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Applications of membrane distillation technology in energy transformation process-basis and prospect

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Membrane distillation technology is a new type of efficient separation technology that combines traditional distillation technology and membrane separation technology. In the study, applications of membrane distillation technology in thermal engineering and refrigerating engineering with typical energy transformation process were presented. Desorption and regeneration process of saline solution by vacuum membrane distillation was proposed on the basis of the concentration and separation properties of membrane distillation. Membrane distillation technology could be used in lithium bromide absorption refrigeration system, energy storage system, and the regeneration process of liquid desiccant solution in temperature-humidity independent control air-conditioning system. The aim of the applications was to use the low-grade energy such as waste heat, solar energy and geothermal energy adequately and to improve the available temperature difference of heat source. According to latent heat transfer and thermal conduction across the membrane in direct contact membrane distillation process, a novel membrane heat exchanger with both heat transfer and mass transfer processes was proposed. The heat exchanger could be used as the solution heat exchanger of lithium bromide absorption refrigeration system and as the special heat exchanger that recovered heat and pure water simultaneously. Some feasible process flows about the applications of membrane distillation technology to energy transformation process were listed and analyzed. Finally, future research emphases were indicated.

membrane distillation, energy transformation, regenerative energy, lithium bromide absorption refrigeration, energy storage, membrane heat exchanger

Membrane distillation technology is a novel and efficient separation method that combines traditional distillation with membrane separation technology. Due to the hydrophobic property and the cellular structure of polymeric membrane, membrane distillation process does not need the solution to be heated to its boiling point and it can keep working as long as the temperature difference exists between the two sides of the membrane. As a result of the lower operating temperature, regenerative energy such as solar energy, geothermal energy and waste heat can be used more adequately in membrane distillation process^[1,2], which is thus expected to become a cheap and efficient separation method^[3].

Microporous hydrophobic membranes like polythene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) are major membrane materials^[4], which are often made into plate and frame module, spiral wound module, tubular module, capillary module, and hollow fiber module. According to the distinctive operating mechanism of water vapor cooling, the membrane distillation mode can be sorted into direct contact membrane distilltion (DCMD), air gap

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membrane distillation (AGMD), sweep gasmembrane distillation (SGMD), and vacuum membrane distillation (VMD)^[1,2]. Among them, VMD and DCMD are the most popular distillation processes. VMD has the most penetration flux because the water vapor pressure difference between the two sides of the membrane is the greatest; DCMD has the merits of simple framework, more penetration flux and being easy to operate. Moreover, hollow fiber membrane module is made up of organic polymer material, it can provide the maximum contact area in limited space, and its volume, weight and floor space reduce remarkably^[5].

Research on the mass transfer across membrane and the applications of membrane distillation process in solution separation has been done in many fields. Membrane distillation technology has been widely used in seawater and brackish water desalinization^[6-10], wastewater treatment^[11-13], water purification^[14, 15], solution concentration and crystallization^[16-20] and deprivation and callback of volatility solute in solution^[21-24]. Besides the merits of simple device, easy control, distillate pureness and being easy to assemble, membrane distillation can be used to treat high concentration solution and even concentrate the solution to saturation state^[3]. Nevertheless, restricted by membrane material, most heat (about 70%) is lost through heat conduction of the membrane wall, resulting in the low thermal efficiency of membrane distillation^[25]. Thus, penetration flux of water vapor still needs improving.

In membrane distillation, heat and mass transfer across membrane is the basic mass transportation and energy transformation process. Enhancement of mass transportation and weakening of heat transfer across membrane is one of the most important research directions in the application of membrane distillation. In thermal engineering and refrigeration system, heat and mass transfer is also the main process of energy transfer, energy transformation and energy utilization. Therefore, based on the mechanism of membrane distillation and the properties of energy transformation in membrane distillation process, this paper aimed to probe into the mechanism and application feasibility of membrane distillation technology in thermal engineering and refrigeration system involving typical energy transformation processes. Firstly, high-density saline solution such as lithium bromide (LiBr) solution, lithium chloride solution (LiCl) and calcium chloride solution (CaCl₂) was concentrated by VMD process. Then, VMD process was

applied to desorption of saline solution in LiBr absorption refrigeration system and energy storage system driven by low-grade energy. It was also applied to the regeneration of liquid desiccant in temperature-humidity independent control air-conditioning system. Secondly, DCMD process was applied to solution heat exchanger design. Thus, a novel solution heat exchanger combining heat and mass transfer process was proposed and applied as solution heat exchanger of lithium bromide absorption refrigeration system. DCMD process was also applied to specific heat exchanger that reclaimed both heat and purified water.

The paper also explored the new characteristics and utilities of membrane distillation in traditional energy transformation process based on the experimental test and mathematical simulation about saline solution and membrane heat exchanger. The issues for further research were also presented prospectively.

1 Mechanism of energy transformation in membrane distillation

In membrane distillation process, heat and mass transfer across membrane is a complicated interactive process. Penetration flux of mass transfer is related to the fundamental properties of membrane material and the water vapor pressure difference between the two sides of the membrane^[26]. Latent heat energy transfers when water vapor diffuses across membrane pores. Heat transfer affects the temperature in membrane wall, then affects the water vapor pressure, and finally affects mass transfer across membrane. If heat conductivity is low and the membrane is thick, the temperature difference between the two sides of the membrane and water vapor pressure difference will be heightened, and then penetration flux will increase, or vice versa^[27]. Distinctive applications of membrane require distinctive membrane material in line with its purpose.

1.1 Description of membrane distillation process

In membrane distillation process, volatile vapor is distilled from aqueous solution using microporous hydrophobic membranes. Figure 1 shows the schematic of membrane distillation process. The diameter of membrane pores is equivalent to water molecular mean free path. The left side of the membrane in touch with the hot feed solution is called the warm side, while the right side is called the cold wall (cold side). The temperature difference between the warm side and cold side causes waENERGY SCIENCE & TECHNOLOGY



Figure 1 Sketch of membrane distillation process

ter vapor pressure difference, so water vapor in the warm side diffuses across membrane pores to the cold side, and is chilled, swept or absorbed by another aqueous solution. The fact that liquid solution can not penetrate the pores because of the hydrophobicity of the membrane and the large contact angle θ between the aqueous solution and membrane pores result in nonwettability between the membrane and aqueous solution, so that liquid phase and gas phase are separated by the membrane^[3]. Taken together, two basic conditions must be satisfied to ensure the normal operation of membrane separation process. One is the hydrophobicity of membrane material, which ensures that only water vapor can diffuse across the membrane pores; the other is the water vapor pressure difference caused by temperature difference between the warm side and cold side of the membrane, which ensures enough driving force for mass transfer^[28].

In membrane distillation process, energy transformation across membrane includes two parts. One is the heat transfer by heat conduction through the membrane wall and residual gas in membrane pores. Heat conduction is decided by thermal conductivity, membrane wall thickness and porosity of membrane material. The other is the latent heat transfer by water vapor diffusion across the membrane. It is worthwhile to mention that temperature polarization and concentration polarization may occur on the membrane surface^[29, 30] because of the thermal layer effect and the heat and mass transfer, which results in the decrease in water vapor pressure difference between the warm side and cold side, the reduction in penetration flux and the weakening of heat transfer. However, moderate disturbance on membrane surface and the increasing of solution flow rate can reduce the negative effect of temperature polarization and

concentration polarization. The flow rate is restricted by the membrane intensity and the Liquid Entry Pressure of water (LEPw) ^[26,31]. Therefore, membrane material with high intensity and high LEPw is always the popular research hotspot in membrane distillation process.

1.2 Membrane distillation process model and its physical characteristics

Figure 2 shows the microscopic description of membrane distillation model. Figure 2(a) shows the schematic diagram of heat and mass transfer across mono-membrane. Hot feed solution (main flow temperature $T_{\rm f}$ and main flow concentration $C_{\rm f}$.) flows in the lumen side of the membrane. The heat, $DQ_{\rm f}$, transfers by heat convection between aqueous solution and the membrane wall. The heat, $DQ_{\rm m}$, transfers across the membrane in two ways, heat conduction through membrane and latent heat transfer across membrane. Obviously $DQ_{\rm f} = DQ_{\rm m}$. Membrane distillation model differs from the traditional heat exchanger in that temperature polarization and concentration polarization occur in membrane wall because of water vapor transfer and latent heat transfer. Temperature polarization means that the temperature near membrane wall $T_{\rm fm}$ is lower than the main flow temperature $T_{\rm f}$ because water vapor absorbs the heat of aqueous solution and transfers across the membrane. Concentration polarization means that the concentration near membrane wall C_{fm} is higher than the main flow concentration $C_{\rm f}$ because of water vapor transfer across the membrane^[32,33]. Temperature polarization and concentration polarization are not beneficial to mass transfer since the water vapor pressure is lower in temperature $T_{f,m}$ and concentration $C_{f,m}$, leading to the decrease in the driving force of mass transfer and the reduction in penetration flux.



Figure 2 Microscopic schematic of membrane distillation model. (a) Mono-membrane; (b) vertical section.

Figure 2 (b) shows the schematic diagram of vertical section of a membrane pipe. The temperature of aqueous solution and the pressure of water vapor in the warm side are higher than those in the cold side. Water vapor diffusion across membrane pores from the warm side to cold side is driven by water vapor pressure difference. Mass transfer can be mathematically described as ^[34-36]:

$$J = K(P_1 - P_2),$$
 (1)

where *J* is the penetration flux, kg/(m²·h); P_1 and P_2 are water vapor pressures in the warm side and cold side, Pa; and *K* is the membrane distillation coefficient, kg/(m²·h·Pa). Membrane distillation coefficient *K* is a complicated parameter related to membrane structure^[37] (including porosity, average pore diameter, membrane wall thickness, tortuosity and contact angle between the aqueous solution and membrane pores) and flow parameters of the aqueous solution.

Figure 3 shows the electron microscopy diagram of PVDF membrane section^[38]. The thickness of membrane wall is 0.15 mm. Pores in the membrane wall do not show uniform diameter or distribution, with finger pores mainly distributing in the membrane wall and spongy pores distributing in the central section of the membrane. Compared with finger pores, spongy pores are more tortuous and compact, which results in the increase in the path length and mass transfer resistance of water vapor diffusion across the membrane. Hence, spongy pores are the major resistance in mass transfer process.



Figure 3 Electron microscopy diagram of PVDF membrane section.

Literatures^[39.41] analyzed three modes of water vapor diffusion across membrane pores and presented a calculation method for membrane distillation coefficient *K* by comparing membrane pore diameter with water vapor mean free path. Water vapor diffusion across the membrane was described as Knusden diffusion, Viscous flow and Molecular diffusion. The Knudsen number (*Kn*) used to indicate the borders of the regions is defined as the ratio of the mean free path of the gas λ to the pore diameter d_p , i.e.

$$Kn = \lambda / d_{\rm p} \,. \tag{2}$$

if Kn > 1, the transport mode is Knudsen diffusion:

$$K = \frac{2}{3} \frac{\varepsilon r}{\tau \delta} \left(\frac{8M}{\pi RT} \right)^{1/2};$$
(3)

if Kn < 0.01, the transport mode is Molecular diffusion:

$$K = \frac{\varepsilon}{\tau \delta} \frac{PD}{P_{\rm a}} \frac{M}{RT}; \qquad (4)$$

if 0.01 < Kn < 1, the mass transport takes place via a combination of Knudsen and Molecular diffusion:

$$K = \left[\frac{3}{2}\frac{\tau\delta}{\varepsilon r} \left(\frac{\pi RT}{8M}\right)^{1/2} + \frac{\tau\delta}{\varepsilon}\frac{P_{\rm a}}{PD}\frac{RT}{M}\right]^{1/2},\qquad(5)$$

where ε is the porosity, τ is the tortuosity, r is the pore radius, δ is the membrane thickness, M is the water molar mass, R is the gas constant, T is the absolute temperature, P_a is the pressure of residual air in pores, P is the total pressure in pores and D is the diffusion coefficient of gas.

1.3 Desorption of high concentration saline solution by vacuum membrane distillation

Vacuum membrane distillation is mainly applied to seawater or saline solution desalination. Seawater or saline solution (concentration 3%-6%) belongs to low concentration solution. Membrane distillation equipment is simple and low temperature heat source such as solar energy, geothermal energy and waste heat can be used as driving heater^[42]. Accordingly, the application of vacuum membrane distillation to the desorption of high concentration saline solution has become a research hotspot in recent years.

As the membrane material develops, applications of VMD process have been extended to higher concentration solution gradually, such as solute purification, separation of saline solution to saturation and even crystallization. However, separation of high concentration solution via VMD process has rarely been mentioned because of the limitations of specialized membrane material and membrane module. Along with the emergence of the high-intensity, large-penetration-flux and small thickness membrane material^[43], the application of VMD process to high concentration of saline solution driven by low temperature heat has become possible. The experimental study of VMD process of high concentration saline solution will be described in detail in section 2.

LiBr aqueous solution used in absorption refrigeration system belongs to high concentration saline solution. The following section will take LiBr solution as an example to illustrate the application of VMD process to high concentration saline solution.

In traditional LiBr absorption refrigeration system, LiBr solution is concentrated and separated in a generator.

The LiBr solution is heated to its boiling point, and water vapor volatilizes from the solution and cools in the condenser. The pressure in the generator is decided by the condensing pressure in the condenser. Generally speaking, the pressure in the generator and condenser are less than 10 kPa. In the energy transformation process in the generator, driving heat source heats LiBr solution, and water vapor takes away latent heat and then is expelled via the condenser.

In VMD process, LiBr solution with high temperature flow lies in the warm side, while the cold side is kept in a vacuum state by the condensing pressure of cooling water. Therefore, the water vapor pressure between the warm side and cold side functions as the driving force of mass transfer. As mentioned above, if the vacuum pressure in the cold side of the membrane in VMD process is close to that in the generator of LiBr absorption refrigeration system, the desorption of LiBr solution by VMD process can be used as the separation mode in the generator.

Figures 2, 3 and eq. (1) show that the driving force of water vapor diffusion across the membrane is the pressure difference between the two sides of the membrane. Water vapor can diffuse across the membrane as long as water vapor pressure difference exists^[2,3]. The penetration flux enhances with the increase of pressure difference. Therefore, mass transfer rate will increase by either increasing the temperature in the warm side or decreasing the pressure in the cold side. What is more, mass transfer can occur with the temperature of hot feed

solution in the warm side far below its boiling point due to the water vapor pressure difference. In addition, membrane material and membrane module provide much larger contact area in limited space than any metal module in limited space, which results in the improvement of the total penetration flux^[44].

In the desorption or regeneration process of LiBr solution in the generator of absorption refrigeration system and the separation process of LIBr solution in VMD process, water vapor is treated in the same way, that is to say, water vapor separated from LiBr solution is cooled in vacuum state and gathered in the condenser. The difference lies in the fact that, in traditional absorption refrigeration system, the LIBr solution must be heated to its boiling point before the desorption or regeneration can operate; while in VMD process, LiBr solution can be concentrated and separated at a temperature far below its boiling point. As a result, low-grade, renewable energy such as solar energy, geothermal energy and waste heat can be efficiently used as the driving heat source in the desorption or regeneration of LiBr solution in VMD process.

1.4 Direct contact membrane distillation and solution heat exchanger

Direct contact membrane distillation (DCMD) is also an important separation mode of aqueous solution. DCMD process differs from VMD process in that cooling water or low temperature aqueous solution flows in the cold side in DCMD process while the cold side in VMD process is kept in a vacuum state by condensate water. Due to the lower water vapor pressure of cooling water or low temperature aqueous solution in the cold side, vapor pressure difference between the two sides drives water vapor to diffuse across the membrane pores from the warm side to the cold side (eq. (1)). However, enhancing mass transfer efficiency and lessening heat transfer across the membrane in both VMD and DCMD processes have become the fundamental aim in nearly all researches^[3].

It is noteworthy that both heat transfer and mass transfer need strengthening in thermal engineering fields. For example, in LiBr absorption refrigeration system, traditional solution heat exchanger can recall heat via the heat exchanger between high temperature solution from the generator and low temperature solution from the absorber. The higher efficiency of solution heat exchanger may lead to the smaller thermal load of the generator and absorber, and thus, to the higher coefficient of performance (COP) of system^[45,46].

According to the concentration difference and temperature difference between the generator and the absorber, it seems wholly possible to apply DCMD process to solution heat exchanger because both heat transfer and mass transfer are beneficial to the generator and absorber. In DCMD process, water vapor diffuses across membrane pores from the warm side to the cold side and heat transfers via latent heat transfer and heat conduction. When DCMD process is applied to the solution heat exchanger of LiBr absorption refrigeration system, the latent heat carried from high temperature solution to low temperature solution by mass transfer not only strengthens heat transfer efficiency, but also increases the solution concentration in the generator and decreases the solution concentration in the absorber. As a result, the deflation scope is enlarged, the thermal load of the generator and the absorber is reduced and the COP is enhanced. That is to say, both heat transfer and mass transfer processes are beneficial to the system.

The experimental and theoretical study of DCMD process in solution heat exchanger will be illustrated in detail in section 3.

1.5 Potential application of membrane distillation in energy transformation process

Based on the mechanism of membrane distillation, the experimental study of VMD process of high concentration saline solution, and the experimental and theoretical study of DCMD process in solution heat exchanger, this paper introduced several potential applications of membrane distillation in energy transformation process, as shown in Figure 4.

High concentration saline solution can be concentrated and separated by VMD process in a way similar to the desorption or regeneration process of LiBr solution in absorption refrigeration system. Moreover, concentrated solution can also act as an energy storage mode due to the transformation of heat energy into solution chemical energy. Therefore, VMD process can be applied to both LiBr absorption refrigeration system and solution chemical energy storage system.



Figure 4 Potential applications of membrane distillation to energy transformation process.

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In temperature-humidity independent control airconditioning system, liquid desiccant like lithium bromide solution, lithium chloride solution and calcium chloride solution absorbs water vapor from fresh air to accomplish dehumidification. The weakened solution needs regeneration for recycle. Membrane distillation process, which uses low-grade energy such as solar energy and geothermal energy as the driving heat energy, can be applied to the regenerative process of the weakened solution.

DCMD process can be used in solution heat exchanger. Both heat transfer and water vapor transfer are beneficial to the chosen system, that is to say, heat transfer and water vapor transfer can occur simultaneously in the same direction in the system. For example, in the membrane heat exchanger of a LiBr absorption refrigeration system, not only is heat transfer realized, but also the deflation ratio is enlarged because of mass transfer, which is wholly beneficial to the improvement of the COP of system. Moreover, DCMD process can be applied to the recovery of both waste heat and pure water according to the accordant direction of heat and mass transfer.

2 Experimental study on desorption of high concentration saline solution by VMD process

Commercial LiBr solution with 50wt% was taken as an example to experimentally verify the feasibility and illustrate the influence factors of desorption or regeneration of high concentration saline solution via VMD process^[47]. The main aim was to study the penetration performance of water vapor at different temperatures and under different flux (in the warm side) and vacuum pressure (in the cold side). The experimental parameters included: (1) temperature scope on the warm side:

. . .

 $65^{\circ}C - 88^{\circ}C$; (2) solution flux scope on the warm side: 40-120 L/h; (3) vacuum degree in the cold side: 0.085-0.095 MPa (absolute pressure: 0.005-0.015 MPa). Membrane material was PVDF, and membrane module was hollow fiber module. Parameters of the membrane material and hollow fiber module are shown in Tables 1 and 2, respectively.

Figure 5 shows the schematic plan of the experimental test of VMD process. The thermostatic water bath controlled the temperature of LiBr solution and the flowmeter controlled the flux of LIBr solution. Adjuster of vacuum pressure and vacuum pump were used to create a vacuum state in the cold side before the experiment. When the vacuum pressure reached the required value, the vacuum pump stopped. After that, the vacuum pressure was decided by the condensing temperature of cooling water. Therefore, the vacuum degree in the cold side was adjusted by the regulating valve of the cooling water flowmeter.

Figure 6 shows the influence of the three parameters on water vapor penetration flux in desorption of LiBr solution by VMD process. Figure 6(a) reveals that water vapor penetration flux increased with the rising of LiBr solution temperature. The increase in LiBr solution temperature caused water vapor pressure to rise and the driving force to increase, according to eq. (1), which resulted in the increase of the water vapor penetration flux. Figure 6(b) shows that water vapor penetration flux increased with the LiBr solution flux rising. As Figure 2 (a) shows that the increase in feed flux resulted in the enhanced disturbance between LiBr solution and membrane wall, the reduced temperature layer and concentration layer and the rising temperature of membrane wall. Moreover, the disturbance was beneficial to water vapor diffusion across membrane pores. Figure 6(c) depicts that water vapor penetration flux increased with the

Table 1 Parameters of PVDF membrane material				
Average aperture (µm)	Porosity	Inner diameter (mm)	Wall thickness (mm)	Outer diameter (mm)
0.16	85%	0.8	0.15	1.1
Table 2 Parameters of hold	ow fiber module			
Outer diameter (mm)	Inner diameter (mm)	Effective length (mm)	Number of membrane	Membrane area (m ²)
50	42	400	300	0.3

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Figure 5 Schematic of the experimental set-up. 1. Thermostat water bath; 2. magnetic pump; 3. flowmeter; 4. membrane module; 5. condenser pipe; 6. cooling water flowmeter; 7. receiving tank; 8. adjuster of vacuum pressure; 9. vacuum pump; 10. temperature probe. pressure sensor; 11. feed thermometer.

vacuum degree rising in the cold side. The increase in the vacuum degree led to the reduction in the absolute pressure in the cold side, according to eq (1), and the increase in the driving force. Thus, the water vapor penetration fluxes enhanceed. It can be concluded from the analysis of orthogonal test of the three parameters that feed temperature had the greatest influence on the water vapor permeation flux, the second influence factor was vacuum pressure in the permeation side, and feed flux had the least influence.

In addition, the electric conductivity used to measure the cooled water in the experiments was below 10 μ s/cm, and the reflection ration of PVDF membrane was calculated to be 99.9% according to the electric conductivity, indicating that the penetrating water had high purity.

3 Experimental and theoretical study of DCMD membrane heat exchanger

Application of DCMD process in special heat exchanger design is considered feasible due to the two properties of the membrane and membrane module: the energy transformation process across the membrane between hot solution and cold solution, and the enormous contact area that hollow fiber membrane module offers.



Figure 6 Influence of three parameters on permeation flux. (a) Influence of feed temperature on permeation flux; (b) influence of feed flux on permeation flux; (c) influence of vacuum degree on permeation flux.



Figure 7 Heat and mass transfer properties under the influence of various flow parameters. (a) Heat and mass transfer of membrane heat exchanger at various inlet temperatures; (b) heat and mass transfer of membrane heat exchanger under various feed fluxes

Hollow fiber membrane heat exchanger applied to the LiBr absorption refrigeration system was analyzed by mathematical simulation^[48]. The result showed that not only was the heat transfer process more sufficiently, but also the mass transfer of water vapor was always from the warm side to the cold side. That is to say, the direction of latent heat transfer was always in line with the direction of heat conduction. Therefore, counter-flow process in membrane heat exchanger seemed more suitable for the flow mode of solution heat exchanger^[49]. Moreover, the quantity of latent heat transfer accounted for nearly 30% of the total amount of heat transfer, the concentration of strong solution increased by about 0.5 wt%, the concentration of weak solution decreased by about 0.5 wt%, and the deflation ratio enlarged by about 1.0 wt%.

Figure 7 shows the experiment results of hollow fiber membrane module as a solution heat exchanger to recover both heat energy and pure water¹⁾. The experiment parameters were similar to those presented in Tables 1 and 2 except that the membrane number was 600 and membrane area was 0.6 m^2 . The working fluid on both sides was water. In counter-flow mode, the main experiment contents included two parts: (1) The feed flux on both sides and the feed temperature on the cold side maintained constant while the feed temperature on the warm side increased gradually. Then the water vapor penetration flux, the quantity of all the transferred heat and the quality of the latent heat transferred from the warm side to the cold side were measured. (2) The feed temperature on both sides maintained constant while the feed flux increased gradually. Then the water vapor penetration flux and the quantity of all the transferred heat and the latent heat transferred from the warm side to cold side were measured. As shown in Figure 7, the quantity of the transferred latent heat amounted to approximately 70 percent of the total transferred heat since the water vapor mass transfer was great. Moreover, compared with traditional metal heat exchanger with similar configuration and size, membrane heat exchanger had high performance in the experimental operating parameters and low flow rate. However, the flow resistance of membrane heat exchanger went up more quickly than traditional mental heat exchanger. Therefore, membrane heat exchanger was fit for low flow velocity conditions.

4 Applications of membrane distillation technology to energy transformation process

The potential applications of membrane distillation technology to energy transformation process, which is shown in Figure 4, are presented in detail below.

4.1 Absorption refrigeration system driven by low-grade energy

Regenerative energy such as solar energy, geothermal

¹⁾ Wang Z S, Feng S Y, Li Y, et al. Experimental and theoretical study on heat and mass transfer of hollow fiber membrane heat exchanger. J Xi'an Jiaotong Univ, 2009, Accepted (in press)

energy and all kinds of waste heat belongs to low-grade energy. The application of such low-grade energy is of great importance either in solving energy shortage problems or in energy saving^[50]. The absorption refrigeration system is an ideal energy saving system because it is driven by heat energy and can recover waste heat energy.

After the experimental study of desorption of LiBr solution by VMD process^[47] and the mathematic simulation of hollow fiber membrane solution heat exchanger^[48], a novel single effect absorption refrigeration system based on membrane distillation technology was developed and shown in Figure 8(a). The membrane desorber could use low-grade energy such as solar energy, geothermal energy and waste heat as the driving heat source.

In the single effect absorption refrigeration system, membrane desorber, which comprised solution heater, hollow fiber membrane module and membrane desorber recycle pump, replaced the traditional generator in order to use lower temperature energy. The solution did not need to be heated to its boiling point and lower temperature energy was efficient enough to drive the system. The pressure on the cold side of membrane desorber was decided by the condensing pressure of the condenser. Moreover, membrane solution heat exchanger took the place of the traditional solution heat exchanger to strengthen mass transfer of water vapor and accordingly, enlarge the deflation ratio of the system. The other components were identical with those used in the traditional absorption refrigeration system. Figure 8(b) shows the comparison between the new cycle and traditional cycle via enthalpy concentration diagram. The process 2-7-5-4-8-9-9'-2 shows the operating process of traditional LiBr absorption refrigeration system, and the process 2-7'-5'-4*-4'-8'-9-9'-2 shows the operating process of the new system. Obviously, the deflation ratio of the new system was enlarged $(\xi_a - \xi'_a) + (\xi'_r - \xi_r)$, suggesting that the circulating ratio in the generator decreased and the COP of the system increased^[51]. The power of recycle pump was so small that it could be ignored, compared with other energy consumption.

4.2 Absorption refrigeration system driven by high-grade energy

As for the LiBr absorption refrigeration system driven by high temperature thermal source, the strong solution from the generator can be further desorbed by VMD process as a second generator due to its high temperature. As shown in Figure 9 (a), component A is the traditional generator driven by high temperature thermal



Figure 8 Single effect LiBr absorption refrigeration system based on membrane distillation. (a) LiBr absorption refrigeration system with hollow fiber membrane desorber and heat exchanger. A: solution heater; B: condenser; C: absorber; D: evaporator; E: membrane heat exchanger; F: expansion valve; G: membrane desorber; K: weak solution pump; L: absorber pump; M: evaporator pump; N: desorber pump; (b) $h-\xi$ diagram.



Figure 9 Absorption refrigeration system based on membrane distillation. (a) LiBr absorption refrigeration system with hollow fiber membrane module desorber and heat exchanger. A: traditional generator; B: vondenser; C: absorber; D: evaporator; E: membrane heat exchanger; F: expansion valve; G: membrane desorber; H: condenser; I: expansion valve; K: weak solution pump; L: absorber pump; M: evaporator pump; N: desorber pump; (b) h- ξ diagram.

source. The strong solution from the generator flowed into the membrane desorber to be further separated. As a result, the deflation ratio increased, the heat load of the generator and absorber reduced, the available temperature difference of thermal source enlarged and above all, the refrigerating capacity increased.

Figure 9(b) shows the enthalpy concentration diagram according to Figure 9(a). The process 2-7'-5'-4-8' -9-9'-2 shows the operating process of traditional LiBr absorption refrigeration system, and the process 2-7-5-4-4'-8-10-10'-2 shows the operating process of the new system with a second auxiliary membrane desorber and a membrane solution heat exchanger. In Figure 9(b), the process 4-4' depicts the membrane desorber process in which the concentration enlarged by $(\xi_0 - \xi_r)$. The processes 2-7 and 4'-8 represent the heat and mass transfer process in membrane heat exchanger in which their concentration increased by $(\xi'_r - \xi_0)$ and $(\xi_a - \xi'_a)$, respectively.

4.3 Absorption energy storage system based on membrane distillation technology

As is known, building energy consumption, along with industrial energy consumption and traffic energy consumption, has become one of the largest energy consumptions. Heating and air-conditioning in buildings consume more than 50 percent of the energy consumed in buildings^[52]. Electricity consumption by refrigeration and air-conditioning accounts for appropriate 20% – 30% of the total power consumption^[53]. Moreover, electric power supplies are unbalanced due to human living and working habits. Therefore, energy shortage and energy waste exist simultaneously at daytime and nighttime. Energy storage is an effective and feasible method to distribute the unbalanced energy supply in a reasonable way. The popular energy storage methods include sensible heat energy storage^[54], ice energy storage^[55], eutectic salt energy storage, phase-change material energy storage^[56] and chemical potential energy storage^[57,58].

In most energy storage systems, energy is transformed into cold energy or heat energy and saved in adiabatic vessel to avoid heat loss. The temperature of cold energy or heat energy is kept at a constant level, but the constant temperature cannot be maintained for a long time. However, in chemical potential energy storage, energy is transformed into chemical potential energy of the working fluid and can be saved there for a long time. Figure 10 shows the flow chart of a LiBr absorption energy storage system based on membrane distillation technology¹. In the system, the membrane

¹⁾ Wang Z S, Gu Z L, Feng S Y, et al. A solar-driven absorption energy storage system based on membrane distillation technology. In: 2009 US-EU-China Thermophysics Conference-Renewable Energy. Beijing University of Technology, Beijing. May 28-30 2009. Accepted (In press)

dsorber replaced the traditional generator and the membrane heat exchanger replaced the traditional solution heat exchanger. Compared with the single effect LiBr absorption refrigeration system shown in Figure 8(a), three main liquid reservoirs, i.e., the coolant reservoir, the strong solution reservoir and the weak solution reservoir, were added to the energy storage system. The heat energy was converted to the chemical potential energy of LiBr solution and coolant water.

LiBr absorption system is an ideal system for chemical potential energy storage. In the energy storage process, heat energy was transformed into chemical potential of LiBr solution and latent energy of refrigerant water. In the exoergic process, rich solution of aqueous LiBr absorbed water vapor from the evaporator and the weakened solution was saved in the weak solution reservoir. Thus, chemical potential was transformed into cold energy in the evaporator or heat energy in the absorber.

The energy storage system shown in Figure 10 could operate continuously as refrigeration system and operate intermittently as a storage energy process or an exoergic process. It could use low-cost heat energy such as industrial waste heat and regenerative energy such as solar energy and geothermal energy. In addition, electric power in valley load and low price period could also be applied to the energy storage system.



Figure 10 Absorption energy storage system based on membrane distillation. A: Solution heater; B: condenser; C: absorber; D: evaporator; E: membrane heat exchanger; F: expansion valve; G: membrane desorber; H: coolant tank; I: strong solution tank; J: weak solution tank; K: weak solution pump; L: absorber pump; M: evaporator pump; M: desorber pump.

4.4 Solution regenerator in liquid desiccant dehumidification air conditioning

Figure 11 shows the liquid desiccant dehumidification system with membrane distillation regenerator. It could be used in temperature-humidity independent control air-conditioning system. Liquid desiccant (such as lithium bromide solution, lithium chloride solution and calcium chloride solution) absorbed the water vapor from fresh air and undertook the whole latent heat loads of building^[59]. Meanwhile, membrane distillation regenerator could concentrate the weak solution using low-grade energy. In decentralized desiccation process, strong solution was pumped into each dehumidifier and absorbed water vapor from fresh air circularly, and then the concentration of liquid desiccant decreased until it could no longer absorb water vapor and became weak solution. Thereafter, the weak solution from each dehumidifier was collected in the weak solution tank and was heated by low-grade energy in the heater. Then, the heated solution was pumped to the hollow fiber membrane module circularly where the concentration of liquid desiccant was recovered. After recovery, the liquid desiccant re-entered into the next cycle. Water vapor diffused across the membrane pores from the warm side to the cold side and were chilled and stored as refrigerant water due to its high purity. The condensate water could also act as coolant refrigerant directly if it flowed into the evaporator. It is shown that the mechanism of membrane distillation regenerator is similar to that of desorption of LiBr solution mentioned above.



Figure 11 Dehumidification and regeneration of liquid desiccant.

5 Discussion and prospect

Membrane distillation is a novel membrane separation technology. This paper discussed the fundamental applications of membrane distillation in energy transformation process and analyzed their potential applications, based on the mechanism of membrane distillation process and the energy transformation process. Due to the feasible application of VMD process to desorption or regeneration of aqueous solution, VMD process could be applied to the LiBr absorption refrigeration system and the LiBr absorption energy storage system. It could also be applied to the regeneration of liquid desiccant in temperature-humidity independent control air-conditioning system. Based on the property of heat and mass transfer in DCMD process, DCMD process could be applied to the solution heat exchanger of LiBr absorption refrigeration system and to special heat exchanger to recover both heat energy and pure water.

Moreover, the advantages of the applications of membrane distillation to energy transformation were analyzed using enthalpy concentration diagram based on the experimental test and mathematical simulation of saline solution desorption and membrane solution heat exchanger. However, the following theoretical and experimental studies are needed to better understand the applications of membrane distillation: the precise diffusion principle and mathematic model, the influence of thermal layer in membrane wall on water vapor diffu sion,

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the influence of temperature polarization and concentration polarization on the partial pressure of water vapor in membrane pores and on the penetration flux, and the thermodynamic equilibrium relations of the unsaturated solution in the interface of membrane pores.

Furthermore, high requirements on the membrane material and membrane module must be satisfied in the applications of membrane distillation process to energy transformation. For example, membrane material should be developed to strengthen penetration flux for the sake of higher separation efficiency, the intension and LEPw of membrane material should be improved in order to increase solution flow velocity, the thickness of thermal layer should be reduced and the negative effect of temperature polarization and concentration polarization should be weakened. Membrane material with low thermal conductivity should be developed so as to increase the thermal efficiency of membrane module, reduce heat loss and improve penetration flux. The membrane module and flow mode should be designed and optimized to be better adapted to energy transformation mode.

With the development of membrane materials and their manufacturing techniques, membrane materials and membrane modules with high performance cost ratio will be more specialized for various applications. In addition, membrane distillation will also be applied to more multi-field studies of different industries.

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