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 \( \text{COP} \) of VMD remains to be elucidated, where, for dehumidification [14,15,18]

\[
\text{COP} = \frac{\text{latent heat removed}}{\text{energy input}}
\]  

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 \( \text{COP} \)? (3) How can substantial improvements in VMD \( \text{COP} \) 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]:

\[
W = -n \, R \, T \, (X_a \ln X_a + X_w \ln X_w)
\]  

(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 \( X_w = x/(a + x) \):

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

(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 \( \Delta x \) mol of water vapor are removed. This reduces \( W(x) \) by \( \Delta W(x) \), which is the minimum work for the reversible separation:

\[
W_{\text{min}} = \Delta W(x).
\]  

(4)

The latent heat removed (\( \Delta H_{\text{lt}} \)) is proportional to \( \Delta x \). Hence, the maximum dehumidification \( \text{COP} \) is

\[
\text{COP}_{\text{max}} = \frac{\Delta H_{\text{lt}}}{W_{\text{min}}} = \frac{(\text{heat of condensation}) \Delta x}{W_{\text{min}}} = \frac{45000 \left( \frac{J}{\text{mol}} \right) \Delta x}{\Delta W(x)}
\]  

(5)

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

\[
RR = \frac{\text{water vapor removed}}{\text{water vapor input}} = \frac{\Delta x}{x}.
\]  

(6)

Higher \( RR \) means drier product air, greater flux, and therefore lower \( \text{COP} \). Figure 3 (a) plots \( W_{\text{min}} \) as a function of \( RR \). Figure 3 (b) shows corresponding results for \( \text{COP}_{\text{max}} \). In the limit of vanishing \( RR \), \( \text{COP}_{\text{max}} \) 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, \( \text{COP}_{\text{max}} \) 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 \( 1/COP \):

\[
SEC = \frac{\text{energy input}}{\text{mass of water removed}} = \frac{\text{heat of condensation}}{COP} = \frac{2500 \left( \frac{1}{\text{kg}} \right)}{3600 \left( \frac{1}{\text{kWh}} \right) \cdot COP} \tag{7}
\]

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 \( COP_{\text{max}} \) strongly depend on the air’s water content. The resulting variation of \( COP_{\text{max}} \) with input \( RH \) (as \( RR \to 0 \) and \( RR \to 1 \)) 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, \( p_{\text{amb}} \). A vacuum pressure, \( p_{\text{vac}} \), 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, \( \Delta p_{w} \), is smaller than the difference \( p_{w} - p_{\text{vac}} \) (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 = $ constant and $pV = $ constant) and isentropic ($pV^{k_w} = $ constant) operation are considered:

$$COP_{iso} = \frac{\Delta H_{lt}}{W_{iso}} = \frac{45000}{RT\ln\frac{p_{amb}}{p_{vac}}}$$

$$COP_{isen} = \frac{\Delta H_{lt}}{W_{isen}} = \frac{45000}{k_w RT\left[\frac{k_w}{k_w - 1}\right]}$$

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 $RR \to 0$ (Supplementary Information 1 (b)). The increase in $COP_{iso}$ with $T$ and with specific humidity ($\omega$) 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:

$$S = \frac{P_w}{P_a}.$$
Along a membrane length increment $dl$ (Fig. 7), the air and water fluxes are, respectively:

\[ df_a = P_a \Delta p_a \, dl \]  
\[ df_w = P_w \Delta p_w \, dl. \]  

(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:

\[ \frac{p_w}{p_a} = \frac{df_w}{df_a} = S \frac{p_w^1 - p_w^2}{p_a^1 - p_a^2}. \]  

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:

\[ F_w = \int df_w \, dl = P_w \int (p_w^1 - p_w^2) \, dl \]  
\[ F_a = \int df_a \, dl = P_a \int (p_a^1 - p_a^2) \, dl. \]

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 $RR \to 0$ or $RR \to 1$. 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):

\[ COP_{iso} = \frac{45000 \left( \frac{1}{m} \right) F_w}{RT(F_w + F_a) \ln \left( \frac{P_{amb}}{P_{vac}} \right)}. \]

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:

$$COP'_{max} = \frac{\Delta H_T}{W_{min}} = \frac{45000 \left( \frac{J}{mol} \right) \Delta x}{W_{min} (RT \Delta x \ln \frac{p_{amb}}{p_{sat}})}.$$  \hspace{1cm} (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 \( \text{COP} \) and \( \text{SEC} \) plotted in Fig. 12 are presented in Supplementary Information 1 (c).

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

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, \( p_{\text{cond}} \), which is slightly above \( p_{\text{sat}} \) at the condenser temperature \( T_{\text{cond}} \). When the water vapor is pumped to or above \( p_{\text{sat}} \), 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 \( \text{COP} \) can be obtained from the electricity for the two pumps. For example, the \( \text{COP} \) with isothermal compression (derived in Supplementary Information 1 (d)) is:

\[
\text{COP}'_{\text{iso}} = \frac{45000 \left( \frac{1}{\text{mol}} \right) F_{W}}{RT(F_{W}+F_{G}) \ln \left( \frac{p_{\text{cond}}}{p_{\text{sat}}} \right) + RT_{\text{cond}}(F_{W} - F_{\text{cond}} + F_{A}) \ln \left( \frac{p_{\text{amb}}}{p_{\text{cond}}} \right)}.
\]  \hspace{1cm} (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 \( \text{COP} \) for VMD with infinite membrane selectivity, for which \( p_{\text{cond}} = p_{\text{sat}} \).
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
- $COP_{\text{max}}$ Thermodynamic limit for $COP$
- $COP_{\text{iso}}$ Maximal $COP$ of VMD with isothermal compression
- $COP_{\text{isen}}$ Maximal $COP$ of VMD with isentropic compression
- $F_{w}$, $F_{a}$ Water vapor flux and air flux, respectively
- $F_{\text{cond}}$ Water vapor condensation flux in the condenser
- $df_{w}$, $df_{a}$ Differentials of water vapor flux and air flux, respectively
- $\Delta H_{lt}$ Latent heat removed
- $k_{w}$ Specific heat ratio
- $dl$ Length differential
- $n$ Number of moles
- $p$ Total pressure
- $p_{w}$ Water vapor partial pressure
- $p_{w/\text{input}}$ 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.
- $p_{\text{amb}}$ Ambient pressure
- $p_{\text{sat}}$ Water vapor saturation pressure
- $p_{\text{vac}}$ Vacuum pressure applied on the permeate side of the membrane
\( p_{\text{cond}} \) Pressure at the condenser
\( \Delta p_w, \Delta p_a \) Difference in partial pressure between the feed and permeate sides, for water vapor and air, respectively
\( P_w, P_a \) Membrane water vapor permeance and air permeance, respectively
\( R \) Gas constant
\( RH \) Relative humidity
\( RR \) Recovery ratio
\( \omega \) Specific humidity
\( S \) Membrane selectivity
\( SEC \) Specific energy consumption
\( SEC_{\text{min}} \) Minimum SEC corresponding to \( COP_{\text{max}} \)
\( T \) Temperature
\( T_{\text{cond}} \) Condenser temperature
\( VMD \) Vacuum-based membrane dehumidification
\( W \) Work to completely separate an ideal-gas mixture at constant \( T \) and \( p \)
\( W_{\text{min}} \) Minimum work for a partial isothermal dehumidification of air
\( W(x) \) \( W \) as a function of \( x \)
\( \Delta W(x) \) Decrease in \( W(x) \) corresponding to a decrease of \( \Delta x \) in \( x \)
\( x, a \) Number of moles of water vapor and air, respectively
\( \Delta x \) Amount of water vapor removed from the humid air stream
\( X_a, X_w \) Mole fractions of air and water vapor, respectively

\'(prime superscript)\' Denotes processes with water vapor separated at \( p_{\text{sat}} \) instead of \( p_{\text{amb}} \)

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Supplementary Information 1:

(a) Thermodynamic limit as RR approaches 0

Since RR approaches 0 as $\Delta x$ approaches 0 (Eq. (6)), $COP_{\text{max}}$ in this limit can be expressed as:

$$COP_{\text{max}}|_{RR\to0} = \frac{45000 \left( \frac{J}{\text{mol}} \right)}{\frac{\Delta W(x)}{\Delta x}|_{\Delta x\to0}}. \quad (S.1)$$

The derivative of $W(x)$, which has a finite, non-zero limit as $\Delta x$ approaches 0:

$$\Delta W(x) |_{\Delta x\to0} = -RT \ln \frac{x}{a+x} = RT \ln \frac{a+x}{x}. \quad (S.2)$$

with which

$$COP_{\text{max}}|_{RR\to0} = \frac{45000 \left( \frac{J}{\text{mol}} \right)}{RT \ln \frac{a+x}{x} \frac{p_{\text{amb}}}{p_{\text{w/input}}}}. \quad (S.3)$$

At $T = 30^\circ\text{C}$ and $RH = 30\%$ (the conditions used for Fig. 2), $p_{\text{w/input}} = 38.2$ mbar and $p_{\text{amb}} = 1013.25$ mbar. Then Eq. (S.3) yields $COP_{\text{max}}|_{RR\to0} = 5.4466$, and Eq. (7) yields a corresponding $SEC_{\text{min}}|_{RR\to0} = 0.1275$ kWh/kg. In Fig. 3 (b), the dependence of $COP_{\text{max}}$ and $SEC_{\text{min}}$ 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:

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

$$p_{\text{vac}} = p_{\text{w/input}} \left(1 - RR \right). \quad (S.5)$$

Therefore, Eq. (8a) becomes

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

As $RR$ approaches 0:

$$COP_{\text{iso}}|_{RR\to0} = \frac{45000 \left( \frac{J}{\text{mol}} \right)}{RT \ln \frac{p_{\text{amb}}}{p_{\text{w/input}}}} \quad (S.7)$$

$$\Rightarrow COP_{\text{iso}}|_{RR\to0} = COP_{\text{max}}|_{RR\to0}. \quad (S.8)$$

(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 \( p_{\text{amb}} \) for the former, and the water saturation pressure \( p_{\text{sat}} \) for the latter. The difference between the minimum work for the two processes is the compression of permeated water vapor from \( p_{\text{sat}} \) to \( p_{\text{amb}} \):

\[
W'_{\text{min}} = W_{\text{min}} - RT \Delta x \ln(p_{\text{amb}}/p_{\text{sat}}). \tag{S.9}
\]

The corresponding \( \text{COP} \) is given by Eq. (14). Since \( RR \) approaches 0 when \( \Delta x \) approaches 0, Eq. (14) becomes

\[
\text{COP}'_{\text{max}} \big|_{RR \to 0} = \frac{45000 \left( \frac{J}{\text{mol}} \right)}{\Delta W'_{\text{x}} \Delta x \to 0 - RT \ln(p_{\text{amb}}/p_{\text{sat}})}. \tag{S.10}
\]

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

\[
\text{COP}'_{\text{max}} \big|_{RR \to 0} = \frac{45000 \left( \frac{J}{\text{mol}} \right)}{RT \ln(p_{\text{sat}}/p_{\text{input}})}. \tag{S.11}
\]

At \( T = 30^\circ \text{C} \) and \( RH = 90\% \) (as in Fig. 11 and used for Fig. 12), \( p_{\text{sat}} \) = 42.4 mbar and \( p_{\text{w/input}} \) = 38.2 mbar. Then Eq. (S.11) yields \( \text{COP}'_{\text{max}} \big|_{RR \to 0} = 171 \), with the corresponding \( \text{SEC} \) from Eq. (7) being

\[
\text{SEC}_{\text{min}} \big|_{RR \to 0} = 4.06 \text{ kWh/kg.}
\]

(d) **Derivation of \( \text{COP}_{\text{iso}} \)**

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

\[
W_{\text{pump}1} = RT(F_w + F_a) \ln(p_{\text{cond}}/p_{\text{vac}}). \tag{S.12}
\]

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

\[
W_{\text{pump}2} = RT_{\text{cond}}(F_w + F_a - F_{\text{cond}}) \ln(p_{\text{amb}}/p_{\text{cond}}). \tag{S.13}
\]

The latent heat removed in the process is

\[
\Delta H_{\text{lt}} = 45000 \left( \frac{kJ}{\text{mol}} \right) F_w. \tag{S.14}
\]
Combining Eq. (14) with Eqs. (S.12)-(S.14) and accounting for the work input of both pumps yields Eq. (15):

\[
\text{COP}_{\text{iso}} = \frac{\Delta H_{\text{it}}}{W_{\text{iso}}} = \frac{\Delta H_{\text{it}}}{W_{\text{pump1}}+W_{\text{pump2}}} = \frac{4\times10^3 \left( \frac{\rho}{\text{mol}} \right) F_w}{R T (F_w+F_a) \ln \left( \frac{P_{\text{cond}}}{P_{\text{vac}}} \right) + R T_{\text{cond}} (F_w+F_a-F_{\text{cond}}) \ln \left( \frac{P_{\text{amb}}}{P_{\text{cond}}} \right)}. \tag{S.15}
\]

**Supplementary Information 2:**

Fig. S.1:

**Supplementary Information 3:**

Fig. S.2:

**Supplementary Information 4:**

Fig. S.3:

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

**Supplementary Information 5:**

Fig. S.4:

**Supplementary Information 6:**

Fig. S.5:

Table S.1:

**Reference for Supplementary Information 6.**


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 $W_{\text{min}}$ 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 $COP_{\text{max}}$ with $RH$ at fixed $T = 30^\circ C$, 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) ($COP_{\text{max}}$) 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 $p_{\text{var}}$, 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 $T = 30^\circ C$ 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) $COP'_{\text{max}}$ and (b) $SEC'_{\text{min}}$ for water removal, for the process portrayed in Fig. 11, where water is removed at $p_{\text{sat}}$. For comparison, $COP_{\text{max}}$ and $SEC_{\text{min}}$ are presented for the process depicted in Fig. 2, where water removal proceeds at $p_{\text{amb}}$.

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 $S \to \infty$), and (c) membrane selectivity (with isothermal compression and $T_{\text{cond}} = 35^\circ\text{C}$), 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 $COP_{\text{max}}$ for VMD via isothermal compression to (a) $T$ (at $\omega = 20 \text{ g/kg}$) and (b) $\omega$ (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 $COP_{\text{iso}}$ on vacuum pressure, $p_{\text{vac}}$

Fig. S.4: The profile of water vapor partial pressure on the feed and permeate sides when vacuum pressure $p_{\text{vac}}$ 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: $p_{\text{cond}}$ at which $COP$ is maximized as a function of $RR$ for a broad range of $S$ values.

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

Fig. 1:

Fig. 2:

Fig. 3
Fig. 4:

(a) Schematic diagram of the working membrane with humid air entering and dry air exiting. The pressure inside the vacuum pump is denoted as $p_{\text{vac}}$.

(b) Pressure profile through the membrane, showing input, along the membrane, and output with the pressure loss $\Delta p_w$.

(c) Description of the process: humid air at 1 atm and 30°C passes through the membrane to produce water vapor at the same conditions. Pumping energy is required to change the state of the water vapor.

Fig. 5:
**Fig. 6:**

- **COP**
- **COP**
- **COP**

**Fig. 7:**

- **Feed side:**
  - Water partial pressure = $p_w^1$
  - Air partial pressure = $p_a^1$
  - Total pressure = $p_w^1 + p_a^1 = p_{amb}$

- **Permeate side:**
  - Water partial pressure = $p_w^2$
  - Air partial pressure = $p_a^2$
  - Total pressure = $p_w^2 + p_a^2 = p_{vac}$

**Pressure**

- $p_{amb}$
- $p_a^1$
- $p_w^1$
- $p_{vac}$
- $p_w^2$
- $p_a^2$

**Along the membrane**

- Input
- Output
- $dI$
- $df_w$
- $df_a$
Fig. 8:

Fig. 9:

Fig. 10:
Fig. 11:

- **COP** vs. RR for both condensation and absorption processes.

Fig. 12:

- Diagram showing the process of condensation and absorption.

Fig. 13:

- Diagram illustrating the process of humid air at 30 °C, ambient pressure, and RH. The condenser is set at 35 °C.
Fig. 14:

A graph showing the relationship between COP and RR for different conditions.

Fig. 15:

A diagram illustrating the flow of humid air through multi-stage processes and the resulting dry air output.
Fig. S.1:

Fig. S.2:

Fig. S.3:
Fig. S.4:

- For $p_{vac} = 40$ mbar, $RR = 0.0315$
- For $p_{vac} = 30$ mbar, $RR = 0.2237$
- For $p_{vac} = 20$ mbar, $RR = 0.4793$
- For $p_{vac} = 10$ mbar, $RR = 0.7392$
- For $p_{vac} = 1$ mbar, $RR = 0.9739$
Fig. S.5:
Table

Table S.1:

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

1 GPU = 3.348 × 10⁻¹⁰ mol/s m² Pa
Highlights

• Prodigous 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