

Supporting Information

Hybrid Pressure Retarded Osmosis – Membrane Distillation System for Power Generation from Low-Grade Heat: Thermodynamic Analysis and Energy Efficiency

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GOVERNING EQUATIONS FOR MASS AND HEAT TRANSFER IN MEMBRANE DISTILLATION AND HEAT EXCHANGER MODULES

Direct Contact Membrane Distillation Module

The governing equations for mass and heat transfer in direct contact membrane distillation (DCMD) are established by coupling the transmembrane mass (or heat) transfer in each differential segment with the changes in mass (or heat) flows in the axial directions. While the equations have been derived in details in our previous work on DCMD modeling,¹ we present the governing equations below for the case of negligible conductive heat transfer across the membrane. Specifically, eqs S-1 and S-2 are for mass transfer, while eqs S-3 and S-4 are for heat transfer:

$$\frac{dQ_F(x)}{dx} = \frac{A_{MD}}{L_{MD}} K_{m,MD} [T_F(x) - T_P(x) - \Delta T_{th}(x)] \quad (\text{S-1})$$

$$\frac{dQ_P(x)}{dx} = \frac{A_{MD}}{L_{MD}} K_{m,MD} [T_F(x) - T_P(x) - \Delta T_{th}(x)] \quad (\text{S-2})$$

$$\frac{d[Q_F(x)h_L(C(x), T_F(x))]}{dx} = \frac{dQ_F(x)}{dx} [h_{vap}(C(x), T_F(x)) + h_L(0, T_F(x))] \quad (\text{S-3})$$

$$\frac{d[Q_P(x)h_L(0, T_P(x))]}{dx} = \frac{dQ_P(x)}{dx} [h_{vap}(0, T_P(x)) + h_L(0, T_P(x)) + c_{p,V}(T_F(x) - T_P(x))] \quad (\text{S-4})$$

The definitions of the variables used in these equations are given in the nomenclature at the end of this Supplementary Information. Eqs S-1 and S-2 relate the changes in mass flow rates along the feed and permeate stream channels to the transmembrane mass transfer driven by partial vapor pressure difference that is induced by temperature difference. Eqs S-3 and S-4 relate the changes in heat flow rates along the feed and permeate stream channels to the transmembrane heat transfer carried by the convective transfer of vapor. Note that eqs S-3 and S-4 implicitly assume that conductive heat transfer through the membrane is negligible and that the transmembrane heat transfer is dominated by the convective transfer of vapor, which carries the enthalpy through the microporous membrane. The full governing equations considering conductive heat transfer can be found in our recent publication.¹

The boundary conditions for eqs S-1 to S-4 are given by

$$Q_F(L_{MD}) = Q_F^0 \quad (\text{S-5})$$

$$Q_P(0) = Q_P^0 \quad (\text{S-6})$$

$$T_F(L_{MD}) = T_F^0 = T_H \quad (\text{S-7})$$

$$T_P(0) = T_P^0 = T_C \quad (\text{S-8})$$

The governing mass and heat transfer equations S-1 to S-4, together with the boundary conditions given by S-5 to S-8, can be solved to yield the distribution of mass flow rate and temperature in the feed and permeate streams, which can then be used for quantitative evaluation of system performance.

Heat Exchanger Module

The governing equations for heat transfer in the heat exchanger (HX) are established by coupling the transverse conductive heat transfer in each differential segment with the changes in heat flows in the axial direction:

$$Q_h \frac{dh_L(0, T_h(x))}{dx} = Q_h c_{p,h} \frac{dT_h(x)}{dx} = K_{c,HX} \frac{A_{HX}}{L_{HX}} [T_h(x) - T_c(x)] \quad (\text{S-9})$$

$$Q_c \frac{dh_L(C_0, T_c(x))}{dx} = Q_c c_{p,c}(C_0) \frac{dT_c(x)}{dx} = K_{c,HX} \frac{A_{HX}}{L_{HX}} [T_h(x) - T_c(x)] \quad (\text{S-10})$$

The definitions of the variables used in these equations are given in the nomenclature at the end of this Supplementary Information. Note that, unlike DCMD, there is no mass exchange between the hot and cold channel flows in HX.

The boundary conditions for eqs S-9 and S-10 are

$$T_h(L_{HX}) = T_P^f \quad (\text{S-11})$$

$$T_c(0) = T_C \quad (\text{S-12})$$

Boundary condition S-11 indicates that the influent temperature of the hot stream in the HX is the effluent temperature (or “final” temperature) of the permeate stream in the MD module

Solving eqs S-9 and S-10 with the boundary conditions S-11 and S-12 yield the temperature distribution in the hot and cold streams in the HX module, which can be used with the results from the MD module modeling to assess the specific heat duty of the MD-HX system.

Table S1. Details of the flow streams in the schematic diagram of the PRO-MD system as presented in Figure 1. Definition of the symbols can be found in the nomenclature table in the end of this document.

Stream Number	Mass Flow Rate	Concentration (Molality)	Temperature	Applied Hydraulic Pressure*
1	Q_1	C_1	$T_C^0 (=T_C)$	0
2	Q_1	C_1	T_C^f	0
3	$(\alpha + \gamma)Q_1$	0	T_h^f	0
4	Q_1	C_1	$T_F^0 (=T_H)$	0
5	$(\alpha + \gamma)Q_1$	0	T_C	0
6	$(1 - \gamma)Q_1$	$\frac{C_1}{1 - (1 + MW)\gamma}$	T_F^f	0
7	αQ_1	0	$T_P^0 (=T_C)$	0
8	$(1 - \gamma)Q_1$	$\frac{C_1}{1 - (1 + MW)\gamma}$	T_C	0
9	$(\alpha + \gamma)Q_1$	0	$T_P^f (=T_h^0)$	0
10	$(1 - \gamma)Q_1$	$\frac{C_1}{1 - (1 + MW)\gamma}$	T_C	p_{PRO}
11	γQ_1	0	T_C	0
12	Q_1	C_1	T_C	p_{PRO}
13	$(\gamma + \zeta)Q_1$	0	T_C	0
14	$(1 - \gamma)Q_1$	C_1	T_C	p_{PRO}
15	ζQ_1	0	T_C	0
16	γQ_1	C_1	T_C	p_{PRO}
17	ζQ_1	0	T_C	0
18	$(1 - \gamma)Q_1$	C_1	T_C	0
19	γQ_1	C_1	T_C	0

* Atmospheric pressure is used as reference (i.e. atmospheric pressure is quantified as zero applied pressure). The over-pressure for circulating the flow, which is theoretically unnecessary but practically unavoidable, is not considered here.

DERIVATION OF THE MAXIMUM POWER EXTRACTABLE IN THE HYBRID SYSTEM

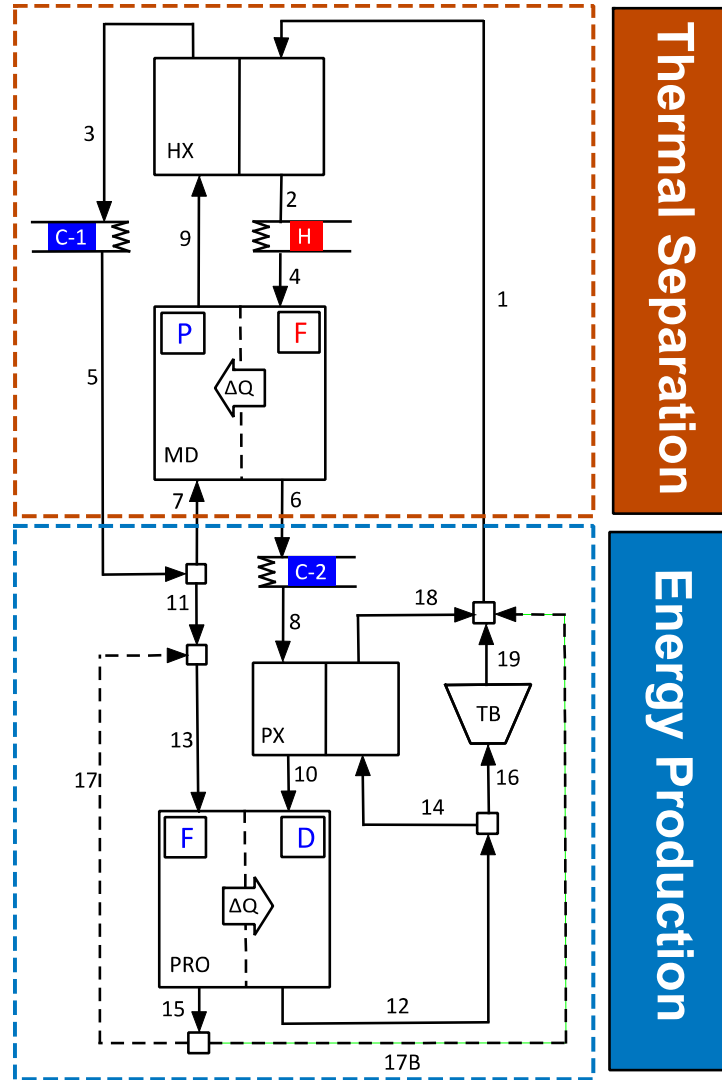


Figure 1. Schematic diagram of the PRO-MD hybrid system. This figure is presented in the main manuscript and is reprinted here to facilitate the understanding of the following derivation.

A hydraulic pressure p_{PRO} is applied to the draw solution such that at a certain axial position at the module, x , the osmotic pressure $\Delta\pi(x)$ is equal to the applied pressure p_{PRO} . No water permeation would occur beyond this position x as the driving force for water permeation vanishes (the analysis of where such a position is also gives the information about required

membrane area). For the analysis presented here, we can use the van't Hoff equation to estimate the osmotic pressure:

$$\Delta\pi(x) \approx \nu RT C_D^f = p_{PRO} \quad (\text{S-13})$$

Note that the van't Hoff equation assumes ideal solution and, hence, is less accurate at higher concentrations. Equation S-13 also assumes that the solute concentration in the feed is zero, which is a reasonable assumption for the permeate of the DCMD and a non-volatile solute (NaCl).

Denoting the increase in volumetric flow rate of the draw solution due to permeation as ΔQ^v , we can apply salt mass balance to determine the final draw concentration C_D^f :

$$C_D^f = C_D^0 \frac{Q_{D,0}^v}{Q_{D,f}^v} = C_D^0 \frac{Q_{D,0}^v}{Q_{D,0}^v + \Delta Q^v} \quad (\text{S-14})$$

Equation S-14 assumes no reverse permeation of solute across the PRO membrane. The power (P) extractable from the turbine is then given by

$$P = p_{PRO} \Delta Q^v = \nu RT C_D^0 \frac{Q_{D,0}^v \Delta Q^v}{Q_{D,0}^v + \Delta Q^v} \quad (\text{S-15})$$

Taking the derivative of P with respect to ΔQ^v yields

$$\frac{dP}{d(\Delta Q^v)} = \nu RT C_D^0 Q_{D,0}^v \frac{1}{(Q_{D,0}^v + \Delta Q^v)^2} > 0 \quad (\text{S-16})$$

which implies that P increases monotonically with ΔQ^v and that the maximum power P_{max} can be attained when permeation of the feed solution is maximized. Because steady state operation requires that the flow rate of the recirculation stream (S_{17} in Figure 1) be constant, the maximum permeation flow rate ΔQ^v is achieved when there is no flow in S_{17B} . When S_{17B} is absent, ΔQ^v is given by the net influent flow rate of the stream entering the PRO feed loop (i.e., $\Delta Q_{max}^v = Q_{11}^v$), and the final draw concentration C_D^f is equal to the working concentration C_1 . Then corresponding applied pressure in the PRO module is thus

$$p_{PRO} \approx \nu RT C_D^f = \nu RT C_1 \quad (\text{S-17})$$

We do not have to rely on the van't Hoff equation any more hereafter, as we no longer need the exact relationship between the osmotic pressure and concentration. Instead, we can describe P_{max} more precisely as

$$P_{max} = p_{PRO} Q_{11}^v \quad (\text{S-18})$$

We can relate the volumetric flow rate Q_{11}^v to the mass flowrate Q_1^m using the mass recovery rate in MD, γ , and the density of the stream 11, ρ_W , which is pure water:

$$Q_{11}^v = \frac{Q_{11}^m}{\rho_{11}} = \frac{\gamma Q_1^m}{\rho_W} \quad (\text{S-19})$$

Therefore, the maximum work extractable from the system under steady state operation is given by

$$P_{max} = p_{PRO} \frac{\gamma Q_1^m}{\rho_W} \quad (\text{S-20})$$

The superscript of Q_1^m in the main text is dropped because all flowrates are defined as mass flow rates in the main text.

ANALYTICAL EXPRESSION FOR THE MAXIMUM MASS RECOVERY IN DIRECT CONTACT MEMBRANE DISTILLATION

Our previous modeling work on direct contact membrane distillation (DCMD) showed that the maximum mass recovery for a given set of system conditions (T_H , T_C , and C_1) is the mass recovery when the operation is in the feed limiting regime (FLR).¹ The maximum mass recovery, γ_{max} , can be described by an analytical expression derived based on thermodynamic principles:¹

$$\gamma_{max} \approx \frac{T_H - T_C^*}{\frac{\bar{h}_{vap,F}}{c_{p,F}} + \frac{c_{p,P}}{c_{p,F}} \frac{T_H + T_C^*}{2} - T_C^*} \quad (\text{S-21})$$

where T_C^* is a function of the working concentration C_1 and the temperature of the heat sink T_C , as defined by

$$p_W(0, T_C) = p_W(C_1, T_C^*) \quad (\text{S-22})$$

with $p_W(C, T)$ being the partial vapor pressure of an NaCl solution of concentration C and temperature T . The $\bar{h}_{vap,F}$ in eq. S-21 is the average enthalpy of vaporization of the permeate and is defined as

$$\bar{h}_{vap,F} \approx \frac{h_{vap}(0, T_H) + h_{vap}(0, T_C^*)}{2} \quad (\text{S-23})$$

Details on the derivation of eq S-21 can be found in our recent publication.¹

IMPACT OF WORKING CONCENTRATION C_1 ON PARAMETERS THAT CONTRIBUTE TO ENERGY EFFICIENCY η

It is observed that the effect of C_1 on the energy efficiency reverses when the extent of heat and mass transfer is varied. As C_1 increases, η_{max}^* decreases when mass and heat transfer kinetics are unlimited (Figure 5B), but η_{OHE} increases with increasing C_1 when mass and heat transfer kinetics are limited (Figure 4). The working concentration C_1 affects the energy efficiency by influencing four parameters in eq 5 (or eq 9, which are repeated below): $c_{p,1}$ and $\pi(C_1)$, which are independent of the mass and heat transfer kinetics, and T_2 and γ , which are dependent on the mass and heat transfer kinetics in the MD-HX.

$$\eta_{OHE} = \frac{P_{max}}{q_H} = \frac{1}{\rho_w} \frac{\pi(C_1)}{\beta} = \frac{\gamma}{\rho_w c_{p,1}} \frac{\pi(C_1)}{(T_H - T_2)} \quad (5)$$

$$\eta_{max}^* = \frac{\gamma_{max}}{\rho_w c_{p,1}} \frac{\pi(C_1)}{(T_H - T_H^*)} \quad (9)$$

The detailed impacts of C_1 on each of these factors are listed in Table S2 and presented in Figures S2-S4 of the Supporting Information. When the mass and heat transfer kinetics are limited, as assumed in Figure 4, the positive impact of C_1 on the osmotic pressure $\pi(C_1)$ is the dominant effect on η_{OHE} . Therefore, the energy efficiency increases with increasing working concentration. However, when the mass and heat transfer kinetics are unlimited, as assumed in Figure 5B, the detrimental impact of a higher C_1 on increasing the minimum temperature difference $\Delta T_{min} = T_H - T_H^*$ outweighs its beneficial impact on raising the osmotic pressure $\pi(C_1)$. Consequently, η_{max}^* decreases slightly with increasing working concentration C_1 .

Table S2. Qualitative description of the impact of working concentration C_1 on parameters that contribute to energy efficiency. “Practical” refers to limited mass transfer in the MD module and heat transfer in the HX module, which occurs in actual operation. “Theoretical” refers to unlimited mass transfer in the MD module and heat transfer in the HX module, which is an ideal scenario that yields the thermodynamic limit of the PRO-MD process.

Parameter		Change	Impact on β	Impact on η_{OHE}
Osmotic pressure $\pi(C_1)$		Increase	----	Positive
Heat capacity $c_{P,F}$		Decrease	Negative	Positive
Mass recovery γ (at optimal α)	Practical	Decrease	Positive	Negative
	Theoretical	Decrease	Positive	Negative
$T_H - T_2$	Practical	Small <i>relative</i> increase	Small positive	Small negative
	Theoretical (= $T_H - T_H^*$)	Large <i>relative</i> increase	Large positive	Large negative

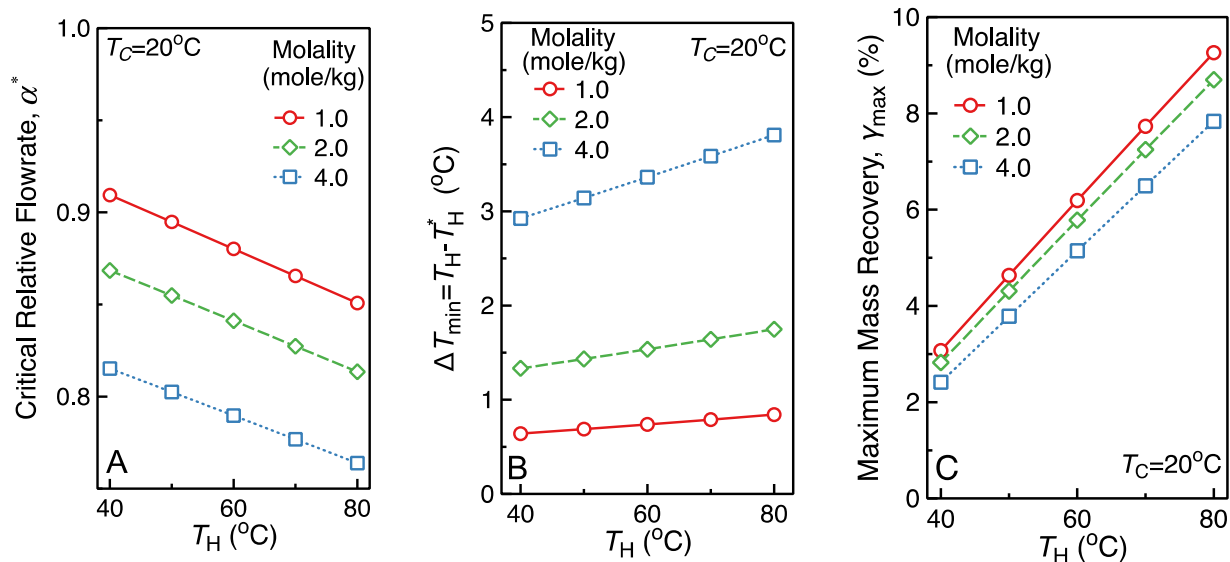


Figure S1. (A) Critical relative flow rate, α^* ; (B) minimum threshold temperature difference at the outlet of the MD permeate stream, $\Delta T_{\min} = T_H - T_H^*$; and (C) maximum mass recovery rate, γ_{\max} , as a function of the temperature of the heat source, T_H , for feed stream concentrations of 1.0, 2.0, and 4.0 mole/kg. In these simulations the cold (heat sink) temperature is set at 20°C .

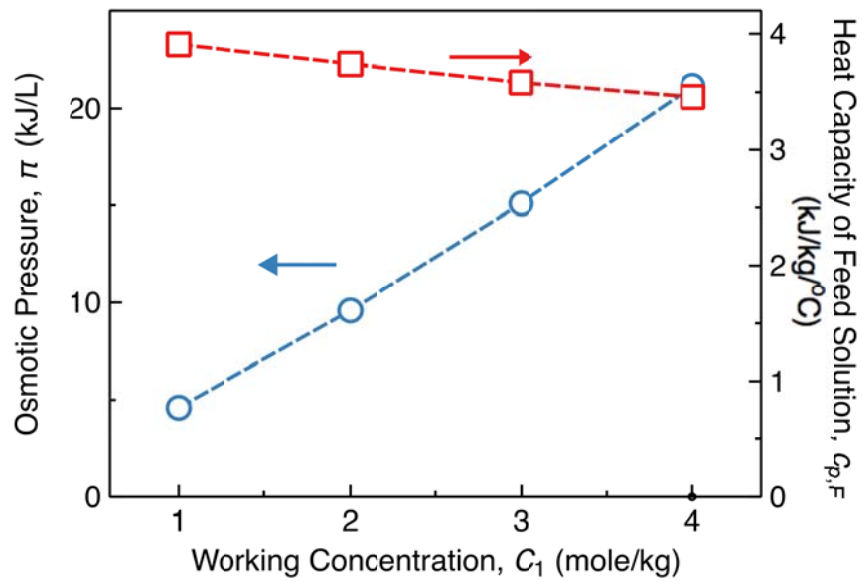


Figure S2. Osmotic pressure of the PRO effluent, π , and heat capacity of the feed influent, $c_{p,F}$, as a function of the solution (NaCl) working concentration C_1 . The dependence on C_1 described in this figure is not affected by the heat and mass transfer kinetics.

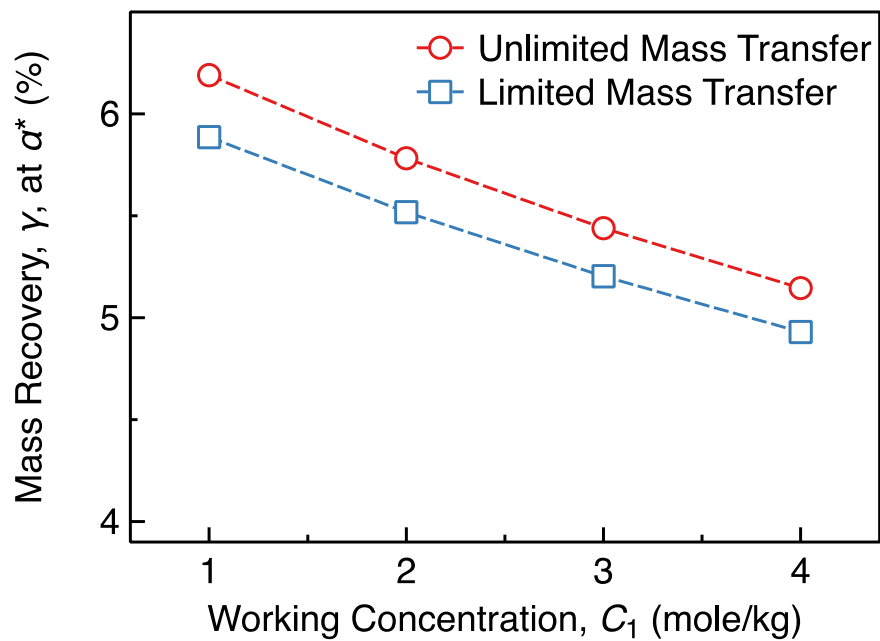


Figure S3. Mass recovery rate as a function of the working concentration C_1 for unlimited and limited mass transfer kinetics.

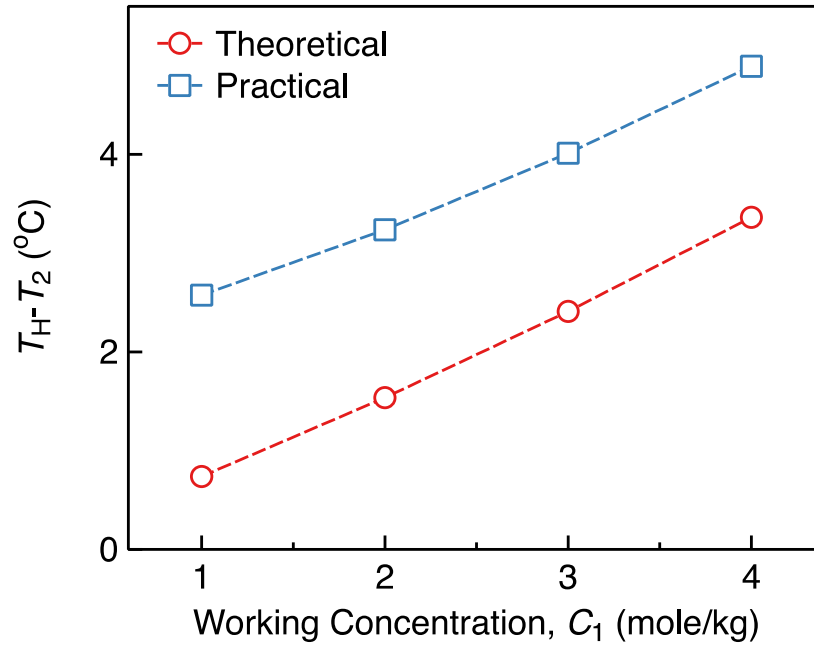


Figure S4. The difference between the working temperature and the effluent temperature of the cold stream in the heat exchanger ($T_H - T_2$) as a function of the working concentration C_1 . Such a temperature difference becomes $T_H - T_H^*$ if the mass transfer kinetics in the MD and heat transfer kinetics in the HX module are unlimited.

NOMENCLATURE

A_{MD}	Membrane area in the MD module	(m ²)
A_{HX}	Exchange area in the HX module	(m ²)
C_1	Electrolyte concentration (in molality) of the NaCl solution in stream 1 (the working concentration)	(mole·kg ⁻¹)
C_D^0, C_D^f	Influent (initial) and effluent (final) concentrations of the draw solution in the PRO module, respectively	(mole·kg ⁻¹)
$c_{p,v}$	Heat capacity of water vapor	(kJ·kg ⁻¹ ·°C ⁻¹)
$c_{p,p}, c_{p,f}$	Heat capacity of the permeate and feed, respectively	(kJ·kg ⁻¹ ·°C ⁻¹)
$c_{p,h}, c_{p,c}$	Heat capacity of the hot stream and cold stream, respectively	(kJ·kg ⁻¹ ·°C ⁻¹)
$h_L(C, T)$	Specific enthalpy of NaCl solution (of concentration C) at temperature T	(kJ·kg ⁻¹)
$h_V(T)$	Specific enthalpy of water vapor at temperature T	(kJ·kg ⁻¹)
$h_{vap}(C, T)$	Specific enthalpy of vaporization of an NaCl solution (of concentration C) at temperature T	(kJ·kg ⁻¹)
$\bar{h}_{vap,F}$	Average specific enthalpy of vaporization of the feed stream, defined by Eq. S-23	(kJ·kg ⁻¹)
$K_{m,MD}$	Mass transfer coefficient in MD	(kg·m ⁻² ·min ⁻¹ ·°C ⁻¹)
$K_{c,HX}$	Heat transfer coefficient in HX	(W·m ⁻² ·°C ⁻¹)
L_{MD}	Length of the MD module	(m)
L_{HX}	Length of the HX module	(m)
MW	Molecular weight of the draw solute	(kg/mole)
P	Power of the power generation stage	(kJ/min)
P_{max}	Maximum power of the power generation stage	(kJ/min)
p_{PRO}	Applied hydraulic pressure in the PRO module	(kJ/L)
$p_W(C, T)$	Partial vapor pressure of the a NaCl solution (of concentration C) at temperature T	(kPa)
Q_i^m	Mass flow rate of stream i	(kg·min ⁻¹)
Q_i^v	Volumetric flow rate of stream i	(L·min ⁻¹)
ΔQ_D^v	Change in the volumetric flow rate of the draw solution in the PRO module	(L·min ⁻¹)
$Q_{D,0}^v, Q_{D,f}^v$	Influent and effluent volumetric flow rates of the draw solution in PRO module, respectively	(L·min ⁻¹)
Q_h, Q_c	Mass flow rates of the hot stream and the cold stream in the HX module, respectively	(kg·min ⁻¹)
Q_F, Q_P	Mass flow rates of the feed and the permeate streams in the MD module, respectively	(kg·min ⁻¹)
Q_F^0, Q_P^0	The initial mass flow rates of the feed and the permeate	(kg·min ⁻¹)

streams in the MD module, respectively

T_i	Temperature of the stream i	(°C)
T_F, T_P	Temperatures of the feed and permeate streams in MD, respectively	(°C)
T_F^0, T_P^0	Influent (initial) temperatures of the feed and permeate streams in MD, respectively	(°C)
T_F^f, T_P^f	Effluent (final) temperatures of the feed and permeate streams in MD, respectively	(°C)
T_h, T_c	Temperatures of the hot and the cold stream in HX, respectively	(°C)
T_h^0, T_c^0	Influent (initial) temperatures of the hot and the cold stream in HX, respectively	(°C)
T_h^f, T_c^f	Effluent (final) temperatures of the hot and the cold stream in HX, respectively	(°C)
T_H, T_C	Temperatures of the heat source and heat sink, respectively	(°C)
$T_H^*(C)$	Temperature of pure water at which its partial vapor pressure is equal to the water partial vapor pressure of an NaCl solution (of concentration C) at temperature T_H	(°C)
ΔT	Difference between the feed and permeate temperatures	(°C)
ΔT_{th}	Threshold temperature difference at which the partial vapor pressures of the feed and the permeate in MD are the same	(°C)
x	Axial position along the MD or HX module	(m)

Greek Symbols

α	Relative mass flow rate between the permeate and the feed in MD	dimensionless
α^*	The critical relative flow rate dividing the FLR and PRL in MD, ($\alpha^* \approx \alpha_{FLR} \approx \alpha_{PLR}$)	dimensionless
γ	Mass recovery rate of the feed	dimensionless
λ	Heat recovery efficiency of the MD-HX system	dimensionless
ν	Dissociation coefficient of electrolyte	dimensionless
$\Delta\pi(x)$	The trans-membrane difference of osmotic pressure at position x of the module	(kJ/L)
ρ_i	Density of stream i	(kg/L)
ρ_W	Density of water	(kg/L)
ζ	Relative PRO feed circulation flow rate (Q_{17}/Q_1)	

References

1. Lin, S.; Yip, N. Y.; Elimelech, M., Direct Contact Membrane Distillation with Heat Recovery--Thermodynamic Insights from Module Scale Modeling. *J Membrane Sci* **2014**, 453, 498-515. DOI: 10.1016/j.memsci.2013.11.016