Membrane contactor air conditioning system: Experience and prospects

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Abstract

This paper presents theoretical and experimental study of humidity control and independently carbon dioxide removal from indoors conditions by means of the pilot recycle membrane contactor air conditioning system (MCACS). The system can be successfully used for indoor air purifying for clean room facilities, industrial processes improvement, food and agricultural products storages and others. Advantages of membrane-absorptive separation method realized in membrane contactors are relative construction simplicity, reliability, high parameters of separation, lower energy consumption and absence of high-pressure drop. Developed air conditioning system represents combination of recycle membrane contactors (RMC) in single block designed to operate with atmosphere restricted air exchange for indoor air purification. Triethylene glycol (TEG) was used as effective hygroscopic liquid carrier for air dehumidification system. Carbon dioxide control system was tested on pure water. Polydimethylsiloxane (PDMS) and polyvinyltrimethylsilane (PVTMS) based nonporous membranes were used in spiral wound and flat frame membrane modules. The experiments with membrane contactor systems demonstrated effective air-drying ($T_{\text{dew point}} = -30$ $^\circ$C) under high gas flow to liquid carrier flow ratio ($G/L = 103$) with membrane absorber and desorber temperature difference about $\Delta T = 30$ $^\circ$C. Carbon dioxide removal system showed possibility of CO$_2$ concentration reduction 10 times.

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1. Introduction

One of the new directions of membrane contactors development lies in the field of climatic technique and connected with new air-conditioning systems creation [1]. Main tasks of such systems are: comfortable temperature keeping, excess moisture, carbon dioxide and organics removal.

Except temperature keeping, each of the processes mentioned above, are realized on membrane contactors [2,3,10]. They can be efficiently applied for indoors air chemical composition control in conditioning systems with restricted or impossible air exchange with outdoor atmosphere. It is especially important for life-support system of submarines, underground shelters, space and aircrafts. MCACS, representing itself serial combination of independent recycle membrane contactors combined with gas separation membrane modules, providing pure air delivering indoors, was developed (Fig. 1). It can independently and simultaneously control humidity rate, carbon dioxide concentration and in case of need provides air enrichment by oxygen independently from outer atmosphere conditions. But the choice of absorbent, that can reversible and selectively interact with oxygen, is still difficult task.

Air drying and carbon dioxide removal stages are based on RMC with gas separation membrane modules with non-porous membranes [4]. All these blocks are combined in gas recycle scheme with two feed flows: external and indoor. The last one is taken from the room and usually possesses excess density of carbon dioxide and moisture. The system has two output flows, one of which, directed indoors, can be depleted by carbon dioxide and water vapor and theoretically a little bit enriched by O$_2$.

Recycle scheme was chosen by reason of high selective component accumulation in the contour of the system: more recirculating flow to feed flow ratio we set, more concentration of penetrated component in absorbent we get. Thus, we can reduce or even shut down for some time external air flow and control room air content independently from outer atmosphere. Developed MCACS can be successfully integrated with conventional central conditioning ventilation systems. Membrane contactors using specific liquid absorbents allow providing air dehumidification without over-cooling it to the dew point in order to condense and recover water vapor. Elevated temperature of room

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Fig. 1. Recycle membrane contactor (RMC) air conditioning system principle.

Air, applied for liquid carrier regeneration in membrane desorber, makes energy consumption of the system essentially lower. As far as energy-consuming units are liquid pump and heater, energy consumption of such a system is comparable with conventional refrigeration air conditioning units or even lower. The system is free of ozone-depleting CFC and HCFC refrigerants currently used in the vapor compression refrigeration cycles. Moreover, membrane contactors allow relative humidity close control (±1%) in the range 12–98%RH.

This paper describes the first step of investigation of air-drying and carbon dioxide removal in recycle membrane contactors with non-porous polymeric membranes in MCACS.

2. Materials and methods

Spiral-wound membrane contactors (“Vladipor”, Russia) with flat nonporous polymeric membranes based on polydimethylsiloxane (PDMS) as the basic elements of the air-drying RMC were used (Fig. 2). Two conventional membrane modules with membrane area $S_{PDMS} = 1.1 \text{ m}^2$ and liquid channels height $h_c = 1 \text{ mm}$ were tested as membrane absorber and desorber. The flow organization in modules is close to counter-current scheme. Applied modules effectively operate in temperature ranges $T = 0–60 \degree\text{C}$ at gas pressure up to $P > 0.5 \text{ MPa}$, that makes them possible operating as absorber at room temperatures, while desorber temperature can be held increased. During the experiments the outlet air humidity and temperature in membrane absorber and desorber were permanently analyzed by digital humidistat (IVTM-7, Russia).

Experiments with carbon dioxide air mixture were carried out on lab scale flat frame membrane contactors, produced by JSC “Aquaservice” (Moscow) with nonporous asymmetric polymeric polyvinyltrimethylsilane (PVTMS) membranes (Fig. 3) [5].

Membrane area of tested flat frame modules was lower than in spiral wound module ($S_{PVTMS} = 0.37$ and $0.12 \text{ m}^2$), liquid channel height was $h_c = 0.1 \text{ mm}$, the achieved length of the channel was $l_c = 170 \text{ mm}$. Gas and liquid flows organization in the module is realized by the counter-current scheme. Carbon dioxide concentration in retentate was checked by carbon dioxide analyzer (“Rikken Keiki”, Japan).

3. Experiments

Gas–liquid membrane contactor is a separating device combining membrane and absorption methods of gas separation, in which selective mass transfer between moving gas and liquid absorbent divided by the membrane is realized. Components can selectively transfer from gas phase into liquid or vice versa, thus realizing the process of separation. The principal scheme of recycle membrane contactor for effective gas mixture separation is shown in Fig. 4. Gas mixture to be separated, consisting, for example, of two gases $(X+Y)$, puts to the membrane absorber. Membrane, installed in the module, passes through only one component of mixture—$(X)$, dissolving in liquid absorbent, circulating in the closed loop. Another low permeable component—$(Y)$ leaves the module as retentate and can be fed to another treating stage of conditioning system. Liquid pump feeds absorbent to the membrane desorber, where dissolved component $(X)$ penetrates through the membrane to...
the gas cavity of the module, from where it can be swept by some part of the feed gas flow or pumped out by the vacuum pump, as it is shown. Heater and cooler are intended to provide high temperature liquid carrier regeneration with subsequent cooling. Thus, it is possible to separate mixtures, containing for example water vapor, hydrogen, methane, ethylene, carbon dioxide, etc.

The schematic diagram of RMC is shown in Fig. 4. This design is suitable for air dehumidification and carbon dioxide removal both [6]. In case of air-drying, RMC operates in non-isothermal mode. Relative humidity of air flow, which must be added to the room must be reduced to $\phi_{\text{out}} < 10\% \text{RH}$. To obtain such a value, effective absorbent regeneration is needed. The heater and cooler are activated for water vapour high temperature recovery from liquid absorbent. After membrane absorber, where air dehumidification process is accomplished, liquid carrier heats to the regeneration temperature ($T_d = 50–60\degree C$) and turns to membrane desorber for regeneration. Sweeping process is realized by preheated part of wet feed air flux, taken from the feed air flow. Absorbent temperature is reduced in water–water spiral heat exchanger to the range of room temperature.

Room air with exceed moisture $\phi = 40\% \text{RH}$ was fed into the gas chamber of the spiral wound membrane absorber at various flow rates $G = 0–1 \text{l/s}$. Triethyleneglycol (TEG), produced by “BioOazis” (Russia), with initial water content about 6.5 mass% was used as standard liquid absorbent for air and natural gas drying. Liquid and gas fluxes, directed to the membrane desorber were heated to $T_d = 55\degree C$.

Carbon dioxide removal from air is effectively realized on high selective membranes and high capacity absorbent. It is known, that the process is slightly affected by temperature of liquid carrier. Thus, the isothermal operating mode of RMC in such case (room temperature of absorber and desorber) can be used for energy reduction. Moreover, for reduction of unit price even distilled water can be applied in the process mentioned above. The external air at atmospheric pressure was applied as sweeping gas in membrane desorber for effective and cheap regeneration.

4. Results and discussion

Direction of driving force of mass transfer process in gas–liquid membrane contactor is determined by the difference of chemical potential gradients between gas and liquid phases. Its value and direction depends generally on the temperature, concentration and pressure, and defines the operating mode of the membrane module: absorber or desorber. Chemical potential of the component in gas phase is determined by its partial pressure and temperature. In liquid phase chemical potential is determined by water vapour activity in liquid absorbent (TEG for air drying) and can be evaluated as equilibrium partial pressure of water vapour to liquid. Henry's law connects this pressure with component activity. Low values of Henry’s constant for TEG/water system at regeneration temperatures, applied in RMC, provides high sorption capacity of water vapour in TEG. Henry’s constant has strong temperature dependence: temperature increase on 10 $\degree C$ leads to partial water vapour pressure in gas phase rise in twice [7].
measured at atmospheric conditions ($T = 20^\circ C$, $P = 0.1$ MPa). Regeneration temperature was kept $T_d = 55^\circ C$.

Room air relative humidity was reduced from $\varphi = 40\%$ RH to 10–12% RH to atmospheric pressure and volume discharge at relatively high gas to liquid flow ratio $G/L = 1000$. It is seen from Fig. 5 that membrane contactor efficiency in air-drying process increases with overall pressure rising in gas chamber of the module. But restriction of operating air flow ranges at various average pressures which corresponding to $\varphi = 16\%$ RH in both cases of air pressure is caused by hydraulic resistance of gas cavity of spiral wound membrane module. It was found, that gas pressure changing in the module leads to so called “critical inversion point” appearance, when equilibrium condition between gas and liquid phases is obtained. After this critical point along the length of the module the partial water vapor pressure in gas phase does not change and the rest part of the membrane does not influence the process. Water vapour penetrates from the absorbent to air and vice versa, mole fraction of water vapour in air at critical point remains constant, that leads to worsening of membrane contactor productivity. Fig. 6 demonstrates the inversion point dependence in the spiral wound membrane module, where $X$ is fraction of operating membrane area in the module [8].

As it can be seen from Fig. 6, with gas flow increasing, more membrane area in the membrane contactor takes part in air-drying process. It can be concluded, that limited PDMS membrane permeability becomes the limiting factor in air-drying process with TEG. That means, that the chosen spiral wound membrane module has exceeded membrane area for the chosen air-drying task and does not suite for it.

The second step of investigation was connected with carbon dioxide removal. As air-drying experiments showed, the construction of this module is effective for separation processes at high gas–liquid ratio. Besides that, big liquid clearance (1 mm) makes this construction possible for use in low gas flows separation processes, as in case of CO2 removal, or for low liquid flows, for example—air drying. Flat frame membrane module has sharp counter-current flow organization and operates with high liquid flows. Two flat frame membrane modules with different membrane area $S_{PVTMS} = 0.37$ and 0.12 m² and spiral wound membrane module with $S_{PDM} = 1.1$ m² were tested for CO2 removal from air at room temperature [6,7].

Air mixture with $C_{CO2} = 45$ mol% at different flows were put to the RMC for carbon dioxide removal investigation. Water discharge was varied from $L = 0–60$ l/h. Relative carbon dioxide concentration, as output $C_t$ and input $C_i$ concentration ratio, on liquid absorbent flow dependence at various gas mixture flows for spiral wound membrane contactor is shown in Fig. 7.

The same dependence for flat frame modules with membrane PVTS are shown at Fig. 8 [4]. For both cases experimental points and theoretical data, obtained with the help of mathematical modeling, are in good agreement with each other [9].

It is seen from the diagram, that flat frame membrane contactor operates more effectively at lower gas flows ($L = 1–10$ l/h). As it is seen from Figs. 7 and 8, membrane area of the flat frame membrane contactor more than four times lower than in the spiral wound, liquid clearances are also smaller, but it is three times more effective. Experimentally obtained effect is 10 times CO2 concentration reduction: from 45 to 4 mole%.

5. Conclusion

Counter-current recycle membrane contactor air conditioning system based on recycle membrane contactors and double-flowing modules providing room air content control with restricted outdoor air exchange at various outdoor atmospheres is suggested. Experimental study of air drying process in recycle membrane contactor with PDMS membranes and TEG as liquid carrier is carried out as the stage of air treatment in conditioning system. The system allows realizing air dehumidification below $T_{dew-point} = -30^\circ C$ at optimum gas–liquid flows ratio above $G/L = 10^3$ under absorption desorption temperature difference $\Delta = T_a - T_d < 30^\circ C$. Thus, it is revealed, that spiral wound membrane contactor design, due to critical inversion point appearance, is not optimal.

Spiral wound and flat frame membrane contactors with non-porous polymeric membranes for effective CO2 removal were tested. Experimentally proved, that the last one membrane contactor design is more effective in the offered recycle system. Membrane contactor allows CO2 10 times reduction without compression for gas flow $G = 40$ l/h on membrane area $S_m = 1$ m² at $G/L = 1/2$ using even water as liquid absorbent.
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