Integrating Membrane Distillation with Waste Heat from Natural Gas Compressor Stations for Produced Water Treatment in Pennsylvania

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Abstract

Direct contact membrane distillation (DCMD) has immense potential in the desalination of highly saline wastewaters where reverse osmosis is not feasible. This study evaluated the potential of DCMD for treatment of produced water generated during extraction of natural gas from unconventional (shale) reservoirs. Exhaust stream from Natural Gas Compressor Station (NG CS), which has been identified as a potential waste heat source, can be used to operate DCMD thereby providing economically viable option to treat high salinity produced water. An ASPEN Plus simulation of DCMD for the desalination of produced/saline water was developed in this study and calibrated using laboratory-scale experiments. This model was used to optimize the design and operation of large scale systems and estimate energy requirements of the DCMD process. The concept of minimum temperature approach used in heat exchanger design was

applied to determine the optimum membrane area for large scale DCMD plants. Energy analysis revealed that the waste heat available from NG CS is sufficient to concentrate all the produced water generated in Pennsylvania to 30 wt.% regardless of its initial salinity.

Keywords

Direct contact membrane distillation, produced water treatment, waste heat utilization, natural gas compressor stations

Introduction

Marcellus Shale is a major natural gas (NG) reservoir with steadily increasing production since 2008 that currently accounts for about 40% of the total U.S. shale gas production [1]. Natural gas extraction from Marcellus shale in Pennsylvania, West Virginia and Ohio is accompanied by large amounts of produced water that contains high total dissolved solids (TDS). Future extraction of shale gas requires economical management of wastewater to minimize potential environmental impacts. Produced water injection into Class II Underground Injection Control (UIC) wells is the dominant management alternative in many shale plays with sufficient disposal capacity [2-4]. In the Marcellus shale region, the average cost of produced water transportation from the well site in Pennsylvania to injection wells in Ohio or West Virginia ranges from 10 to 20 \$/barrel (bbl) [5, 6]. In addition, the costs associated with deep well injection is estimated at \$1/bbl [5]. However, while there is a total of 12,000 Class II saline water disposal wells in Texas, only 8 such wells are currently available in Pennsylvania [7]. Lack of sufficient disposal capacity in Pennsylvania requires the development of alternative approaches

for management of high TDS produced water [8]. Recent studies have documented concerns over induced seismic activities due to deep well injection [9-12], further emphasizing the need for the development of innovative management strategies for produced water to avoid unintended environmental consequences.

Among different wastewater treatment technologies, emerging membrane distillation (MD) process is particularly attractive because of its low capital investment, low operating temperature, and thus the ability to operate using low grade (waste) heat. MD is a vapor pressure driven process that has been known for over four decades. The first MD patent was filed in 1963 by Bodell [13], while the first paper was published in 1967 by Findley [14]. Direct contact membrane distillation (DCMD) is the most commonly studied MD configuration in which a hydrophobic micro-porous membrane is in direct contact with a hot feed stream on one side and a cold recirculating permeate stream on the other. The volatile vapors from the feed side traverse across the membrane and are condensed on the permeate side. The nonvolatile compounds in the feed stream, such as salts, suspended solids, and macromolecules are retained in the feed solution due to the hydrophobic nature of the membrane. The permeate solution will be free from impurities as long as the membrane is not wetted [15, 16] and as long as there are no volatile contaminants in the feed stream that can permeate across the membrane.

DCMD is a non-isothermal separation process that involves simultaneous heat and mass transfer and operates on the principle of vapor-liquid equilibrium. In the last decade, researchers have developed several predictive models for DCMD systems by combining heat and mass transfer principles [17-22]. Heat transfer models comprise of Nusselt number-based empirical correlations to evaluate the heat transfer coefficients [23-25], while mass transfer is typically expressed as a linear function of the vapor pressure difference across the membrane [24-27].

Moreover, different types of heat recovery approaches have been described in the literature [28-32] to recover the energy lost to the permeate side stream from the feed stream and increase the overall energy efficiency of the process. DCMD is being explored for diverse applications such as desalination of water, concentration of aqueous solutions in the food industry and concentration of acids [33-37]. MD processes are able to distill water at operating temperatures of 30-90°C, which is significantly lower than the conventional thermal treatment processes. The lower operating temperature of MD also offers an excellent opportunity to integrate MD processes with waste heat sources to further reduce the operating cost. Furthermore, MD operates at lower hydrostatic pressure compared to conventional pressure-driven membrane technologies, such as reverse osmosis and nano-filtration [38]. Membrane distillation has been evaluated for desalination of seawater and brine from thermal desalination plants in pilot-scale studies [39-42], but the commercialization of this technology is hindered by high energy cost [43]. Kesieme et al. [44] estimated that the MD treatment cost decreased from \$2.2/m³ to \$0.66/m³ when a waste heat source was employed to drive the process. In comparison, the operating cost of reverse osmosis treatment was estimated at \$0.80/m³ [44].

While many studies reported that integrating MD with waste heat sources can lower its operating cost [44-46], the focus of those studies was often on a qualitative understanding without identifying specific sources of waste heat or conducting a systems analysis to integrate full scale MD technology with actual waste heat sources. Furthermore, there are no studies in the literature that are focused on the feasibility of MD technology utilizing waste heat for treatment of high salinity produced water from shale gas extraction. Relatively abundant and unutilized source of waste heat is available in the natural gas compressor stations (NG CS) in the U.S [47]. The U.S. natural gas pipeline network is an integrated transmission and distribution network

consisting of more than 210 pipeline systems, 300,000 miles of transmission pipelines, and 1,799 compressor stations with more than 17 million installed horsepower (HP) for continuous delivery of natural gas [48]. In most CS, a portion of NG is combusted to provide the energy required by the compressor engine that is usually an internal combustion engine or a gas turbine. Despite the high thermal efficiency of compressor engines, about two-thirds of the fuel energy is lost as waste heat [49]. A recent study revealed that a huge quantity of waste heat is available at NG CS in the form of hot exhaust gases [47]. It is estimated that an average of 610 TJ/day of waste heat is released in the hot flue gas of compressor engines in the U.S. at temperatures above 900 K [47]. This offers a potential to collocate wastewater treatment facilities with NG CS to offset the energy requirements of the MD process.

This study evaluated the synergies and potential of MD technology for treatment of shale gas produced water utilizing waste heat available from NG CS. A mathematical model based on the fundamentals of heat and mass transfer processes was developed and calibrated for a DCMD process using laboratory-scale experiments. The model was then used to optimize design and operating parameters for a full-scale DCMD system. The energy analysis from this model was combined with the information about available waste heat at NG CS in Pennsylvania (PA) region of Marcellus shale to estimate the amount of produced water that can be treated in distributed DCMD wastewater treatment plants. Results from this study provide important insights in the operation of an integrated system and can be extended to other sources of industrial waste heat combined with other thermally-driven water treatment technologies.

112

113 **Theory and Methodology**

114 Mathematical model of DCMD

115 In DCMD, the hot feed (liquid to be separated or treated) evaporates at the membrane
 116 surface and vapors travel across the membrane to be condensed in a recirculating cold liquid on
 117 the other side of the membrane. The permeate flux across the membrane can be determined by
 118 Equation (1) [50], where J is the mass flux ($\text{kg/m}^2/\text{s}$), C is the membrane distillation coefficient
 119 ($\text{kg/m}^2/\text{s}/\text{Pa}$), $p_{m,f}$ and $p_{m,p}$ are vapor pressures (Pa) at the feed-membrane and permeate-
 120 membrane interface corresponding to membrane surface temperatures $T_{m,f}$ and $T_{m,p}$, respectively.
 121 The MD coefficient, C , is considered fairly constant as it is weakly dependent on temperature
 122 [51, 52].

$$J = C(p_{m,f} - p_{m,p}) \quad (1)$$

123 The schematic of the heat and mass fluxes in DCMD is displayed in Figure 1. The
 124 presence of boundary layers at the membrane surface substantially contributes to the heat
 125 transfer resistances. Heat transfer in DCMD occurs in the following steps:

- 126 a) heat transfer from the bulk feed to the surface of the membrane (Q_f) (Equation (2)),
- 127 b) heat transfer across the membrane (Q_m) (Equation (3)),
- 128 c) heat transfer from membrane surface at the permeate side to the bulk permeate (Q_p)
- 129 (Equation (4))

$$Q_f = h_f(T_{b,f} - T_{m,f}) \quad (2)$$

$$Q_m = J\Delta H + \frac{k_m}{\delta}(T_{m,f} - T_{m,p}) \quad (3)$$

$$Q_p = h_p(T_{m,p} - T_{b,p}) \quad (4)$$

where, h_f and h_p are the heat transfer coefficients (W/m²/K) on the feed and permeate side respectively, ΔH is the latent heat of vaporization of water (J/kg), k_m is the membrane thermal conductivity (W/m/K), δ is the membrane thickness (m), and $T_{b,f}$ and $T_{b,p}$ are the bulk feed and permeate temperatures, respectively.

All three heat fluxes are equal at steady state (Equation (5)).

$$Q_f = Q_m = Q_p \quad (5)$$

Heat transfer across the boundary layer can offer substantial resistance leading to a difference between the membrane surface temperature and the bulk temperature of the fluid [53]. Yun et al. [17] have shown that the membrane surface temperatures can be calculated using Equations (6) and (7) that are derived from Equations (1) – (5). The authors also included constants C'_p and ΔH^0 to account for the variation in latent heat of vaporization of water with membrane surface temperature.

$$T_{m,f} = \frac{\left[1 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right] (h_f T_{b,f} - J\Delta H^0) + JC'_p \left(T_{b,p} + \frac{h_f}{h_p} T_{b,f}\right) \left[2 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right]}{h_f \left[1 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right] + JC'_p \left\{1 + \frac{h_f}{h_p} \left[2 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right]\right\}} \quad (6)$$

$$T_{m,p} = \frac{\left[1 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right] (h_p T_{b,p} + J\Delta H^0) + JC'_p \left(T_{b,f} + \frac{h_p}{h_f} T_{b,p}\right)}{h_p \left[1 - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right] + JC'_p \left[2 + \frac{h_p}{h_f} - \exp\left(-JC'_p \frac{k_m}{\delta}\right)\right]} \quad (7)$$

where, $C'_p = 1900$ J/kg/K and $\Delta H^0 = 2967.3$ kJ/kg [17].

The heat transfer coefficients for the feed and the permeate sides can be calculated using Equations (8) and (9) [23], where Nusselt number (Nu) is evaluated from a correlation with Reynolds number (Re) and Prandtl number (Pr).

$$h = Nu \frac{k}{d_h} = \left[0.664 k_{dc} Re^{0.5} Pr^{0.33} \left(\frac{2d_h}{l_m} \right)^{0.5} \right] \frac{k}{d_h} \quad (8)$$

$$k_{dc} = 1.654 \left(\frac{d_f}{H} \right)^{-0.039} \phi^{0.75} \left[\sin \left(\frac{\theta}{2} \right) \right]^{0.086} \quad (9)$$

145 where, k is the thermal conductivity of the fluid, d_h is the hydraulic diameter of the channel, l_m is
 146 the distance between filaments of the spacer, d_f is the thickness of spacer filament, H is the
 147 thickness of the spacer, ϕ is the porosity of the spacer and θ is the hydrodynamic angle between
 148 the crosslinked spacer filaments. The correction factor k_{dc} is included to account for the effects
 149 of spacer characteristics on heat transfer.

150 A step-wise approach to modeling heat and mass transfer in DCMD described by
 151 Gustafson et al. [54] for large scale systems was employed to obtain the temperature and
 152 flowrate profiles along the length of the membrane module. According to this approach, the
 153 membrane is divided into several sections (Figure 1) and Equations (1) to (9) are used in
 154 conjunction with energy and mass balance for each section of the membrane module to obtain
 155 temperature and flow distribution across the membrane. The mass flow rates of the feed and the
 156 permeate in a section of the membrane can be evaluated by:

$$M_{f,i+1} = M_{f,i} - J_i A_i \quad (10)$$

$$M_{p,i} = M_{p,i+1} + J_i A_i \quad (11)$$

157 where, M ($\text{kg}\cdot\text{s}^{-1}$) is the mass flow rate, A_i (m^2) is the area of the membrane in a section and J_i
 158 ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the mass flux across the membrane section. The subscripts 'i' refers to the feed
 159 inlet and permeate outlet for the i^{th} section, while 'i+1' refers to the feed outlet and permeate
 160 inlet for the same section of membrane (Figure 1). The energy balance across the i^{th} section can

be used to calculate the enthalpy, and hence temperatures, of the streams leaving the section as follows:

$$M_{f,i}E_{f,i} = M_{f,i+1}E_{f,i+1} + Q_{m,i}A_i \quad (12)$$

$$M_{p,i}E_{p,i} = M_{p,i+1}E_{p,i+1} + Q_{m,i}A_i \quad (13)$$

where, E ($\text{J}\cdot\text{kg}^{-1}$) refers to the specific enthalpy and $Q_{m,i}$ ($\text{W}\cdot\text{m}^{-2}$) refers to the heat flux across the membrane.

Figure 1. (a) Temperature profile in DCMD module, (b) enlarged section of DCMD module

Coupling mathematical model with Aspen Plus simulation for DCMD

The equations listed in the previous section (Eqn. (1) to (13)) were used to simulate operation of a DCMD system in Aspen Plus (Version 8.8) as a user defined unit operation. These user-defined blocks were arranged in series with the feed and permeate flow in a countercurrent direction to obtain the temperature, concentration and flow profiles of all streams. According to

the flowchart for one such block shown in Figure 2, the temperatures of the entering streams ($T_{f,i}$ and $T_{p,i+1}$) were used as the initial guesses of the membrane surface temperatures ($T_{m,f}$ and $T_{m,p}$) to calculate the associated liquid vapor pressures ($p_{m,f}$ and $p_{m,p}$). An initial value of the flux (J) was then calculated using Equation (1) with a membrane distillation coefficient (C) of 5.6 kg/m²/hr/kPa determined in a previous laboratory-scale study which employed a polytetrafluoroethylene membrane with a polypropylene support [55]. The properties of the membrane and spacer used in these experiments are shown in Supplementary Information. Heat transfer coefficients (h_f and h_p) were calculated using Equation (8) and used to determine the membrane surface temperatures ($T'_{m,f}$ and $T'_{m,p}$) using Equations (6) and (7). These values were then used to calculate the flux (J') corresponding to the adjusted membrane surface temperatures. This iterative procedure was repeated until the relative difference between J' and J reached a selected tolerance of 0.1%.

Figure 2. Algorithm used for the simulation of DCMD

The permeate flux obtained using this approach was used to calculate the heat flux across the membrane ($Q_{m,i}$) using Equation 3, and the mass flow rates of the feed and permeate streams

($M_{f,i+1}$ and $M_{p,i}$) leaving the membrane section using Equations (10) and (11), respectively. Equations (12) and (13) were then used to calculate the specific enthalpy of feed and permeate streams ($E_{f,i+1}$ and $E_{p,i}$) leaving the module section, which were then used to calculate the temperatures of these streams ($T_{f,i+1}$ and $T_{p,i}$). Finally, the averages of the feed and permeate bulk temperatures ($T_{f,avg}$ and $T_{p,avg}$) were calculated and the initial guesses of membrane surface temperatures ($T_{m,f}$ and $T_{m,p}$) were updated with these values. The same procedure was repeated until the relative difference between the values calculated in subsequent iterations was below 0.1%. The mass and heat fluxes across the membrane section were determined at the average values of stream properties for each section of the membrane to prevent overestimation of the fluxes. For example, if the feed stream enters a membrane section at 60 °C and the permeate stream enters on the other side of the module at 40 °C, it is reasonable to assume that the feed stream would leave the membrane section at a lower temperature (e.g., 58 °C) while the permeate side stream would leave that same section at a higher temperature (e.g., 42 °C). The flux values are generally calculated at the feed inlet temperature (i.e., 60 °C) and permeate inlet temperature (i.e., 40 °C) in most theoretical models, which can lead to overestimation of fluxes as the predicted vapor pressure difference would be greater than is the case in reality. Hence, calculating the flux using the average feed temperature (i.e., 59 °C) and average permeate side temperature (i.e., 41 °C) would result in a more accurate flux prediction. It should be noted that these calculations were carried out assuming negligible heat loss to the surroundings. The physical properties of the streams were obtained from the electrolytic Non-Random Two-Liquid (NRTL) model available in Aspen Plus.

Calibration of the mathematical model

Previous work by the authors showed that the concentration polarization could result in up to 30% increase in the salt concentration at the feed-membrane surface at high salinities [55]. The model used in this study was therefore calibrated to account for this reduction in the driving force (vapor pressure) at higher salt concentration due to concentration polarization. Model calibration was carried out using the experimental data with the feed temperature of 60 °C and feed flow rate of 1.9 L/min. To calibrate the model, the difference in the predicted flux and experimentally observed flux values at different salinities was evaluated and the predicted flux was adjusted according to the experimentally observed concentration polarization coefficient. The experimental setup and the composition of produced water samples used for model calibration and validation is discussed elsewhere [55].

Results and Discussion

Calibration/validation of the DCMD model

As shown in Figure 3, the model that was calibrated using the data collected at 60 °C was able to predict experimentally measured permeate flux at different feed temperatures, flow rates and salinities with a root mean square error of 6%, which is satisfactory for industrial applications [56]. The results shown in Figure 3 indicate that the impact of feed flow rate on permeate flux is significantly lower than that of the feed temperature. For instance, a three-fold increase in the feed flow rate from 1.1 L/min ($Re = 1,330$) to 3.4 L/min ($Re = 4,000$) increases the permeate flux by only 17% at a feed temperature of 60°C (Figure 3(a)). On the other hand, increasing the feed temperature from 50 to 60 °C at a feed flow rate of 1.1 L/min increases the

permeate flux by 103%. While increasing the feed flow rate helps to decrease the effects of temperature polarization and improves mass transfer [57], the feed temperature is directly responsible for the driving force. This effect of temperature and flow rate on the permeate flux is consistent for varying salt concentrations as shown in Figure 3 and is in agreement with other studies [58, 59].

Figure 3. Comparison of simulated DCMD process with the experimental results obtained for (a) a TDS of 92.8 g/l and (b) TDS of 308.3 g/l. Permeate temperature and flow rate were 30 °C and 1.9 l/min, respectively.

Calibrated and validated model was used to predict flux and temperature profiles for large scale systems using the approach that was successful in predicting the permeate flux for a hollow fiber polypropylene membrane area of up to 0.66 m² [39]. Commercial microfiltration membrane assemblies commonly use membrane areas of 0.1 to 0.2 m² [60] and the area of a single flat-sheet membrane chosen for this simulation was 0.2 m². The number of membrane modules in series or the effective membrane area governs the temperature change on both feed and permeate side. As discussed before, increasing the feed flow rate enhances permeate flux across the membrane; the same is true for permeate side flow rate [38, 61]. However, this increase in permeate flux due to higher feed- or permeate-side flow rates eventually reaches a plateau after which increasing the flow rates has no effect on the permeate flux. Hence, a

minimum Reynolds number of 1,000 was used for simulating large scale membrane modules to ensure higher permeate flux across the membrane. Similarly, the temperature difference between the feed inlet and the permeate inlet streams were chosen to achieve maximum permeate flux and heat recovery. More information on the choice of temperatures is provided in the later section that discusses heat recovery and specific thermal energy requirements.

As can be seen in Figure 4, the permeate flux decreases with an increase in membrane area because of the decrease in temperature difference between the feed and permeate sides that occurs when more modules are added in series. Consequently, the total permeate flow initially increases with an increase in membrane area (Figure 4) but it levels off after a certain point when adding more modules in series offers limited benefit to the overall system performance.

Figure 4. Minimum temperature difference, flux, and permeate flow profiles as a function of membrane area in a counter-current DCMD system. The feed and permeate flow rate was 1500 kg/hr while the inlet feed and permeate temperatures were fixed at 90 °C and 30 °C, respectively.

A minimum temperature approach similar to that used for the design of heat exchangers [62] was employed in this study to evaluate the maximum possible number of membrane modules in series. For heat exchangers, a minimum temperature difference of 10 °C between the hot and the cold side has been established as a thumb rule for effective heat transfer [63, 64]. Therefore, the minimum temperature difference between the feed outlet and the permeate side inlet in any module of a DCMD array was set at 10 °C to ensure that a reasonable driving force would be maintained in all modules. The maximum membrane area that meets this condition for

the feed inlet temperature of 90 °C and the permeate inlet temperature of 30 °C was 3.6 m², which corresponds to 18 modules in series. The average flux obtained for these conditions was 26.5 kg/m²/hr, which is significantly higher than 8.1 kg/m²/hr reported for a similar case in the literature [39]. This difference can be attributed to a considerably higher MD coefficient of the membrane used in this study [55] because of the highly porous and thin membrane selected for this application as shown in Supplementary Information.

The objective of this study was to assess the energy requirements for produced water treatment using available waste heat from NG CS and these calculations were scaled up to a large scale systems by simply putting the arrays of 18 modules in series in a parallel arrangement to achieve a desired total system capacity as illustrated in Supplementary Information.

DCMD system with heat recovery

Heat recovery in DCMD system has been analyzed previously [28-30, 65] and the process flow diagram used in this study depicted in Figure 5 is similar to a recent case study of DCMD based desalination [29]. While the previous study [29] focused on concentrating the seawater from a TDS of 28,050 mg/l to about 140,000 mg/l, this study evaluated the use of DCMD to concentrate produced water from TDS of 100,000 mg/l (10 wt.%) to 300,000 mg/l (30 wt.%). Flue gas from an NG CS was incorporated in the system as a source of waste heat using intermediate steam loop to drive the MD process. Heat exchanger HX-4 is used to generate steam at 3.6 bar (140 °C) using the hot flue gas, which is then utilized to increase the temperature of the MD feed stream to a desired operating temperature. Because the permeate stream is heated as it travels through the MD array, the heat exchanger HX-2 is added to recover some of that heat for preheating the feed stream. The permeate stream leaving HX-2 is cooled down to 30 °C

in heat exchanger HX-1 by contacting with fresh produced water feed. It is assumed that a sufficient quantity of produced water is available at 20 °C to cool down the permeate stream in heat exchanger HX-1.

The salinity of produced water depends on the location and age of the fractured well with sodium chloride as the major constituent. For the purpose of this study, the salinity of the feed water was assumed to be 10 wt.% sodium chloride solution, while that of the brine leaving the system was fixed at 30% to yield the overall water recovery factor of 66.7%. It should be noted that a large volume of feed has to be recycled through the MD array because of the low water recovery rate in a single pass through a DCMD and that the flowrate of brine that is purged from the system is significantly lower than the flowrate of recycled brine. A full-scale system would typically include a pretreatment step to remove the scale forming salts prior to DCMD treatment. Hence, it is assumed that the flux decrease due to membrane fouling would be negligible.

Figure 5. Schematic flow diagram of the DCMD desalination plant treating 100 kg/s (stream 4)

of feed water. DCMD feed and permeate inlet temperature are 90 °C and 30 °C respectively, whereas the required membrane area is 9102 m².

Simulations of system performance were performed at different feed temperatures to determine the optimum range based on the specific thermal energy consumption (kWh/m³) and the results are shown in Figure 6. As expected, the permeate flux increases with an increase in feed temperature. It must be noted that the fraction of recovered energy also increases with temperature because the permeate stream leaves the DCMD system at higher temperatures when the feed temperature is increased. As shown in Figure 6(b), the energy required per m³ of permeate increased from 527 to 565 kWh/m³ as the feed temperature decreased from 90 to 60 °C; hence, it is preferable to operate DCMD at a higher temperature where almost 37% of the energy needed for system operation can be recovered using heat exchangers HX-1 and HX-2. The lowest specific thermal energy required to operate DCMD was reported by Lin et al. [66] as 27.6 kJ/kg (or 7.67 kWh/m³) but the values reported in the literature are at least one order of magnitude higher than this thermodynamic minimum. Khayet et al. [67] obtained a specific thermal energy consumption of 600 kWh/m³ for a DCMD pilot study with a membrane area of 4 m², which is comparable to the values determined in this study. Khayet and Matsuura [68] reported the specific thermal energy requirement for a theoretical 24,000 m³/day DCMD desalination plant studied by Al-Obaidani [69] of 39.7 kWh/m³. However, these calculations assume a very high water recovery of 80% from DCMD without any recirculation of the feed side stream while the thermodynamic maximum for single pass recovery that can be attained in a DCMD system is 6.4% [66].

Figure 6. (a) Average flux and percentage heat recovery as a function of feed temperature, (b) Specific thermal energy required to concentrate produced water from 10% to 30% TDS as a function of feed temperature.

The Gain Output Ratio (GOR), which is defined as the ratio of the amount of permeate generated to the amount of saturated steam provided to the system [70], can theoretically be as high as 21 for DCMD systems [71] while the highest value of GOR obtained experimentally was between 5 and 6 [30, 72]. However, the temperature difference between the hot and the cold streams for both membrane modules and heat exchangers used for heat recovery would have to be around 1-2 °C to achieve such high GOR. Such low temperature difference would require enormous membrane and heat exchanger area and will detrimentally impact the economics of the overall treatment process (i.e., capital cost). In addition, the flow rate of feed and permeate side streams in the DCMD system must be very low to obtain high water recovery and achieve higher GOR value [72]. While this makes the process more energy efficient, it significantly decreases the permeate flux because the temperature difference between the feed and the permeate side is drastically reduced due to increased residence time. Both these factors would lead to a substantial increase in the membrane area to achieve desired water recovery. Therefore, the

minimum temperature approach was utilized in this study to optimize the membrane and heat exchanger area, which yielded a maximum GOR of 1.07 when the feed temperature was 90 °C.

Produced water treatment by DCMD in PA

To evaluate the potential of DCMD to treat produced water from unconventional gas extraction using waste heat available at NG CS in Pennsylvania (PA), it is necessary to estimate the volume of produced water generated in PA. The total shale gas production on a county level in Marcellus shale play in PA was based on the most updated information (January-July 2014) published by the Pennsylvania Department of Environmental Protection (PA DEP) [73]. There were 5,188 active unconventional gas wells operating in 2014 in PA with a total natural gas production of $5.1 \times 10^{10} \text{ m}^3$ [74]. The amount of produced water per unit volume of gas production varies across different states and shale plays due to the differences in shale formation characteristics. Previous studies have shown that 300 barrels (47.7 m^3) of brine are produced per MCM (million cubic meter) of shale gas recovered in PA [75]. Brine production per day is calculated based on the total amount of produced water and the number of production days for each well provided by PA DEP [73]. Figure 7 shows estimated aggregate amount of produced water on a county level in PA during the first half of 2014. The results indicate that produced water generation ranged from $0.014 \text{ m}^3/\text{day}$ in Cambria County to $3,211.5 \text{ m}^3/\text{day}$ in Susquehanna County. Based on this analysis, it can be estimated that a total of about 2.78 MCM of produced water is generated in PA in the first six months of 2014, which is equivalent to $630 \text{ m}^3/\text{hr}$.

Figure 7. Estimated quantity of produced water on a county level in Pennsylvania

Previous study estimated that a total of 43.4 TJ/day of waste heat is available at natural gas compressor stations in PA [47]. The amount of energy required to concentrate the produced water generated in PA to 30% salinity can be estimated based on the DCMD specific thermal energy consumption shown in Figure 6(b). For example, the specific thermal energy consumption with respect to produced water with a TDS of 10 wt.% is 382 kWh/m³ when the feed temperature is 60 °C. While this is the net energy requirement of the process, the actual energy requirement depends on the efficiency of steam generation. Assuming the efficiency of steam generation of 80%, it can be estimated that a total of 26 TJ/day of energy would be needed to treat 630 m³/hr of produced water generated in PA if DCMD process is operated using the feed temperature of 60 °C. Figure 8(a) shows the amount of energy required to concentrate the produced water generated in PA to 30% as a function of feed temperature. The energy requirement in Figure 8 is calculated assuming 80% efficiency for steam generation. If the feed

temperature is increased to 90 °C, only 56% of the total waste heat available from NG CS in PA is sufficient to concentrate the produced water generated in PA to 30% salinity. The effect of changes in produced water salinity on the energy requirements for DCMD process is shown in Figure 8(b). The results in this figure indicate the energy required to treat produced water would be lower than the available waste heat energy regardless of the feed water salinity. A maximum of 32.2 TJ/day of energy would be required to treat all produced water in PA even if the feed salinity is just 3%.

Figure 8. (a) Thermal energy required to concentrate produced water in PA to 30% salinity using DCMD as a function of feed temperature at a fixed initial TDS of 10% (w/v), (b) Total thermal energy and specific thermal energy with respect to feed as a function of the feed salinity when the feed temperature is 90 °C and is concentrated to 30% salinity.

Practical constraints such as transportation of produced water to the source of waste heat are likely to limit the application of MD technology. This issue can be clearly seen in Figure 9 which displays the spatial distribution of theoretical DCMD treatment capacity at NG compressor stations and the estimated quantity of produced water generated in each county. The results in Figure 9 were developed assuming that the DCMD system is operated at an inlet feed temperature of 90 °C and the theoretical amount of produced water that could be treated utilizing

the waste heat from NG CS in PA was estimated based on the installed capacity at each compressor station [47]. Transportation of produced water to NG CS sites may be feasible in counties that have several NG CS (e.g., Greene County) as it is likely to have a limited impact on the overall produced water management cost. However, water transportation costs may become significant and prohibitive for counties that do not have NG CS in close proximity (e.g., Susquehanna County in the northwest corner of the state that generates the highest amount of produced water in PA). Future analysis should focus on the economic feasibility of using DCMD for treatment of produced water utilizing waste heat to identify major cost drivers.

Figure 9. Spatial distribution of estimated produced water and treatment capacity using available waste heat at NG CS in PA

412

413 **Conclusions**

414 A mathematical model using fundamental heat and mass transfer equations and literature
415 correlations was developed in this study to predict the performance of large scale DCMD
416 systems. The model was calibrated using the results of laboratory-scale studies and the concept
417 of minimum temperature similar to that employed in the design of heat transfer equipment was
418 used to obtain the optimum membrane area when several membrane modules are arranged in
419 series. It was found that a minimum temperature difference of 10 °C between the feed and the
420 permeate-side streams yielded an optimum membrane area for permeate flux across the
421 membrane. Using sensitivity analysis, it was established that the heat recovery efficiency and
422 permeate flux increase with an increase in the DCMD feed temperature, which reduces the
423 specific thermal energy consumption of this treatment process. A plant scale DCMD system with
424 optimum membrane area, external heat recovery, and utilizing waste heat from NG CS was
425 evaluated for its potential to treat produced water in PA region of Marcellus Shale. It was found
426 that the amount of energy required to concentrate produced water in PA to 30% salinity was
427 much lower than the amount of waste heat available from NG CS irrespective of the produced
428 water salinity. The key findings of this study suggest that DCMD is capable of concentrating all
429 the produced water in PA if the waste heat from NG CS can be utilized. However, the economic
430 feasibility of this approach needs to be evaluated to identify major cost drivers and barriers.

431 **Nomenclature**

432 A = area of membrane

433 C = membrane distillation coefficient ($\text{kg.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$)

434	d_f	= diameter of spacer filament (m)
435	d_h	= hydraulic radius (m)
436	E	= specific enthalpy ($J.kg^{-1}$)
437	h	= heat transfer coefficient ($W.m^{-2}.K$)
438	ΔH	= latent heat of vaporization for water ($J.kg^{-1}$)
439	H	= spacer thickness (m)
440	J	= permeate flux ($kg.m^{-2}.s^{-1}$)
441	k	= thermal conductivity ($W.m^{-1}.K^{-1}$)
442	k_{dc}	= correction factor for spacer geometry
443	l_m	= spacer mesh size (m)
444	M	= mass flow rate ($kg.s^{-1}$)
445	Nu	= Nusselt number
446	p	= vapor pressure (Pa)
447	Pr	= Prandtl number
448	Q	= heat flux ($W.m^{-2}$)
449	Re	= Reynold number
450	T	= absolute temperature (K)
451	TDS	= total dissolved solids
452	Greek	
453	δ	= membrane thickness (m)
454	θ	= hydrodynamic angle
455	ϕ	= spacer voidage
456	Subscripts	

457 b,f = bulk at feed side
 458 b,p = bulk at permeate side
 459 f = feed
 460 m = membrane
 461 m,f = membrane surface at the feed side
 462 m,p = membrane surface at the permeate side

463

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467

468 **References:**

- 469 [1] Marcellus Region production continues growth, in, U.S. Department of Energy, Energy
 470 Information Administration, 2014.
 471 [2] K.B. Gregory, R.D. Vidic, D.A. Dzombak, Water management challenges associated with the
 472 production of shale gas by hydraulic fracturing, *Elements*, 7 (2011) 181-186.
 473 [3] J.A. Veil, M.G. Puder, D. Elcock, R.J. Redweik Jr, A white paper describing produced water
 474 from production of crude oil, natural gas, and coal bed methane, Argonne National Laboratory,
 475 Technical Report, (2004).
 476 [4] J. Gao, F. You, Optimal design and operations of supply chain networks for water
 477 management in shale gas production: MILFP model and algorithms for the water-energy nexus,
 478 *AIChE Journal*, 61 (2015) 1184-1208.
 479 [5] J.A. Slutz, J.A. Anderson, R. Broderick, P.H. Horner, Key Shale Gas Water Management
 480 Strategies: An Economic Assessment, in, Society of Petroleum Engineers.
 481 [6] T. Hayes, T. Smith, Techno-economic Assessment of Water Management Solutions,
 482 Marcellus Shale Gas Water Management Initiative, Canonsburg, PA, (2011).
 483 [7] R. McCurdy, Underground injection wells for produced water disposal, in: *Proceedings of*
 484 *the Technical Workshops for the Hydraulic Fracturing Study: Water Resources Management.*
 485 EPA, 2011.
 486 [8] D.M. Kargbo, R.G. Wilhelm, D.J. Campbell, Natural gas plays in the Marcellus shale:
 487 Challenges and potential opportunities, *Environmental science & technology*, 44 (2010) 5679-
 488 5684.
 489 [9] W.L. Ellsworth, Injection-induced earthquakes, *Science*, 341 (2013) 1225942.

490 [10] M. Zoback, S. Kitasei, B. Copithorne, Addressing the environmental risks from shale gas
491 development, Worldwatch Institute, 2010.

492 [11] K.M. Keranen, M. Weingarten, G.A. Abers, B.A. Bekins, S. Ge, Sharp increase in central
493 Oklahoma seismicity since 2008 induced by massive wastewater injection, *Science*, 345 (2014)
494 448-451.

495 [12] A. McGarr, B. Bekins, N. Burkardt, J. Dewey, P. Earle, W. Ellsworth, S. Ge, S. Hickman,
496 A. Holland, E. Majer, J. Rubinstein, A. Sheehan, Coping with earthquakes induced by fluid
497 injection, *Science*, 347 (2015) 830-831.

498 [13] B. Bodell, Silicone rubber vapor diffusion in saline water distillation, United States Patent
499 Serial, (1963).

500 [14] M. Findley, Vaporization through porous membranes, *Industrial & Engineering Chemistry*
501 *Process Design and Development*, 6 (1967) 226-230.

502 [15] F. Edwie, T.-S. Chung, Development of simultaneous membrane distillation–crystallization
503 (SMDC) technology for treatment of saturated brine, *Chemical Engineering Science*, 98 (2013)
504 160-172.

505 [16] G. Rácz, S. Kerker, Z. Kovács, G. Vatai, M. Ebrahimi, P. Czermak, Theoretical and
506 Experimental Approaches of Liquid Entry Pressure Determination in Membrane Distillation
507 Processes, *Periodica Polytechnica Chemical Engineering*, 58 (2014) 81-91.

508 [17] Y. Yun, R. Ma, W. Zhang, A. Fane, J. Li, Direct contact membrane distillation mechanism
509 for high concentration NaCl solutions, *Desalination*, 188 (2006) 251-262.

510 [18] I. Hitsov, T. Maere, K. De Sitter, C. Dotremont, I. Nopens, Modelling approaches in
511 Membrane Distillation: A critical review, *Separation and Purification Technology*, (2014).

512 [19] F. Laganà, G. Barbieri, E. Drioli, Direct contact membrane distillation: modelling and
513 concentration experiments, *Journal of Membrane Science*, 166 (2000) 1-11.

514 [20] M. Khayet, A. Velázquez, J.I. Mengual, Modelling mass transport through a porous
515 partition: effect of pore size distribution, *Journal of Non-Equilibrium Thermodynamics*, 29
516 (2004) 279-299.

517 [21] M. Khayet, Membranes and theoretical modeling of membrane distillation: a review,
518 *Advances in colloid and interface science*, 164 (2011) 56-88.

519 [22] T.-C. Chen, C.-D. Ho, H.-M. Yeh, Theoretical modeling and experimental analysis of direct
520 contact membrane distillation, *Journal of Membrane Science*, 330 (2009) 279-287.

521 [23] J. Phattaranawik, R. Jiraratananon, A. Fane, Heat transport and membrane distillation
522 coefficients in direct contact membrane distillation, *Journal of Membrane Science*, 212 (2003)
523 177-193.

524 [24] V.A. Bui, L. Vu, M. Nguyen, Modelling the simultaneous heat and mass transfer of direct
525 contact membrane distillation in hollow fibre modules, *Journal of Membrane Science*, 353
526 (2010) 85-93.

527 [25] M. Qtaishat, T. Matsuura, B. Kruczek, M. Khayet, Heat and mass transfer analysis in direct
528 contact membrane distillation, *Desalination*, 219 (2008) 272-292.

529 [26] J. Phattaranawik, R. Jiraratananon, A. Fane, Effects of net-type spacers on heat and mass
530 transfer in direct contact membrane distillation and comparison with ultrafiltration studies,
531 *Journal of membrane science*, 217 (2003) 193-206.

532 [27] J. Zhang, J.-D. Li, S. Gray, Effect of applied pressure on performance of PTFE membrane
533 in DCMD, *Journal of Membrane Science*, 369 (2011) 514-525.

534 [28] A. Fane, R. Schofield, C. Fell, The efficient use of energy in membrane distillation,
535 *Desalination*, 64 (1987) 231-243.

- [29] K.K. Sirkar, L. Song, Pilot-Scale Studies for Direct Contact Membrane Distillation-Based Desalination Process, in: USBR (Ed.), 2009.
- [30] Y. Zhang, Y. Peng, S. Ji, Z. Li, P. Chen, Review of thermal efficiency and heat recycling in membrane distillation processes, *Desalination*, 367 (2015) 223-239.
- [31] Y. Henderyckx, Evaporation-condensation recovery of a solution component using vapor-per-meable wall spaced from a cold wall, in, Google Patents, 1971.
- [32] A. Criscuoli, Improvement of the Membrane Distillation performance through the integration of different configurations, *Chemical Engineering Research and Design*, 111 (2016) 316-322.
- [33] V. Alves, I. Coelho, Orange juice concentration by osmotic evaporation and membrane distillation: a comparative study, *Journal of Food Engineering*, 74 (2006) 125-133.
- [34] S. Gunko, S. Verbych, M. Bryk, N. Hilal, Concentration of apple juice using direct contact membrane distillation, *Desalination*, 190 (2006) 117-124.
- [35] S. Nene, S. Kaur, K. Sumod, B. Joshi, K. Raghavarao, Membrane distillation for the concentration of raw cane-sugar syrup and membrane clarified sugarcane juice, *Desalination*, 147 (2002) 157-160.
- [36] A. Alklaibi, N. Lior, Membrane-distillation desalination: status and potential, *Desalination*, 171 (2005) 111-131.
- [37] M. Tomaszewska, M. Gryta, A. Morawski, Study on the concentration of acids by membrane distillation, *Journal of Membrane Science*, 102 (1995) 113-122.
- [38] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, *Desalination*, 287 (2012) 2-18.
- [39] L. Song, Z. Ma, X. Liao, P.B. Kosaraju, J.R. Irish, K.K. Sirkar, Pilot plant studies of novel membranes and devices for direct contact membrane distillation-based desalination, *Journal of Membrane Science*, 323 (2008) 257-270.
- [40] S. Adham, A. Hussain, J.M. Matar, R. Does, A. Janson, Application of membrane distillation for desalting brines from thermal desalination plants, *Desalination*, 314 (2013) 101-108.
- [41] E. Guillen-Burrieza, A. Ruiz-Aguirre, G. Zaragoza, H.A. Arafat, Membrane fouling and cleaning in long term plant-scale membrane distillation operations, *Journal of Membrane Science*, 468 (2014) 360-372.
- [42] A.E. Jansen, J.W. Assink, J.H. Hanemaaijer, J. van Medevoort, E. van Sonsbeek, Development and pilot testing of full-scale membrane distillation modules for deployment of waste heat, *Desalination*, 323 (2013) 55-65.
- [43] P. Wang, T.-S. Chung, Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring, *Journal of Membrane Science*, 474 (2015) 39-56.
- [44] U.K. Kesieme, N. Milne, H. Aral, C.Y. Cheng, M. Duke, Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation, *Desalination*, 323 (2013) 66-74.
- [45] Y. Xu, B.-K. Zhu, Y.-y. Xu, Pilot test of vacuum membrane distillation for seawater desalination on a ship, *Desalination*, 189 (2006) 165-169.
- [46] J.H. Hanemaaijer, J. van Medevoort, A.E. Jansen, C. Dotremont, E. van Sonsbeek, T. Yuan, L. De Ryck, Memstill membrane distillation – a future desalination technology, *Desalination*, 199 (2006) 175-176.

- [47] S. Tavakkoli, O.R. Lokare, R.D. Vidic, V. Khanna, A Systems-level Analysis of Waste Heat Recovery Opportunities from Natural Gas Compressor Stations in the US, ACS Sustainable Chemistry & Engineering, (2016).
- [48] Energy Information Agency, US Natural Gas Pipeline, in.
- [49] INGAA, Natural Gas Pipeline and Storage Infrastructure Pojections Trough 2030 Prepared for INGAA Foundation, Inc. by: ICF International, (2009).
- [50] M. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, Journal of Membrane Science, 285 (2006) 4-29.
- [51] L. Song, B. Li, K.K. Sirkar, J.L. Gilron, Direct Contact Membrane Distillation-Based Desalination: Novel Membranes, Devices, Larger-Scale Studies, and a Model, Industrial & Engineering Chemistry Research, 46 (2007) 2307-2323.
- [52] R.W. Schofield, A.G. Fane, C.J.D. Fell, R. Macoun, Factors affecting flux in membrane distillation, Desalination, 77 (1990) 279-294.
- [53] K.W. Lawson, D.R. Lloyd, Membrane distillation, Journal of membrane Science, 124 (1997) 1-25.
- [54] R.D. Gustafson, J.R. Murphy, A. Achilli, A stepwise model of direct contact membrane distillation for application to large-scale systems: Experimental results and model predictions, Desalination, 378 (2016) 14-27.
- [55] O.R. Lokare, S. Tavakkoli, S. Wadekar, V. Khanna, R.D. Vidic, Fouling in direct contact membrane distillation of produced water from unconventional gas extraction, Journal of Membrane Science, 524 (2017) 493-501.
- [56] G. Guan, X. Yang, R. Wang, R. Field, A.G. Fane, Evaluation of hollow fiber-based direct contact and vacuum membrane distillation systems using aspen process simulation, Journal of Membrane Science, 464 (2014) 127-139.
- [57] F. Macedonio, A. Ali, T. Poerio, E. El-Sayed, E. Drioli, M. Abdel-Jawad, Direct contact membrane distillation for treatment of oilfield produced water, Separation and Purification Technology, 126 (2014) 69-81.
- [58] M.A. Izquierdo-Gil, C. Fernández-Pineda, M. Lorenz, Flow rate influence on direct contact membrane distillation experiments: different empirical correlations for Nusselt number, Journal of Membrane Science, 321 (2008) 356-363.
- [59] K. He, H.J. Hwang, M.W. Woo, I.S. Moon, Production of drinking water from saline water by direct contact membrane distillation (DCMD), Journal of Industrial and Engineering Chemistry, 17 (2011) 41-48.
- [60] C. Shaw, in, Alfa Laval Inc., 2015.
- [61] Y.M. Manawi, M. Khraisheh, A.K. Fard, F. Benyahia, S. Adham, Effect of operational parameters on distillate flux in direct contact membrane distillation (DCMD): Comparison between experimental and model predicted performance, Desalination, 336 (2014) 110-120.
- [62] U.V. Shenoy, Heat exchanger network synthesis: process optimization by energy and resource analysis, Gulf Professional Publishing, 1995.
- [63] T.F. Russell, A.S. Robinson, N.J. Wagner, Mass and heat transfer: analysis of mass contactors and heat exchangers, Cambridge University Press, 2008.
- [64] S.M. Hall, Rules of thumb for chemical engineers, Butterworth-Heinemann, 2012.
- [65] F. He, J. Gilron, K.K. Sirkar, High water recovery in direct contact membrane distillation using a series of cascades, Desalination, 323 (2013) 48-54.

- [66] S. Lin, N.Y. Yip, M. Elimelech, Direct contact membrane distillation with heat recovery: Thermodynamic insights from module scale modeling, *Journal of Membrane Science*, 453 (2014) 498-515.
- [67] M. Khayet, J. Mengual, G. Zakrzewska-Trznadel, Direct contact membrane distillation for nuclear desalination, Part II: experiments with radioactive solutions, *International journal of nuclear desalination*, 2 (2006) 56-73.
- [68] M.S. Khayet, T. Matsuura, *Membrane Distillation : Principles and Applications*, Elsevier Science & Technology, Saint Louis, MO, USA, 2011.
- [69] S. Al-Obaidani, E. Curcio, F. Macedonio, G. Di Profio, H. Al-Hinai, E. Drioli, Potential of membrane distillation in seawater desalination: thermal efficiency, sensitivity study and cost estimation, *Journal of Membrane Science*, 323 (2008) 85-98.
- [70] A. Kayvani Fard, Y.M. Manawi, T. Rhadfi, K.A. Mahmoud, M. Khraisheh, F. Benyahia, Synoptic analysis of direct contact membrane distillation performance in Qatar: A case study, *Desalination*, 360 (2015) 97-107.
- [71] J. Gilron, L. Song, K.K. Sirkar, Design for Cascade of Crossflow Direct Contact Membrane Distillation, *Industrial & Engineering Chemistry Research*, 46 (2007) 2324-2334.
- [72] H. Lee, F. He, L. Song, J. Gilron, K.K. Sirkar, Desalination with a cascade of cross-flow hollow fiber membrane distillation devices integrated with a heat exchanger, *AIChE Journal*, 57 (2011) 1780-1795.
- [73] PADEP, Pennsylvania Department of Environmental Protection, <http://www.depweb.state.pa.us/> (accessed July 15, 2015), (2015).
- [74] PADEP, Pennsylvania Department of Environmental Protection, http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?%2fOil_Gas%2fOil_Gas_Well_Historical_Production_Report (accessed May 15, 2015), (2015).
- [75] D. Yoxtheimer, Appalachian shale energy produced fluids management and UIC well disposal trends, http://www.saferpa.org/Documents/Resources/TechBrief-08-2015/Appalachian-Shale-Energy-Produced-Fluids-Management-UIC-Well-Disposal-Trends_SaferPA-08-20-2015.pdf (accessed May 20, 2015), (2015).