We report the application of porous polypropylene hollow fiber membranes with 100×500 nm slit pores in membrane contactor for air dehumidification using triethylene glycol (TEG) as an absorbent. Experiment geometry with gas flow through the lumen of fiber and absorbent circulated on the shell side was utilized to enhance water vapor stage cut. The influence of gas flow rate, liquid circulation rate and water content in triethylene glycol solution on the performance of membrane contactor was studied. The obtained results reveal that the limiting step of water vapor absorption for lumen gas flow configuration is the diffusion of water into TEG volume. Using dry TEG solution and high circulation rate the dew point of feed gas can be decreased down to \(\sim -30^\circ C\) for the membrane contactor performance of 30 – 60 l/(m\(^2\)h), while with reducing dew point requirements to \(\sim -10^\circ C\) the performance of the contactor over 1 m\(^3\)/h is achievable.

Keywords: dehumidification, membrane contactor, polypropylene membrane, gas-liquid contactor.

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1. Introduction

Gas dehumidification is known as one of the most common technical tasks required in various industrial applications, such as natural gas treatment, air drying, pneumatic fluids conditioning, etc. Dehumidification can be accomplished using cooling cycles [1], including those based on vapor capillary condensation effect [2, 3], vapor absorption [4] or adsorption [5] with desiccants and exploiting membrane separation equipment [6]. Among the methods mentioned, gas, dehumidification by vapor absorption with hygroscopic liquids gained most widespread use due to low energy consumption, the absence of water droplets and its high efficiency.

Two types of hygroscopic liquid absorbents are applied commonly for water vapor capture: aqueous solutions of hygroscopic salts (such as, LiCl, LiBr or CaCl\(_2\)) which are typically utilized for humidity control in residential or commercial buildings and di- or triethylene glycols (DEG or TEG) used primarily for industrial facilities. The main disadvantages of salt solutions are related to corrosion and salt crystallization [7]. The utilization of salt solutions for apartment air dehumidification is governed by the absence of desiccant pick-up due to the much lower salt vapor pressure in comparison with glycols [8]. Moreover, the comfort humidity values for working and living spaces is ranges from 30 % to 60 %. These humidity values can be achieved by using salt solutions and there is no need to utilize strong absorbents like TEG. At the same time, technological applications, such as gas pipeline transport, air compression for pneumatic systems required very low dew point values from \(-60^\circ C\) to \(-40^\circ C\), which can be achieved only by using 99.99 % TEG as a desiccant [9].

Typically gas dehumidification is realized by direct gas-liquid contact in packed columns or bubble towers [4]. However, the interfacial contact area of those contactors depends strongly on the operation conditions, such as flow rate or operating pressure. Tight control of the operation parameters is required to avoid foaming, channeling, flooding or unloading of the dehumidification columns. Gas-liquid membrane contactors where the liquid and gas phases are separated by a semipermeable membrane (especially hollow fiber membranes) were suggested as an alternative technology for overcoming drawbacks of direct gas-liquid contactors [10–12]. Moreover, utilization of membrane contactors allows to increase interfacial contact area over 2000 m\(^2\)/m\(^3\) compared to 50 – 600 m\(^2\)/m\(^3\) typical for classic contact devices [13].

Membrane contactors are generally divided into two groups: non-porous contactors (usually having an asymmetric structure with selective layer) and porous contactors. Despite providing much better isolation of contacting phases, non-porous contactors generally have much lower permeability for the target components, resulting in proportional growth of capital and operational costs in industrial uses. In the case of porous contactors, the gas-liquid interface is formed at the pore necks. Depending on the membrane’s hydrophobicity and the type of absorbent, the diffusion of gas molecules or diffusion of absorbed molecules in the liquid occurs within the pores. In the second case, the resistance of membrane is significantly higher due to lower diffusivity in liquid phase in comparison with the gas phase. This necessitates the use of hydrophobic membrane material for dehumidification issues.
The first demonstration of air drying by membrane contactors was reported by Isetti and Nannei using LiCl and CaCl$_2$ saturated solutions as absorbents [14]. Further studies of heat and mass transfer in membrane contactors during dehumidification with aqueous LiCl have been performed by Zhang et al. [15–17]. In contrast, until now, only a little attention has been paid to membrane contactor dryers with DEG or TEG absorbents [18,19]. Moreover, all reports found in the literature consider contactors with absorbent flowing to the lumen side of fibers and gas flowing from the shell side. Despite the fact that using lumen liquid in hollow fiber seems logical from a practical viewpoint, as the feed stream flux generally exceeds that of absorbent many times, this configuration significantly decreases the probability that gas molecules will be drawn into the pores of membrane. This potentially leads to incomplete removal of absorbate and failure to achieve equilibrium vapor pressure. Moreover, the usage of lumen liquid requires the use of powerful pumps to push viscous absorbent through small-diameter fibers.

Thus, in the present study, we report the use membrane contactors with opposite configuration: gas flowing in the lumen side of fibers and absorbent flowing over the shell side. Hydrophobic polypropylene (PP) hollow fiber was used in contactor to avoid filling the pores with a liquid. TEG was applied as an ultimate absorbent allowing the attainment of minimal humidity levels. A schematic representation of the dehumidification process is provided in Fig. 1a. The effects of gas and liquid flow rates as well as TEG water content on the performance of polypropylene hollow-fiber membrane contactor were elucidated.

![Figure 1. Scheme of membrane contactor dehumidification process (a) and experimental setup for air dehumidification (b)](image)

2. Experimental

Nanoporous polypropylene hollow fiber membranes were supplied by Zena S.R.O. (Czech Republic). A schematic diagram of air dehumidification setup is represented in Fig. 1b. The flux of compressed air was controlled with two mass-flow controllers SLA5850 (Brooks, USA). Air was saturated with water vapor in the humidifier by direct air-water contact. Air temperature and humidity on the inlet and outlet of membrane contactor was monitored by HIH-4000 (Honeywell, USA) sensors. The dew point temperature of treated air was also determined by dew-point hygrometer TOROS-3VY (Ukraine). Lumen side (gas) and shell side (liquid) pressures were controlled by Carel SPKT00E3R pressure transducers and kept at required values to avoid bubble formation in liquid and penetration of liquid droplets into the air stream. A peristaltic pump (BT300-2J, Longer Pump Co, China) was used for TEG circulation. At each run fresh TEG with purity higher than > 99.5% was used. All dehumidification experiments were carried using feed air with relative humidity 95 – 97 % at the temperature of 23 °C. To ensure the steady state conditions of absorption were achieved, every measurement was performed 3 times in 30 minute intervals.

To characterize contactor performance, two major parameters of contactor devices (water absorption flux and water vapor stage cut) were extracted for each experimental conditions:

\[
J = \frac{Q_{in} \cdot \frac{P_{sat}(H_2O)}{P_{in}} \cdot RH_{in} - Q_{out} \cdot \frac{P_{sat}(H_2O)}{P_{out}} \cdot RH_{out}}{S},
\]

where \(J\) – water absorption flux [mol/m$^2$/s], \(Q_{in}\) and \(Q_{out}\) – inlet and outlet gas flux, respectively, \(RH_{in}\) and \(RH_{out}\) – inlet and outlet relative humidity, \(P_{sat}\) – saturated water vapor pressure at given temperature (calculation was performed via Antoine Equation with coefficients determined by Stull [20] for temperature below 0 °C and
TABLE 1. Characteristics of PP membrane contactor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber outer diameter, mm</td>
<td>0.31</td>
</tr>
<tr>
<td>Fiber inner diameter, mm</td>
<td>0.24</td>
</tr>
<tr>
<td>Average pore size, nm</td>
<td>200</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>45</td>
</tr>
<tr>
<td>Module length, cm</td>
<td>50</td>
</tr>
<tr>
<td>Number of fibers in module</td>
<td>1200</td>
</tr>
<tr>
<td>Module contact area, m²</td>
<td>0.584</td>
</tr>
</tbody>
</table>

coefficients determined by Bridgeman and Aldrich [21] for temperature above 0 °C, $P_{in}$ and $P_{out}$ – inlet and outlet air pressure and $S$ – membrane area:

$$\eta = \frac{Q_{in} \cdot \frac{P_{sat}(H_2O)}{P_{in}} \cdot RH_{in} - Q_{out} \cdot \frac{P_{sat}(H_2O)}{P_{out}} \cdot RH_{out}}{Q_{in} \cdot \frac{P_{sat}(H_2O)}{P_{in}} \cdot RH_{in}},$$

where $\eta$ – water vapor stage cut.

Membrane surface and porous structure were characterized by scanning electron microscopy (SEM) using Supra 50VP instrument.

3. Results and discussion

Micrographs of polypropylene hollow-fiber are represented on Fig. 2. Membrane porosity is represented by slit-like pores with sizes of $100 \times 500$ nm (average pore size $\sim 200$ nm), typical for hot-stretched polymers. Such geometry of the pores can be considered optimal for providing maximal contact area while maintaining small pore sizes in the membrane. The last parameter is crucial to maximize critical pressure difference needed to overcome capillary forces for polymer wetting or bubbling at the gas-membrane-liquid interface. General characteristics of hollow fiber membrane and membrane contactor module are listed in the Table 1.

The experiments in air dehumidification were started with revealing the role of humid air flow rate on the membrane contactor performance. Water vapor stage cut and vapor flux through the membrane show a strong dependence of residual water content on the air flow rate in the 300 – 3500 ml/min range (Fig. 3). Notably, the attained water dew point temperature in the retentate goes below $-28$ °C, illustrating efficiency of the lumen gas configuration as compared to earlier reports [19]. Increasing the gas flux leads to an increase in the water dew point and water vapor stage cut. To determine the limiting stage of absorption process, we have extracted the flux...
of water absorbed in the contactor (Fig. 3b) and compared the values with theoretical diffusion flux through the membrane. The diffusion flux of vapor was estimated using Knudsen diffusion mechanism [22] and the assumption that the membrane pores were filled with gas and absorption occurred at the external surface of fibers:

\[ J = -D_{Knudsen} \left( \frac{P_{H_2O,air} - P_{H_2O,TEG}}{L \cdot RT} \right), \]

where \( P_{H_2O,air} \) – partial pressure of water vapor in the inlet air, \( P_{H_2O,TEG} \) – equilibrium pressure of water vapor at the triethylene glycol-air interface at a given water content in a liquid (for TEG concentration 99.8 % the equilibrium partial pressure equals 0.0177 mol/m\(^3\)), \( L \) – membrane thickness, \( R \) – gas constant, \( T \) – temperature, \( D_{Knudsen} \) – Knudsen diffusion coefficient, determined as:

\[ D_{Knudsen} = \frac{\varepsilon d}{3\tau} \sqrt{\frac{8RT}{\pi M}}, \]

where \( \varepsilon \) is the membrane porosity, \( d \) – average pore diameter, \( \tau \) – pore tortuosity, \( M \) – water molecular weight. The estimated value of tortuosity in hot-stretched PP membranes was suggested to equal 2 [23]. The resulting Knudsen diffusion coefficient for average pore diameter of 200 nm and porosity of 0.45 is valued as \( 8.88 \cdot 10^{-6} \) m\(^2\)/s. Using the value with experimental partial pressure of water in humid air of 1.17 mol/m\(^3\), equilibrium partial pressure over 99.8 % TEG solution of 0.0177 mol/m\(^3\), and membrane layer thickness of 35 mm, one can estimate the water flux through the membrane in Knudsen regime as 0.293 mol/(m\(^2\)s). The derived flux exceeds experimental value by three orders of magnitude, suggesting absorption reaction or absorbent feed to be the limiting step of the process.

\[ \text{Fig. 3. Effect of gas flow rate on the water vapor stage cut, outlet gas dew point (a) and water vapor absorption flux (b). Inlet relative humidity – 96 % at 23 °C, TEG circulation rate 1000 ml/min and concentration 99.8 %} \]

To check the effect of absorbent flux on the performance of membrane contactor, experiments with TEG circulation rate ranging from 166 ml/min to 1000 ml/min were carried out (Fig. 4). Moderate influence of TEG circulation rate on water vapor stage cut and dew point temperature of retentate flow was revealed. Increasing the circulation rate \( \sim 7 \) times leads to increase the absorption flux of only 5 %. This can be explained by a laminar flow of absorbent in the membrane contactor – for the given size of absorber (the inner diameter of 40 mm and the length of 400 mm) liquid velocity is ranged from 0.002 to 0.012 m/s. These results suggest water diffusion into TEG volume to be a limiting stage of absorption process.

As the partial pressure of water vapor is strongly affected by H\(_2\)O content in TEG, we have analyzed the role of this parameter on the contactor efficiency. Increasing water content in TEG solution leads to drastic decrease of water vapor stage cut and increase of dew point temperature of retentate due to growth of equilibrium water vapor pressure over the absorbent (Fig. 5). Nevertheless even at 3 % water content in TEG, the dew point of the retentate is reduced to relatively low value of 4 °C with vapor stage cut over 50 %. Thus water pressure over contacting liquid is seemed to be key parameter for the contactor performance. Notably, the outlet gas dew points were found relatively close to equilibrium values, especially in case of high vapor humidity [9]. This illustrates an efficiency of the proposed method for gas dehumidification. Using a lean TEG solution and a high circulation, the rate dew point of feed gas can be decreased down to \(-30 \) °C for the contactor performance of 30 – 60 l/(m\(^2\)h). This result demonstrates that membrane contactors with shell side flow of TEG can be utilized for air and natural gas dehumidification.
4. Conclusions

Thus, porous hollow-fiber membrane used in gas-liquid membrane contactors with lumen gas flow configuration can be successfully utilized for air dehumidification using the triethylene glycol as a desiccant. Examination of feed gas flow, absorbent circulation rate and TEG water content effects on water vapor transport through membrane reveal partial water pressure over absorbent at gas-liquid interface to be the key parameter for the contactor performance, while diffusion of dissolved water into glycol volume appears as a limiting stage of absorption process. Utilization of dry TEG solution at high absorbent circulation rates allows one to decrease the dew point of the feed gas down to \( \sim -30 \) °C from 96 % humidity level at standard conditions. These results reveal the potential of using porous membrane contactors with lumen gas flow configuration for air dehumidification and natural gas conditioning for pipeline transport.
Acknowledgements


References