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A thermodynamic perspective to study energy performance of vacuum-based membrane dehumidification

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Abstract

In humid environments, decoupling the latent and sensible cooling loads - dehumidifying - can significantly improve chiller efficiency. Here, a basic limit for dehumidification efficiency is established from fundamental thermodynamics. This is followed by the derivation of how this limit is modified when the pragmatic constraint of a finite flux must be accommodated. These limits allow one to identify promising system modifications, and to quantify their impact. The focus is on vacuum-based membrane dehumidification. New high-efficiency configurations are formulated, most notably, by coupling pumping with condensation. More than an order-of-magnitude improvement in efficiency is achievable. It is contingent on water vapor exiting at its saturation pressure rather than at ambient pressure. Sensitivity studies to recovery ratio, temperature, relative humidity and membrane selectivity are also presented.

Keywords: Vacuum-based membrane dehumidification, dehumidification energy efficiency, coefficient of performance, thermodynamic limit, latent heat

1. INTRODUCTION

Dehumidification can comprise a substantial fraction of cooling loads in hot humid environments. For example, 70-80% of the total energy consumed by a vapor-compression chiller comes from direct cooling at a relative humidity RH of 70-95%. Outdoor air (point O) and return air (point R) are mixed in an air-handling unit (Fig. 1). The mixed air (point M) is then passed over the cooling coil, where both sensible and latent heat are removed. To meet the required humidity for thermal comfort, the surface temperature of the cooling coil is set below the dew point temperature of the supply air. Then, the off-coil air is reheated to raise its temperature (T) and lower its RH (point S). The considerable energy consumption in both the cooling step (when the cooling coil operates at lower surface temperatures) and the reheating step diminishes air-conditioning efficiency [1,2].

This motivates decoupling moisture removal from sensible cooling [1,2]. Efforts to date have been based on solid [3-8] and liquid [4,9-13] desiccant dehumidifiers. These include three-fluid energy exchangers and other novel methods for improving heat and mass transfer [10,12]. The process is illustrated by pathway $M \rightarrow D \rightarrow S$ in Fig. 1. The mixed humid air is first passed through the desiccant module, removing the water vapor. But the exothermic sorption between water vapor and desiccant warms the air stream ($M \rightarrow D$). The air is then cooled to the desired temperature ($D \rightarrow S$) by a conventional vapor compressor chiller. The desiccant is regenerated thermally after each cycle. The Coefficient Of Performance (COP - see Eq. (1) below) of desiccant dehumidification is low because of the excessive energy to regenerate the desiccant at high temperature [4,7,8,14].

This study relates to the strategy of Vacuum-based Membrane Dehumidification (VMD) [14-18], illustrated by path $M \rightarrow I \rightarrow S$ in Fig. 1. Mixed air is first passed over a membrane surface at ambient pressure. A vacuum pressure is applied to the opposite side of the membrane to create a driving force for water permeation. An advantage of VMD is that air is dehumidified isothermally ($M \rightarrow I$). The dried air is cooled to the thermal comfort level with minimal energy consumption ($I \rightarrow S$). No thermal regeneration is needed for continuous operation.

Substantial efforts to develop suitable highly permselective polymeric [17-22], inorganic [14,19,23], liquid [24,25] and mixed matrix [26,27] membranes have been explored. However, precisely how membrane permeance and selectivity affect the *COP* of VMD remains to be elucidated, where, for dehumidification [14,15,18]

$$COP = \frac{\text{latent heat removed}}{\text{energy input}} \quad (1)$$

and is the principal measure of dehumidification efficiency.

The vacuum pump is a critical part of a VMD system. It creates a continuous driving force for water vapor permeation. It also pumps and discharges permeate vapor from the membrane module to ambient pressure. It is essentially the only source of energy consumption in VMD. The key practical limitation in VMD systems to date has been requiring a pump that can handle large volumes of water vapor at high compression ratio (~ 100) [16].

Here, a fundamental thermodynamic approach to answer three important questions is developed. (1) What are the energy efficiency bounds of VMD imposed by thermodynamics? (2) How do the key physical variables affect VMD *COP*? (3) How can substantial improvements in VMD *COP* be realized? Our findings are vital for designing an efficient membrane vacuum system for dehumidification and gas separation.

2. VACUUM-BASED MEMBRANE DEHUMIDIFICATION

2.1 Thermodynamic analysis of ideal gas separation

The incoming humid air, along with the outgoing dry air and water vapor (Fig. 2), can be treated as ideal gases for the temperatures and pressures of common cooling applications. The minimum work input for the complete separation of water vapor from humid air at constant pressure (p) and temperature is the reversible limit [28]:

$$W = -n R T (X_a \ln X_a + X_w \ln X_w) \quad (2)$$

where n is the total number of moles, R is the gas constant, and X_a and X_w are the mole fractions of dry air and water, respectively. Namely, for input humid air with a moles of dry air and x moles of water vapor, for which $X_a = a/(a + x)$ and $X_w = x/(a + x)$:

$$W(x) = -RT \left[a \ln \left(\frac{a}{a+x} \right) + x \ln \left(\frac{x}{a+x} \right) \right]. \quad (3)$$

The impact of distinct separation strategies will now be analyzed. The most efficient dehumidification scheme - an isothermal process at constant atmospheric pressure (1 atm) - is considered first. The separation and condensation processes can be analyzed separately (Fig. 2). Because condensation proceeds at ambient temperature, cooling can be very efficient, representing only a negligible fraction of the total energy consumption.

In a partial separation process, only Δx mol of water vapor are removed. This reduces $W(x)$ by $\Delta W(x)$, which is the minimum work for the reversible separation:

$$W_{min} = \Delta W(x). \quad (4)$$

The latent heat removed (ΔH_{lt}) is proportional to Δx . Hence, the maximum dehumidification COP is

$$COP_{max} = \frac{\Delta H_{lt}}{W_{min}} = \frac{(\text{heat of condensation}) \Delta x}{W_{min}} = \frac{45000 \left(\frac{J}{mol} \right) \Delta x}{\Delta W(x)} \quad (5)$$

Actual systems operate irreversibly at finite flux. This prompts consideration of how COP depends on Recovery Ratio (RR):

$$RR = \frac{\text{water vapor removed}}{\text{water vapor input}} = \frac{\Delta x}{x}. \quad (6)$$

Higher RR means drier product air, greater flux, and therefore lower COP . Figure 3 (a) plots W_{min} as a function of RR . Figure 3 (b) shows corresponding results for COP_{max} . In the limit of vanishing RR , COP_{max} approaches ~ 5.4 (expanded in Supplementary Information 1 (a), which rigorously accounts for the proper limit when two variables each approach 0 but their quotient approaches a finite non-zero value). In the opposite limit of RR approaching 1, COP_{max} approaches ~ 4.2 .

Dehumidification has also been proposed as an alternative to desalination for producing potable water from ambient air. The principal energetic measure is then Specific Energy Consumption SEC (typically in kWh/kg), which is proportional to $1/COP$:

$$SEC = \frac{\text{energy input}}{\text{mass of water removed}} = \frac{\text{heat of condensation}}{COP} = \frac{2500 \left(\frac{J}{kg} \right)}{3600 \left(\frac{J}{kWh} \right) \cdot COP} \quad (7)$$

where the conversion factor in the denominator of Eq. (7) ensures that the units of SEC are kWh/kg.

The minimum energy for water reclamation increases from 0.13 to 0.17 kWh/kg over the full range of RR values (Fig. 3 (b) and Supplementary Information 1 (a)). In contrast, the corresponding SEC limit for seawater desalination is more than two orders of magnitude lower [29,30]. Vacuum-based membrane systems have also been developed for thermally-driven desalination [31] (in contrast to electrically-driven reverse osmosis).

The latent heat and minimum work for calculating COP_{max} strongly depend on the air's water content. The resulting variation of COP_{max} with input RH (as $RR \rightarrow 0$ and $RR \rightarrow 1$) is shown in Fig. 4.

2.2 Thermodynamic analysis of vacuum-based membrane dehumidification

The isothermal separation of water vapor from air requires membranes with high water vapor permeability and selectivity. A cross-flow membrane dehumidifier is shown in Fig. 5 (a). Its pressure profile is drawn in Fig. 5 (b). Humid air is passed over the membrane at ambient pressure, p_{amb} . A vacuum pressure, p_{vac} , is applied on the permeate side of the membrane. This creates a driving force for water vapor to be selectively sieved out of the air stream, pumped, and discharged to ambient. In practice, there is a pressure loss through the membrane, reducing the driving force for water vapor permeation. The apparent driving force, Δp_w , is smaller than the difference $p_w - p_{vac}$ (Fig. 5 (b)). This pressure drop is caused by concentration polarization and flow maldistribution, depending on the specific membrane material structure and configuration [32-34]. However, a negligible pressure loss is adopted here in order to ascertain limiting performance.

The water vapor partial pressure (p_w) decreases along the membrane. With sufficient contact time between the feed air and the membrane, p_w can reach the vacuum pressure at the outlet. Lowering p_{vac} leads to more water vapor being removed and hence drier product air.

The energy flows for VMD are indicated in Fig. 5 (c). The major energetic virtue of VMD is condensing water at ambient temperature. The cooling process can then be highly efficient while using standard components only. The energy consumption for cooling the condenser is not taken into account in evaluating the *COP* of conventional vapor-compression chillers - a convention also used here.

The work input is the electrical energy to compress water vapor from p_{vac} to p_{amb} . The pump works most efficiently in an isothermal process, and far less efficiently in an isentropic process. In reality, the pump drives a polytropic process. To appreciate the *COP* limits, the two extremes of isothermal ($T = \text{constant}$ and $pV = \text{constant}$) and isentropic ($pV^{k_w} = \text{constant}$) operation are considered:

$$COP_{iso} = \frac{\Delta H_{lt}}{W_{iso}} = \frac{45000 \left(\frac{\text{J}}{\text{mol}} \right)}{RT \ln \frac{p_{amb}}{p_{vac}}} \quad (8a)$$

$$COP_{isen} = \frac{\Delta H_{lt}}{W_{isen}} = \frac{45000 \left(\frac{\text{J}}{\text{mol}} \right)}{\frac{k_w RT}{k_w - 1} \left[\left(\frac{p_{amb}}{p_{vac}} \right)^{\frac{k_w - 1}{k_w}} - 1 \right]} \quad (8b)$$

where k_w is the specific heat ratio and V denotes volume.

For negligible pump inefficiency and a perfectly selective membrane, the maximum *COP* for isothermal and isentropic VMD (COP_{iso} and COP_{isen}) is plotted in Fig. 6 as a function of *RR*. VMD via isothermal compression is closest to the limiting process in Fig. 2. COP_{iso} approaches COP_{max} as $RR \rightarrow 0$ (Supplementary Information 1 (b)). The increase in COP_{iso} with T and with specific humidity (ω) is presented in Supplementary Information 2, and is consistent with the results shown in Fig. 4.

Next, the sensitivity of VMD efficiency to membrane selectivity S is considered. When S is finite, air permeation must be considered. For membrane permeances P_w and P_a to water and air:

$$S = \frac{P_w}{P_a}. \quad (9)$$

Along a membrane length increment dl (Fig. 7), the air and water fluxes are, respectively:

$$df_a = P_a \Delta p_a dl \quad (10a)$$

$$df_w = P_w \Delta p_w dl. \quad (10b)$$

The ratio of water vapor partial pressure to air partial pressure on the permeate side is equal to the ratio of water flux to air flux:

$$\frac{p_{w2}}{p_{a2}} = \frac{df_w}{df_a} = S \frac{p_{w1} - p_{w2}}{p_{a1} - p_{a2}}. \quad (11)$$

From Eq. (11) and the boundary conditions for water vapor partial pressure at the entrance and exit, a 1D model is considered. Water and air fluxes through the entire membrane are then:

$$F_w = \int df_w dl = P_w \int (p_{w1} - p_{w2}) dl \quad (12a)$$

$$F_a = \int df_a dl = P_a \int (p_{a1} - p_{a2}) dl. \quad (12b)$$

Figure 8 (a) shows the effect of membrane selectivity on RR as a function of p_{vac} . Figure 8 (b) illustrates how COP_{iso} varies with RR , and includes the sensitivity to S , with COP_{iso} not vanishing for any of the curves in the limit of $RR \rightarrow 0$ or $RR \rightarrow 1$. Lower p_{vac} leads to a higher driving force for water vapor permeation and to a higher RR . At lower S , a larger fraction of air permeates the membrane. This reduces the water vapor partial pressure on the permeate side. A greater driving force for permeation is then created (Supplementary Information 3). High RR can then be obtained even at $p_{vac} > p_{w/input}$. In addition, lower S results in higher RR . A similar observation was reported in [18]. The dehumidification COP is obtained from the water and air fluxes, from Eq. (8a):

$$COP_{iso} = \frac{45000 \left(\frac{J}{mol} \right) F_w}{RT(F_w + F_a) \ln \left(\frac{p_{amb}}{p_{vac}} \right)}. \quad (13)$$

Dehumidification COP is independent of the membrane's water vapor permeability, and instead strongly depends on S (Eqs. (11)-(13) and Fig. 8). The fact that higher RR is obtained at lower S does not mean that poorer selectivity implies higher energy efficiency. The reason is that there is a large energy requirement for pumping the unusable permeated air. COP peaks as a function of RR (Fig. S.3 in Supplementary Information 4) - consistent with the results reported in [18]. One valuable conclusion

from these results is that higher S reduces the required membrane area, and therefore reduces the capital cost. Also, higher S increases dehumidification COP , and therefore decreases operation costs.

In Fig. 8 (b) - which re-plots the results for COP_{iso} from Fig. S.3 so as to show its explicit dependence on RR - all the curves exhibit a local minimum at sufficiently low RR (except for limit of infinite S). This local minimum - arising from competing effects delineated in Supplementary Information 4 - occurs at a sufficiently small value of RR as to be imperceptible for membranes with high S values, but becomes evident for the lowest S values considered (100 and 50). Results are included for S as low as 50 in order to provide the full perspective, even though commercial off-the-shelf membranes of considerably higher S values are readily procurable.

2.3 Engineering solutions to improve VMD energy efficiency

The COP of VMD - even in the best-case scenario of isothermal compression - falls below the constrained thermodynamic limit, increasingly so as RR increases (Fig. 6). The shortfall follows from the loss of input work, resulting from only one vacuum pressure being applied to the entire membrane. This work loss can be reduced. The vacuum pressure profile applied to the permeate side should be as close to the water vapor partial pressure profile on the feed side of the membrane as possible.

This prompts trying to improve VMD efficiency by two engineering solutions: (1) a multi-stage process (Fig. 9), and (2) a closed-loop configuration (Fig. 10). Both solutions have been proposed for seawater desalination [30,31], but never explored for dehumidification.

In a multi-stage process, the membrane module is divided into several independent stages. Figure 9 (a) illustrates a two-stage system. The pressure is varied stepwise so as to achieve the highest COP in each stage. The work loss, as well as the work input, can then be reduced significantly (Fig. 9 (b)). By increasing the number of stages, the vacuum pressure profile approaches the feedwater vapor partial pressure profile. Then COP_{iso} for VMD can approach the thermodynamic limit.

In the closed-loop configuration (Fig. 10), humid air is circulated through the membrane module several times before it exits and is replaced by fresh humid air. The pressure level in each loop is reduced until the desired RR is obtained. Similarly, increasing the number of loops increases COP_{iso} . However, even with these improvements, the VMD COP does not prominently exceed that of today's best commercial vapor-compression chillers. Therefore, this line of analysis is not considered further.

Rather, serious consideration of VMD technology necessitates roughly an order-of-magnitude improvement in COP . The underlying thermodynamics points the way - elaborated in the following section. Specifically, because water vapor is a condensable gas with a low saturation pressure, it is proposed that VMD be coupled with a condensing unit. Then the pressure ratio of the vacuum pump can be reduced dramatically, with an attendant prodigious increase in COP .

3 COUPLING PUMPING AND CONDENSATION

In this section, a modified VMD strategy with the potential of an order-of-magnitude improvement in COP is elucidated.

3.1 Thermodynamic analysis

The limiting COP_{max} for air-water vapor separation (Figs. 3 and 4) was derived via an isothermal process in which pure water is obtained at ambient pressure. This engenders a minimum work input, W_{min} . But if pure water can be obtained at its saturation pressure p_{sat} (Fig. 11), then the work input can be lowered appreciably to W'_{min} (Eqs. (3)-(4)). This is due to not having to compress water vapor from p_{sat} to p_{amb} . The energy efficiency of this modified process is:

$$COP'_{max} = \frac{\Delta H_{lt}}{W'_{min}} = \frac{45000 \left(\frac{J}{mol} \right) \Delta x}{W_{min} - RT \Delta x \ln \left(\frac{p_{amb}}{p_{sat}} \right)}. \quad (14)$$

COP'_{max} and its corresponding SEC_{min} are graphed in Fig. 12. The difference between the separation processes portrayed in Figs. 3 and 12 is that water vapor is separated at different pressures. In Fig. 2, it is ambient pressure p_{amb} . In Fig. 11, it is the water saturation pressure p_{sat} . A derivation and

evaluation of the different functions for *COP* and *SEC* plotted in Fig. 12 are presented in Supplementary Information 1 (c).

The striking result is that an order-of-magnitude improvement in *COP* (Fig. 12 (a)) and in *SEC* (Fig. 12 (b)), is possible at practical *RR* values if water is removed at p_{sat} instead of p_{amb} .

3.2 Realizing maximum performance

The high efficiency of the process in Fig. 11 is method-independent and represents its thermodynamic limit. This process can realistically be achieved with the modified VMD system displayed schematically in Fig. 13. The permeated gas and vapor are compressed by pump 1 to the condenser pressure, p_{cond} , which is slightly above p_{sat} at the condenser temperature T_{cond} . When the water vapor is pumped to or above p_{sat} , it condenses to a liquid. The liquid has a much higher density, and hence does not contribute to the pressure accumulation inside the condenser. Pump 2 contributes only marginally to the work for creating and sustaining the condenser's operating pressure. The condenser can be designed to connect with a container that stores the condensed water. When it is full, this container can be disconnected, and the water can be discharged. The work of pump 2 to evacuate the container can be negligible. The reason is that the volume of the container is very small compared to the volume of the water vapor.

Since condensation takes place at ambient temperature, it is not necessary to use an energy-intensive chiller for the cooling process. A conventional cooling tower can suffice. The system's *COP* can be obtained from the electricity for the two pumps. For example, the *COP* with isothermal compression (derived in Supplementary Information 1 (d)) is:

$$COP'_{iso} = \frac{45000\left(\frac{J}{mol}\right) F_w}{RT(F_w + F_a) \ln\left(\frac{p_{cond}}{p_{vac}}\right) + RT_{cond}(F_w - F_{cond} + F_a) \ln\left(\frac{p_{amb}}{p_{cond}}\right)}. \quad (15)$$

Results for the corresponding VMD system of Fig. 13 are presented in Fig. 14 (for a pump efficiency of 100%). Figure 14 (a) plots *COP* for VMD with infinite membrane selectivity, for which $p_{cond} = p_{sat}$.

Figure 14 (b) accentuates that greater power is required to pump the permeate water vapor to p_{sat} at higher T_{cond} .

When S is finite, p_{cond} must be higher than p_{sat} . This is required for water condensation, due to the air content in the permeate gas. One can then readily compute the p_{cond} value at which COP is maximized (Supplementary Information 5). When S exceeds $\sim 10^4$ (attainable with current membranes as shown in Supplementary Information 6), COP can well exceed that of state-of-the-art vapor compression chillers (Fig. 14 (c)). Higher S has the added advantage of reducing operating costs.

The COP of our modified VMD is below the thermodynamic limit (Fig. 14 (a)). The thermodynamic limit can be approached by introducing a multi-stage process and a closed-loop configuration (Fig. 15), albeit at higher capital cost. In the absence of the experimental realization of even the single-stage open-loop design, these possibilities are simply noted. Detailed evaluation is deferred to future investigations.

4 CONCLUSIONS

Thermodynamic bounds for dehumidification efficiency have been established here. This allows assessing the room for improvement of any given system. It also illuminates the physical bases for superior strategies. For example, water is commonly removed from the input humid air at ambient pressure. This severely restricts the attainable coefficient of performance, which then is not patently superior to current vapor compression chillers.

The advantages of relaxing the constraint on exit water vapor partial pressure have been expounded. Permitting that pressure to reach its saturation value allows a dramatic reduction in the input energy. There is a concomitant order-of-magnitude improvement in dehumidification efficiency.

Here, the focus is on vacuum-based membrane dehumidification (VMD). Sensitivity studies subsumed recovery ratio, temperature, relative humidity and membrane selectivity. Basic thermodynamics indicates that our approach should offer massive increases in COP . This is equivalent

to sizable decreases in specific energy consumption. A key element is coupling pumping and condensation so that water vapor exits at its saturation pressure.

Finally, the analysis has been strictly thermodynamic. Namely, there is no pretense of economic optimization. Nonetheless, one could ask why finite values of recovery ratio should be considered if only the limit of vanishing recovery ratio yields maximum efficiency. However, the limit of vanishing flux is decidedly uneconomical. Cost factors unrelated to the coefficient of performance shift system design to higher recovery ratio. There is a tradeoff, because efficiency worsens as recovery ratio increases. All this has been derived and quantified here. These results point the way to dramatic performance improvements in realistic dehumidifiers.

Nomenclature

COP	Coefficient of performance
COP_{max}	Thermodynamic limit for COP
COP_{iso}	Maximal COP of VMD with isothermal compression
COP_{isen}	Maximal COP of VMD with isentropic compression
F_w, F_a	Water vapor flux and air flux, respectively
F_{cond}	Water vapor condensation flux in the condenser
df_w, df_a	Differentials of water vapor flux and air flux, respectively
ΔH_{lt}	Latent heat removed
k_w	Specific heat ratio
dl	Length differential
n	Number of moles
p	Total pressure
p_w	Water vapor partial pressure
$p_{w/input}$	Water vapor partial pressure of input humid air
p_{w1}, p_{a1}	Partial pressure of water vapor and feed air, respectively.
p_{w2}, p_{a2}	Partial pressures of water vapor and permeate air, respectively.
p_{amb}	Ambient pressure
p_{sat}	Water vapor saturation pressure
p_{vac}	Vacuum pressure applied on the permeate side of the membrane

297	p_{cond}	Pressure at the condenser
298	$\Delta p_w, \Delta p_a$	Difference in partial pressure between the feed and permeate sides, for water
299		vapor and air, respectively
300	P_w, P_a	Membrane water vapor permeance and air permeance, respectively
301	R	Gas constant
302	RH	Relative humidity
303	RR	Recovery ratio
304	ω	Specific humidity
305	S	Membrane selectivity
306	SEC	Specific energy consumption
307	SEC_{min}	Minimum SEC corresponding to COP_{max}
308	T	Temperature
309	T_{cond}	Condenser temperature
310	VMD	Vacuum-based membrane dehumidification
311	W	Work to completely separate an ideal-gas mixture at constant T and p
312	W_{min}	Minimum work for a partial isothermal dehumidification of air
313	$W(x)$	W as a function of x
314	$\Delta W(x)$	Decrease in $W(x)$ corresponding to a decrease of Δx in x
315	x, a	Number of moles of water vapor and air, respectively
316	Δx	Amount of water vapor removed from the humid air stream
317	X_a, X_w	Mole fractions of air and water vapor, respectively
318	' (prime superscript)	Denotes processes with water vapor separated at p_{sat} instead of p_{amb}

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Supplementary Information 1:

(a) Thermodynamic limit as RR approaches 0

Since RR approaches 0 as Δx approaches 0 (Eq. (6)), COP_{max} in this limit can be expressed as:

$$COP_{max}|_{RR \rightarrow 0} = \frac{45000 \left(\frac{J}{mol} \right)}{\left. \frac{\Delta W(x)}{\Delta x} \right|_{\Delta x \rightarrow 0}}. \quad (S.1)$$

$\left. \frac{\Delta W(x)}{\Delta x} \right|_{\Delta x \rightarrow 0}$ is the derivative of $W(x)$, which has a finite, non-zero limit as Δx approaches 0:

$$\left. \frac{\Delta W(x)}{\Delta x} \right|_{\Delta x \rightarrow 0} = -RT \ln \frac{x}{a+x} = RT \ln \frac{a+x}{x} \quad (S.2)$$

with which

$$COP_{max}|_{RR \rightarrow 0} = \frac{45000 \left(\frac{kJ}{mol} \right)}{RT \ln \frac{a+x}{x}} = \frac{45000 \left(\frac{J}{mol} \right)}{RT \ln \frac{P_{amb}}{P_{w/input}}}. \quad (S.3)$$

At $T = 30^\circ\text{C}$ and $RH = 30\%$ (the conditions used for Fig. 2), $p_{w/input} = 38.2$ mbar and $p_{amb} = 1013.25$ mbar. Then Eq. (S.3) yields $COP_{max}|_{RR \rightarrow 0} = 5.4466$, and Eq. (7) yields a corresponding $SEC_{min}|_{RR \rightarrow 0} = 0.1275$ kWh/kg. In Fig. 3 (b), the dependence of COP_{max} and SEC_{min} on RR is plotted on the left-hand and right-hand ordinates, respectively.

(b) Maximal COP for VMD with isothermal compression as RR approaches 0

For arbitrary recovery ratio:

$$RR = \frac{\text{water vapor removed}}{\text{water vapor input}} = \frac{P_{w/input} - P_{vac}}{P_{w/input}} \quad (S.4)$$

$$P_{vac} = P_{w/input} (1 - RR). \quad (S.5)$$

Therefore, Eq. (8a) becomes

$$COP_{iso} = \frac{\Delta H_{lt}}{W_{iso}} = \frac{45000 \left(\frac{J}{mol} \right)}{RT \ln \frac{P_{amb}}{P_{w/input} (1-RR)}}. \quad (S.6)$$

As RR approaches 0:

$$COP_{iso}|_{RR \rightarrow 0} = \frac{45000 \left(\frac{J}{mol} \right)}{RT \ln \frac{P_{amb}}{P_{w/input}}} \quad (S.7)$$

$$\Rightarrow COP_{iso}|_{RR \rightarrow 0} = COP_{max}|_{RR \rightarrow 0}. \quad (S.8)$$

(c) Derivation of COP when water vapor is separated at different pressures

The separation processes in Figs. 2 and 11 differ in the pressure at which water vapor is separated: ambient pressure p_{amb} for the former, and the water saturation pressure p_{sat} for the latter. The difference between the minimum work for the two processes is the compression of permeated water vapor from p_{sat} to p_{amb} :

$$W'_{min} = W_{min} - RT\Delta x \ln(p_{amb}/p_{sat}) . \quad (S.9)$$

The corresponding COP is given by Eq. (14). Since RR approaches 0 when Δx approaches 0, Eq. (14) becomes

$$COP'_{max}|_{RR \rightarrow 0} = \frac{45000 \left(\frac{J}{mol}\right)}{\frac{\Delta W(x)}{\Delta x}|_{\Delta x \rightarrow 0} - RT \ln(p_{amb}/p_{sat})} . \quad (S.10)$$

Now substituting Eq. (S.2) into Eq. (S.10) yields

$$COP'_{max}|_{RR \rightarrow 0} = \frac{45000 \left(\frac{J}{mol}\right)}{RT \ln(p_{sat}/p_{input})} . \quad (S.11)$$

At $T = 30^\circ\text{C}$ and $RH = 90\%$ (as in Fig. 11 and used for Fig. 12), $p_{sat} = 42.4$ mbar and $p_{w/input} = 38.2$ mbar. Then Eq. (S.11) yields $COP_{max}|_{RR \rightarrow 0} = 171$, with the corresponding SEC from Eq. (7) being $SEC_{min}|_{RR \rightarrow 0} = 4.06$ kWh/kg.

(d) Derivation of COP_{iso}

Equation (15) for COP_{iso} for the dehumidification process of Fig. 11 will now be derived. In Fig. 11, the air-water mixture is pumped by pump 1 from p_{vac} to p_{cond} . For isothermal compression, the pump's work consumption is

$$W_{pump1} = RT(F_w + F_a) \ln(p_{cond}/p_{vac}) . \quad (S.12)$$

At the condenser, part of the water vapor is condensed at flow rate F_{cond} . The rest of the air-water mixture leaving the condenser is pumped by pump 2 from p_{cond} to p_{amb} . Its work consumption is

$$W_{pump2} = RT_{cond}(F_w + F_a - F_{cond}) \ln(p_{amb}/p_{cond}) . \quad (S.13)$$

The latent heat removed in the process is

$$\Delta H_{lt} = 45000 \left(\frac{kJ}{mol}\right) F_w . \quad (S.14)$$

Combining Eq. (14) with Eqs. (S.12)-(S.14) and accounting for the work input of both pumps yields Eq. (15):

$$COP_{iso} = \frac{\Delta H_{lt}}{W_{iso}} = \frac{\Delta H_{lt}}{W_{pump1} + W_{pump2}} = \frac{45000 \left(\frac{J}{mol} \right) F_w}{RT(F_w + F_a) \ln\left(\frac{p_{cond}}{p_{vac}}\right) + RT_{cond}(F_w + F_a - F_{cond}) \ln\left(\frac{p_{amb}}{p_{cond}}\right)} \quad (S.15)$$

Supplementary Information 2:

Fig. S.1:

Supplementary Information 3:

Fig. S.2:

Supplementary Information 4:

Fig. S.3:

COP_{iso} possess a maximum because the water flux increases and then decreases with lower vacuum pressure (also illustrated in Fig. S.4). With $p_{vac} < 350$ mbar, COP_{iso} peaks at around $p_{w/input}$ and increases with S . At $p_{vac} > 350$ mbar, COP_{iso} is basically independent of S and increases with p_{vac} . The rise of COP_{iso} at $p_{vac} > 350$ is because of the low energy input for the required compression ratio (Eq. 8 (a)), and local minima occur at $p_{vac} \approx 350-400$ mbar. At $p_{vac} > 350$ mbar, COP_{iso} has little practical significance because RR then approaches 0. This point is sharpened in Fig. 8 (b) where COP_{iso} is graphed against RR .

Fig. S.4:

Supplementary Information 5:

Fig. S.5:

Supplementary Information 6:

Table S.1:

Reference for Supplementary Information 6.

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Figure captions:

Fig. 1: Psychrometric chart. Air-conditioning processes are indicated, from mixed air (point M, mixing return air at point R and outdoor air at point O) to supply air (point S). With a conventional air-handling unit, the path is $M \rightarrow \text{off-coil} \rightarrow S$. Using a desiccant, $M \rightarrow D \rightarrow S$. Using vacuum-based membrane dehumidification, $M \rightarrow I \rightarrow S$.

Fig. 2: Schematic of the separation process at constant T and p , for parameters common to cooling in humid environments.

Fig. 3: (a) Sensitivity of W_{min} to RR for the conditions noted in Fig. 2. (b) The maximum COP and minimum SEC for water removal from air, as functions of RR (double-ordinate plot).

Fig. 4: Variation of COP_{max} with RH at fixed $T = 30^\circ\text{C}$, in the limits of RR approaching 0 and 1.

Fig. 5: Schematic of (a) cross-flow VMD, (b) the water vapor pressure profile along the membrane and (c) the flow of liquid water and water vapor.

Fig. 6: COP as a function of RR for VMD with isothermal vs. isentropic compression. The environmental conditions are the same as in Fig. 2. The corresponding method-independent limit for ideal-gas separation from Fig. 3 (b) (COP_{max}) is included for comparison.

Fig. 7: Water vapor and air partial pressure profiles on both sides of the membrane when S is small. The inset indicates pressure conditions on both sides of the membrane.

Fig. 8: (a) The effect of membrane selectivity S on (a) RR as a function of p_{vac} , with the vertical dotted line indicating the input water vapor partial pressure; and (b) maximal COP via isothermal compression as a function of RR (at $T = 30^\circ\text{C}$ and $RH = 90\%$).

Fig. 9: Schematic of (a) a two-stage configuration and (b) the corresponding pressure profile.

Fig. 10: Schematic of (a) a closed-loop configuration and (b) the pressure profile of the water vapor, p_w , in a three-loop system.

Fig. 11: Schematic of an isothermal separation process, but with water vapor being separated at its saturation pressure (rather than at atmospheric pressure).

Fig. 12: (a) COP'_{max} and (b) SEC'_{min} for water removal, for the process portrayed in Fig. 11, where water is removed at p_{sat} . For comparison, COP_{max} and SEC_{min} are presented for the process depicted in Fig. 2, where water removal proceeds at p_{amb} .

Fig. 13: Schematic of a VMD design with coupling between pumping and condensation.

Fig. 14: Effects of (a) compression strategy, (b) condensing temperature (with isothermal compression and $S \rightarrow \infty$), and (c) membrane selectivity (with isothermal compression and $T_{cond} = 35^\circ\text{C}$), on maximum COP for the VMD design that couples pumping and condensation.

Fig. 15: Schematics of a (a) multi-stage and (b) closed-loop configuration for the design that couples pumping and condensation.

Fig. S.1: Sensitivity of COP_{max} for VMD via isothermal compression to (a) T (at $\omega = 20$ g/kg) and (b) ω (at $T = 30^\circ\text{C}$).

Fig. S.2: The profiles of water vapor partial pressure on the feed and permeate sides when membrane selectivity, S , varies. F_w is proportional to the shaded area between p_{w1} and p_{w2} . The driving force for water vapor permeation increases with lower membrane selectivity.

Fig. S.3: Dependence of COP_{iso} on vacuum pressure, p_{vac}

Fig. S.4: The profile of water vapor partial pressure on the feed and permeate sides when vacuum pressure p_{vac} varies. Membrane selectivity $S = 10000$. F_w is proportional to the shaded area between p_{w1} and p_{w2} . F_w increases and then decreases when vacuum pressure decreases from 40 to 1 mbar.

Fig. S.5: p_{cond} at which COP is maximized as a function of RR for a broad range of S values.

Table caption

Table S. 1: Several composite membranes with high water vapor permeance and selectivity for air dehumidification

540

Figures:

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Fig. 1:

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Fig. 2:

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Fig. 3

Fig. 4:

Fig. 5:

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Fig. 7:

Fig. 8:

Fig. 9:

Fig. 10:

Fig. 11:

Fig. 12:

Fig. 13:

Fig. 14:

(a)

(b)

Fig. 15:

Fig. S.1:

Fig. S.2:

Fig. S.3:

Fig. S.4:

Fig. S.5:

Table

Table S.1:

Active layer material	membrane structure	Water vapor	Selectivity	Ref.
SPEEK	A 2–5 μm -thick top layer on polyethersulfone microfiltration hollow fiber (OD = 1.2 mm, ID = 0.8 mm)	1500-2500	115000-192000 (N_2)	[1]
PVA/gelatin–silica	The top layer is dip-coated on porous polysulfone hollow fiber substrate. [ID=150 μm ; OD=350 μm]	4.1-15	2980-67511 [C_3H_6]	[2]
Ionic liquids [emim][Tf2N] [N[4]111][Tf2N] [emim][BF4]	The ionic liquids are spread over hydrophilic polyethersulfone [PES] flat substrate with a thickness of 132 μm	635 570 1050	3843(N_2) 3290(N_2) 16300(N_2)	[3]
PVA/gelatin–silica	The top layer is dip-coated on porous polysulfone hollow fiber substrate. Skin layer 2 μm .	2390-5380	>15000 [C_3H_6]	[4]
Pebax®1657	A 2 mm-thick Pebax® 1657 layer on an intermediate microporous support on a flat-sheet polyester substrate	1800 [with substrate] 6000 [without substrate]	1800(N_2) 6000(N_2)	[5]
PVA/LiCl blend	Intermediate TiO_2 powder layer and PVA/LiCl top layer are consecutively coated on a fine stainless steel wire mesh	1790-4780	1000-5000 (air)	[6]
TEG PEG	50 μm top layer is supported on a highly hydrophobic flat substrate [pore size = 0.1 μm , thickness = 125 μm ; and porosity = 70%]	180-270 150	1700-2500(N_2) 2000(N_2)	[7]
TEG	18 μm TEG liquid layer spreads, wets and then soaks on the top hydrophilicized surface of a flat hydrophobic substrate [0.1 μm micropores and 95 μm thickness].	706	2420(N_2)	[8]

1 GPU = $3.348 \times 10^{-10} \text{ mol/s m}^2 \text{ Pa}$

Highlights

- Prodigious efficiency gains in Vacuum-based Membrane Dehumidification (VMD)
- Thermodynamic perspective unifying the evaluation of dehumidification methods
- Novel high-efficiency VMD strategies stemming from basic thermodynamics