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Performance Test of Dense Membrane for Vacuum Membrane Dehumidification System

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Abstract

A membrane mass exchanger where water vapor is exchanged in a vacuum membrane dehumidification (VMD) system utilizes the vapor pressure difference between the permeate side and the feed side. However, differently from a typical moisture selective membrane, this membrane is located under pressure difference to accelerate the separation. Thus, a new approach to validate performance of the water vapor selective membrane is required. In order to quantitatively measure the effect of this phenomenon on the moisture permeability, an experimental system was setup to measure water vapor selectivity and permeance under the presence of absolute pressure difference before and after the membrane. So far, it is known that the performance of membrane is only a function of partial pressure of vapor. However, from the experiment, it is observed that selectivity and permeance are also changeable by absolute pressure difference due to the physical deformation caused by absolute pressure difference across the membrane.

Keywords: Permeance, Selectivity, Dense membrane, Dehumidification ;

1. Introduction

The energy consumption for air conditioning is constantly increasing. And dehumidification loads account for a large part of the cooling load. Therefore, many systems are currently being developed to replace the vapor compression cycle, and membrane heat pumps have been selected as one of the most feasible system [2].

As a key component of membrane heat pumps, studies have continued to improve membrane performance. Membrane dehumidification models for performance analysis are considered ideal models operated only by the vapor pressure difference, which is different from the actual phenomenon. This difference is expected to be attributed to the influence of absolute pressure on the selectivity of the membrane separation. Bui et al. [3] study shows that the COP of the membrane heat pump changes depending on the selectivity of the membrane applied to the system. Therefore, the exact COP value of the designed model can only be calculated by pre-checking the selectivity and permeability of the membrane to be used according to the operating pressure in the system configuration. However, the membrane characteristic values mentioned in various existing papers are often the result of no specified experimental conditions, or only simple diffusion model, which is different from the actual system's conditions. So, in this work, we construct conditions similar to real-systems and then experimentally calculate selectivity and permeability.

2. Background

2.1. Dense membrane

The major purpose of membrane-based vacuum dehumidification is to separate water vapor from the air without vapor-liquid phase change. Thus the type of membrane is gas-gas separation type one. Gas separation

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membrane can selectively separate substance and can separate mixture using chemical potential difference between membrane sides. It can be made using various materials such as metal, ceramic and liquid, and mainly uses polymers that are easy to form. It can be largely divided into porous and dense membrane, of which no physical porosity exists that allows a substance to pass through a membrane.

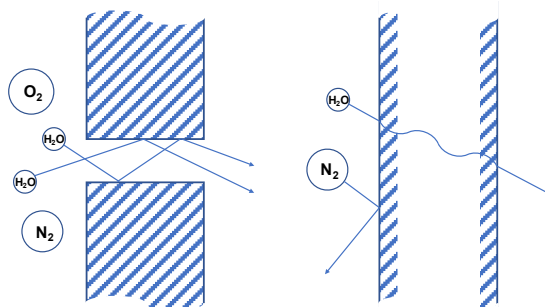


Fig. 1. Water vapor permeation in porous/dense membrane

In the case of dense membrane for water vapor separation, hydrophilic materials are usually bonded to hydrophobic polymer-based materials to form ion-nano channel in which water vapor molecules can move. Therefore, the solution-diffusion model can explain the movement of the substances, and steam vapor difference on both sides of the membrane acts as a driving force.

If you look at the previous analytical research data, it is often assumed that the selectivity is infinite using a dense membrane. However, in actual condition, the dense membrane also has a large but finite value. In this case, the design and operation of the system will be different, and not only steam but also air will pass through, so a method of periodically vacuuming should be devised.

2.2. Test method for water vapor permeability

The cup method measures the change in cup weight in an environment where water or desiccant filled cup is kept constant temperature and humidity [12]. If water is contained, the relative humidity inside the cup is assumed to be 100% and the amount of evaporated water is calculated. If desiccant is used, the water vapor mass is calculated through the vapor absorbed as 0% relative humidity. Although it is the most commonly used method, it has the disadvantage of creating a boundary layer according to the concentration of substance before and after the membrane. Accordingly, the measurement varies greatly depending on the distance from the water and desiccant to the membrane, so error analysis is essential. There are also disadvantages of not being able to add various experimental variables such as pressure changes.

To overcome these disadvantages, devices have been suggested that not only measure simply by gravimetric but also reflect various experimental conditions such as spring stiffness. A typical example is constant-volume variable-pressure method that permeates water vapor from feed side to the permeate side [13]. Depending on the amount of water vapor permeated in the device, the pressure on the permeate side changes, which allows the permeability to be calculated. However, in the case of gases mixed with other gases and water vapor, only the permeation of water vapor can be measured.

Therefore, this work uses experimental methods that combine different experimental methods.

3. Experiment

3.1. Experimental setup

As explained above, the experimental device was built based on the cup method and constant-volume variable-pressure method among the measurements described earlier. In the constant-volume variable-pressure method, the permeated water vapor is the cause of pressure rise, allowing the measurement of the permeability to be made through pressure change and time flow, but not the permeability of the additional substances. Considering this, the desiccant of cup method is applied to ensure that all permeated water vapor is absorbed into the absorbent, and the increase in pressure is the result of nitrogen. This allows for the calculation of permeability for both substances.

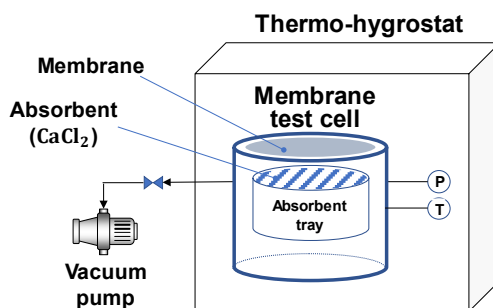


Fig. 2. Schematic diagram of test setup

The above figure represents the whole experimental device. The test cell has two tabs for the sensor, one for decompression or pressurization. In the experiment, the gas must pass through the membrane to enter the test cell, and the O-ring was installed in double to prevent leakage to the side of the membrane. The test cell was used in the experiment after checking its confidentiality through a pressure test in advance. In addition, a tray containing calcium chloride, was built in the test cell to keep the relative humidity at 0% and to measure the weight of the transmitted water vapor. During the experimental procedure, absolute pressure difference was generated before and after the membrane by vacuum pump or nitrogen tank, and the test cell was inserted into the thermo-hygrostat so that the experiment could be carried out at a constant temperature and humidity.

3.2. Membrane sample

The membrane used in this study was produced by dispersing silica particles, which are hydrophilic inorganic nanoparticles, to polyurethane, a hydrophobic material, and then joining them to polyamide supports. Membrane produced in this way is not over-spoiled by moisture, so its durability is complemented so that frequent replacement is not required.

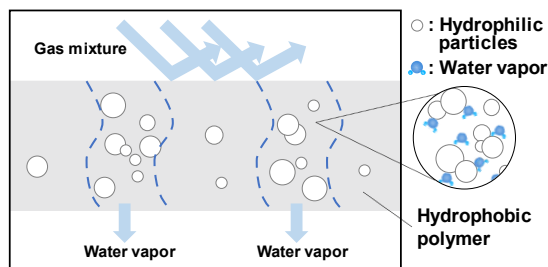


Fig. 3. Characteristic diagram of membrane sample used in experiment

The figure above shows the cross section of the membrane sample used. When hydrophilic particles are placed in the membrane as shown without being concentrated or too dispersed, ion-nano channels are created. In this case, water vapor inside the membrane moves in a molecular state by repeatedly adsorption and desorption to the hydrophilic particle surface.

3.3. Test condition and test

The experimental conditions were created close to the environment in which the actual system could be applied, considering the problems described earlier. It is arranged in the table below. The experiment was conducted in two main ways. The first is to compare two cells with nitrogen permeation set in opposite directions to see if nitrogen permeation affects water vapor permeability in a dense membrane. In addition, the experiment was conducted with the existing cup method, comparing the variation in the permeability with the occurrence of absolute pressure difference. Second, we measured the permeance and selectivity changes by changing humidity. The data from the measurements allow us to predict indicators in different humidity conditions with extrapolation.

Table 1. Experimental conditions for test setup

Variables	Value
Absorbent tray mass	70g - 100g
Distance from membrane to absorbent	5mm
Relative humidity	30% - 70%
Temperature	30°C
Test unit pressure (abs)	40kPa, 160kPa

3.4. Membrane performance unit

First, weight change of the absorbent tray, the area of the membrane through which the substance can be permeated in the cell, and the measurement time can be used to obtain the mass flux of water vapor.

$$J_{\text{H}_2\text{O}} = \frac{\Delta m_{\text{CaCl}_2}}{A_m \Delta t} \quad (1)$$

Since the above value does not consider the volume of the gas, the molar mass of H_2O is distributed to convert the mass of water vapor into mole. Since driving force of water vapor movement is vapor pressure difference, we separated steam pressure out of the mass flux to calculate the permeance. Since the steam pressure inside the cell is zero, the steam pressure difference can be calculated through the humidity of the chamber. In addition, multiplying the constants to fit the units allows the expression to be arranged as follows.

$$P_{\text{H}_2\text{O}} = \frac{\Delta m_{\text{CaCl}_2}}{M_{\text{H}_2\text{O}} p_v A_m \Delta t} \times \frac{10^{10}}{3.35} \quad (2)$$

The unit of GPU value obtained by the above formula is $\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$. The volume inside the cell is constant but the pressure continues to change, so the mass of permeated nitrogen can be calculated through the ideal gas equation. The slight change in volume due to compression of the O-ring, deformation of the membrane was ignored and the volume and pressure changes in the cell were calculated by the ideal gas equation. The mass flux of nitrogen obtained through this process is as follows.

$$J_{\text{N}_2} = \frac{\Delta m_{\text{N}_2}}{A_m \Delta t} = \frac{\Delta p V / R_{\text{N}_2} T}{A_m \Delta t} \quad (3)$$

R_{N_2} is the ideal gas constant of nitrogen. As with water vapor permeability calculations, the mass of nitrogen is divided into the molar mass of nitrogen. And in this experiment, the driving force of nitrogen is the absolute pressure difference excluding water vapor pressure, so the formula was calculated by dividing the formula by $(p_{\text{atm}} - p_v) - p$.

$$P_{\text{N}_2} = \frac{\Delta p V / R_{\text{N}_2} T}{M_{\text{N}_2} [(p_{\text{atm}} - p_v) - p] A_m \Delta t} \times \frac{10^{10}}{3.35} \quad (4)$$

The unit is $\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$, such as the water vapor permeance value. The selectivity of membrane is calculated by the permeance of water vapor and nitrogen calculated from the above equations.

$$\alpha = P_{\text{H}_2\text{O}} / P_{\text{N}_2} \quad (5)$$

Calculated from the data measured at intervals of five minutes using the above expression, the sum of the values and the values calculated at the beginning and end of the experiment were consistent with the error range. Therefore, it can be said that the assumptions included during the composition process of the expression are reasonable.

Table 3. Real-time measurement data of the representative Test A and test B

Test 1			Test 2	
Time [hr]	p(abs) [kPa]	Absorbent mass [g]	p(abs) [kPa]	Absorbent mass [g]
0	42.22	77.31	41.98	79.92
12	58.78	-	57.36	-
24	69.02	-	67.68	-
36	76.76	-	75.19	-
48	82.48	80.60	80.97	83.21

4. Result and discussion

4.1. Measurement data

The experimental data were recorded using the LabVIEW program. For the weight of the absorbent tray, the cells were dismantled before and after the experiment and measured using the scale. The above table shows the representative case data that have been repeated under certain measurement conditions. After 48 hours of experimentation, both cells increased by about 40 kPa to measure the amount of nitrogen passed, and it can be confirmed that the weight of the absorbent tray has increased due to the permeation of water vapor.

Figure 4 shows the change in pressure within the cell over the measurement period. Since it was assumed that all the water vapor passed into the cell is absorbed by the absorbent, the cause of the increased pressure is the result of the permeation of nitrogen. The slope of the graph decreases over time, which can be interpreted as a weaker driving force as the absolute pressure difference decreases. Therefore, it was confirmed that the drive forces of nitrogen and air can work even in a dense membrane and that consideration is required.

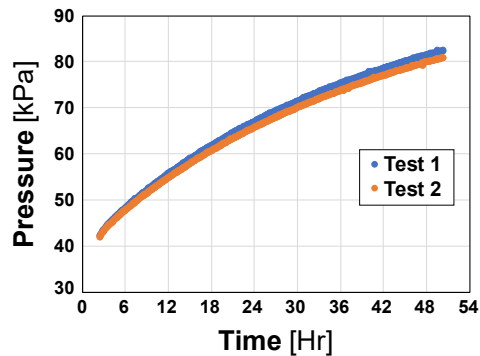


Fig. 4. Pressure variation in test cell

4.2. Calculation result

4.2.1. Effect of absolute pressure difference

This section presents the experimental results for checking the effects of absolute pressure difference in a water vapor permeability of dense membrane. At the start of the experiment, the absolute pressure difference before and after the membrane formed by pressurization or decompression is the same as 60 kPa, but both nitrogen and water vapor are brought into the cell for Test A, and Test B allows nitrogen to penetrate outward. The data measured under the same 50% relative humidity conditions are listed.

As nitrogen permeates, it can be confirmed that the cell pressure in Test A increases, and the pressure in Test B decreases. The above measurements were presented by converting them into performance factors. The data measured by the cup method are also listed for comparison. The relative humidity was measured at 70% for the cup method measurement.

The selectivity was not indicated for Test B because it was the ratio of the substance permeated in the same direction, nor was the test cup measurement recorded because it was not possible to measure the permeance of nitrogen. When looking at the data, we can see that the permeability of the water vapor was measured the highest at Test A with the same direction of permeation of nitrogen and water vapor. Depending on the direction in which nitrogen is permeated in the test cell, and partly confirmed that the presence of absolute pressure difference affects the permeability of water vapor.

Table 4. Real-time measurement data of the Test A and Test B which has opposite directions of nitrogen permeation

Time [hr]	Test A		Test B	
	p(abs) [kPa]	Absorbent mass [g]	p(abs) [kPa]	Absorbent mass [g]
0	42.25	89.19	162.46	75.78
12	58.24	-	153.40	-
24	68.95	-	144.95	-
36	76.58	-	138.03	-
48	82.43	92.38	132.22	77.76

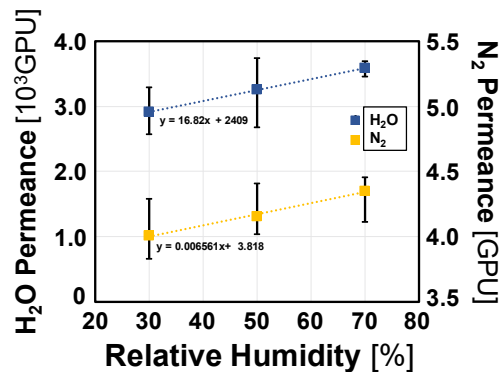
Table 5. Membrane performance factor values of Test A, Test B and cup method

Performance factor	Test A	Test B	CUP
Permeance (H ₂ O) [GPU]	3.56×10 ³	2.08×10 ³	1.68×10 ³
Permeance (N ₂) [GPU]	4.40	2.52	-
Selectivity [-]	808.29	-	-

Among the membrane-based vacuum dehumidification systems introduced in the introduction, in the case of the W-MVD system, the membrane is mounted before and after the vacuum compressor, and each condition creates the direction of the pressure difference, such as Test A and Test B. The experimental results show different indicator values even for the same membrane sample and should be used to take this part into account during the analysis process.

4.2.2. Membrane performance according to relative humidity

This section describes the changes in permeability measured by varying relative humidity. The relative humidity was changed from 30% to 70% according to the conditions set earlier, and the error value due to membrane damage was removed during the experiment. After converting the measurements into performance factor, it was expressed as an average. Calculations showed that the permeance of both H₂O and N₂ increased as the relative humidity increased, but the permeance increase of H₂O was greater, so was the value of selectivity.

Fig. 5. Permeance variation of H₂O and N₂ according to relative humidity

The result of the calculation shows the data on the graph. The water vapor permeance formula used in this study is linearly proportional to changes in water vapor pressure, and data presented as actual averages can also be found to be close to linearity. The permeance of nitrogen also appears to be increasing like water vapor, which is interpreted as the effect of absolute pressure difference in the calculation formula has decreased as the water vapor pressure rises. Because both performance indicators exhibit linearity, the permeance of nitrogen and water vapor with changes in humidity was predicted through extrapolation. The trend line was calculated through the MATLAB curve fitting tool and the results were shown on the graph. Using this expression, the permeance and selectivity values for relative humidity of 0% were calculated, as shown in Table 1. The permeance value of H₂O is calculated as 2409 GPU and the permeance value of N₂ is 3.818 GPU and has a selectivity value of approximately 630.96. The following sections compare with data from existing studies.

4.3. Membrane performance factors comparison

The results of this experiment and analysis, and the conditions of the experiment were summarized in Table 6. Units were unified for comparison with the data previously investigated. Since permeance is an indicator calculated without considering membrane thickness, the measured membrane thickness average of 75 μm was multiplied by the result and converted to permeability.

Except for the test cases of the reverse direction and the cup method where selectivity data were unavailable, the remaining five results were placed on the Fig. 2 to compare with the data in the previous paper. From the results, water vapor permeability was high without considering experimental conditions. However, as the

selectivity is relatively low, additional device is required to prevent pressure rise of the compressor due to permeated N_2 if the corresponding membrane is used in the system configuration.

Table 6. Membrane factors data and condition in this paper

Test method	RH [%]	H ₂ O permeability [Barrer]	N ₂ permeability [Barrer]	Selectivity [-]
Cup method	70	11390.51	-	-
Reverse permeation of N ₂	50	15608.44	18.93	-
Test result	30	21821.67	30.08	725.56
	50	24425.44	31.16	783.81
	70	26868.04	32.04	838.47
Extrapolation	0	18067.5	28.64	630.96
	100	30682.5	33.56	914.37

5. Conclusion

In this study, experiments were conducted through simple experimental device to check the effect of absolute pressure difference on the performance of a dense membrane with water selective properties. There are several methods for measuring permeability and selectivity, but each threshold exists. Thus, in order to improve the shortcomings, a new experimental device was formed that fused the cup method with the constant-volume variable-pressure method.

The results of the cup method and reverse pressure gradient experiments show that there is an effect of absolute pressure difference on the movement of water vapor in a dense membrane, and it is concluded that consideration is necessary accordingly.

Nomenclature

A_m	area of membrane [m ²]	p_s	water saturation pressure [kPa]
b	width of masked edge [m]	p_v	water vapor pressure [kPa]
d	distance of absorbent from membrane [m]	Δp	pressure difference [kPa]
D	diffusion coefficient [-]	P_{H_2O}	water vapor permeance [mol/m ² sPa]
J_{H_2O}	mass flux of H ₂ O [g/m ² s]	P_{N_2}	nitrogen permeance [mol/m ² sPa]
J_{N_2}	mass flux of N ₂ [g/m ² s]	R_{H_2O}	ideal gas constant of H ₂ O [kJ/kgK]
Δm_{CaCl_2}	mass variation of CaCl ₂ [g]	R_{N_2}	ideal gas constant of N ₂ [kJ/kgK]
Δm_{N_2}	mass variation of N ₂ [g]	Δt	time variation [s]
M_{H_2O}	molar mass of H ₂ O [g/mol]	T	temperature [°C]
M_{N_2}	molar mass of N ₂ [g/mol]	V	volume of cell [m ³]
p	pressure of test cell [kPa]	α	selectivity [-]
p_{atm}	atmospheric pressure [kPa]	δ	specimen thickness [m]

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