Preliminary study of wet-free CO₂ absorption through membrane diffuser

I G Wenten¹,², A K Wardani¹, K Khoiruddin¹ and D Ariono¹

¹ Department of Chemical Engineering, Institut Teknologi Bandung, Jl. Ganesha No.10, Bandung, 40132, Indonesia
² Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha No.10, Bandung, 40132, Indonesia

E-mail : igw@che.itb.ac.id

Abstract. Wetting phenomenon is major drawback of membrane contactor in CO₂ absorption which limits the performance stability. In this study, hollow fiber membrane diffuser was proposed for providing wet-free gas absorption. The performance of membrane diffuser as function of operating pressure (0.5-3.0 bar), membrane hydrophobicity (hydrophobic and superhydrophobic polypropylene membrane), and membrane type (polypropylene and polysulfone) was investigated. Result shows that CO₂ concentration in absorbent increases with operating pressure. Superhydrophobic polypropylene membrane exhibits higher CO₂ transfer than the hydrophobic membrane. Meanwhile, the CO₂ absorption by PSf membrane is relatively low.

1. Introduction
The capture of carbon dioxide (CO₂) has gained great interest due to the increased concerns of global warming and greenhouse gas emissions as well as the exhaustion of easily accessible fossil fuel resources [1]. The capture of CO₂ from natural gas is important in order to meet the specifications required by consumers, while CO₂ capture from flue gas is needed to mitigate the increasing concentration of CO₂ in the atmosphere. Currently, various CO₂ capture technologies have been developed, including absorption, solid adsorption, cryogenic distillation, and membrane-based processes. Among them, absorption is the most mature and widely used CO₂ capture technology. Absorption involves the use of a liquid sorbent (e.g. monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), potassium carbonate, and water) to separate CO₂ from natural/flue gases [2]. This process is limited by the requirement of solvent regeneration that leads to high energy consumption. Cryogenic distillation is also extremely energy-intensive and is not considered economical for industrial applications [3, 4]. Meanwhile, solid adsorbents (e.g. zeolites, silica, metal-organic frameworks, activated carbons, and graphene) that chemically adsorb CO₂ in active sites can lose efficiency very quickly with high temperatures [3, 5].

Membrane as a relatively new CO₂ capture technology offers advantages of low cost, low energy, flexible in operation, and modularity [6-10]. The membrane can also be integrated with another process such as gas absorption, called membrane contactor. Membrane contactor combines the benefit...
of high selectivity from chemical solvent and modularity and compactness of membrane permeation [11-14]. The use of porous membrane to replace conventional packing provides an extra area for contact between the gas and liquid phases and able to avoid the dispersion between them [15]. In addition, the flow of gas and liquid phases can be controlled independently which provides better optimization of both phases. However, the operation of membrane contactor is still limited by wetting phenomenon which affects its performance stability. Wetting leads to the increased membrane resistance that may result in a significant drop of CO₂ absorption efficiency [16]. It has been proved by Wang et al. [17] where the CO₂ absorption in non-wetted membrane contactor is six times higher than that in the wetted one.

To prevent the wetting in membrane-based CO₂ capture, various researches and developments have been conducted, including membrane material design and membrane system engineering [2]. Membrane material design focuses on synthesis or modification of membrane to obtain desirable membrane hydrophobicity [18-20]. Meanwhile, membrane system engineering aims to develop membrane-based CO₂ capture processes with optimal configurations to achieve the separation target. Membrane diffuser can be a promising approach in membrane system engineering to obtain wet free CO₂ absorption. In membrane diffuser, CO₂ is transferred through the membrane pores and partitions into a liquid [21, 22]. This method allows high interaction of gas-liquid and possible to operate at lower gas pressures, as there is no need to counterbalance hydrostatic heads [23]. Since the gas phase is operated under dead-end mode, it is possible to keep the pore filled by the gas. This configuration is expected to avoid pore membrane wetting.

Kumar et al. [21] investigated the performance of a hollow fiber membrane diffuser for CO₂ sequestration from combustion gas coupled with wastewater treatment. The membrane was a composite laminated hollow fiber with a thin dense polyurethane layer sandwiched between two microporous polyolefin layers. The results showed that the use of hollow fiber membrane diffuser was able to obtain high CO₂ mass transfer efficiencies with minimal loss of CO₂ to the atmosphere. The same configuration was used by Jana et al. [24] using ceramic hydrophobic membrane for providing CO₂ in algal photobioreactor during cultivation of *Arthrospira* sp. An enhanced overall mass transfer coefficient of about $38\times10^{-4}$ m/s was obtained using 19.5% CO₂ gas mixture and 0.23 m/s gas velocity. Jana et al. also showed that the membrane was efficient in removal of dissolved oxygen produced during photosynthesis, resulting in higher algal growth and higher CO₂ sequestration. Meanwhile, Nordin et al. [25] compared the performance of a polyvinylidene fluoride (PVDF) membrane diffuser and a bubble diffuser. The size of the bubbles produced from the membrane diffuser was much smaller compared to the bubble diffuser, thus the total amount of bubbles produced and the total contact area provided per minute by the membrane diffuser was quite higher than the bubble diffuser.

In this work, a preliminary study was conducted to investigate the performance of wet-free CO₂ absorption through polypropylene (PP) and polysulfone (PSf) hollow fiber membrane diffuser. The influence of operating pressure on CO₂ concentration was investigated. In addition, the effect of membrane hydrophobicity and material was also examined.

### 2. Materials and Methods

#### 2.1. Materials

PP and PSf hollow fiber membranes were provided by GDP Filter, Indonesia. The diameter and pore size of the membranes are summarized in Table 1. CO₂ gas (purity 99.5%) and demineralized water were used for filtration tests.

| Table 1. Membrane characteristic |
|----------------------------------|
| **Membrane** | **PP** | **PSf** |
| Outlet diameter (mm) | 0.4 | 2.2 |
| Inlet diameter (mm) | 0.3 | 1.8 |
| Average pore size (nm) | 50 | 10 |
2.2. CO₂ absorption and analysis
Filtration test was conducted by flowing the CO₂ gas from inside out through the hollow fiber membranes that have soaked in demineralized water, as shown in Figure 1. The operating pressure of the CO₂ gas was varied from 0.5 to 3 bar. The flowrate of inlet gas was constant at 100 mL/minute and the ratio of water volume to membrane area was 30.5 m³/m². The pH of demineralized water was measured every minute by electrode pH analyzer (LUTRON PE-03). The pH value was then converted to the CO₂ concentration by carbonate equilibria approach using “Bjerrum plot” [26, 27]. “Bjerrum plot” portrays the relation of pH value to the concentration of CO₂, HCO₃⁻, and CO₃²⁻. Meanwhile, to measure the water contact angle, a droplet of demineralized water was placed on the membrane surface using a micro-syringe 10µL. The water droplet was recorded by a digital camera and the contact angle was determined from the digital image of the water drop on the membrane surface. The water contact angle was measured at 5 different locations of individual membrane surface to minimize experimental errors.

3. Results and Discussion
3.1. The effect of operating pressure
In this work, the operating pressure was varied from 0.5 to 3 bar to study its effect on the CO₂ concentration. Figure 2 shows that the CO₂ concentration increases by increasing the operating pressure. In 0.5 bar, the CO₂ concentration is almost constant for 13 minutes of measurement. The CO₂ concentration then slowly increases for operating pressure of 1-2.5 bar. Meanwhile, there is a huge jump of CO₂ concentration when operated in 3 bars. These results are due to the decrease of the CO₂ gas volume at higher pressure, thus increases the absorption of CO₂ molecules in water. In addition, the CO₂ is able to be absorbed in water by physical absorption which the solvent absorption capacity increases nearly linearly with pressure following Henry's law [28]. Therefore, the CO₂ solubility in water is enhanced at higher pressure, resulting in an increase of CO₂ concentration. Meanwhile, the operating time has an almost similar effect on all operating pressure, where the CO₂
concentration increases as the increase of operating time. It is due to the accumulation of CO$_2$ in the solution.

![Figure 2](image.png)

**Figure 2.** Effect of operating pressure on CO$_2$ concentration (PP hydrophobic membrane)

3.2. The effect of membrane hydrophobicity
To study the effect of membrane hydrophobicity on CO$_2$ concentration, two types of PP membranes were used in this work. The first PP membrane has a water contact angle (WCA) of 118.4±1.5°, namely as a hydrophobic PP membrane. The second PP membrane has WCA more than 150°, namely as a superhydrophobic PP membrane. The two PP membranes were operated at 1.5 bar and the results are depicted in Figure 3. It can be seen that the increase of hydrophobicity of the membrane leads to the increase of CO$_2$ concentration. The superhydrophobic PP membrane results in higher CO$_2$ concentration than the hydrophobic PP membrane. It is due to the lower surface energy and polarity of superhydrophobic membrane, resulting in a weak covalent interaction between water and membrane surface [29]. This weak interaction between water and membrane surface may reduce the resistance on membrane surface, thus CO$_2$ is able to easily permeated through the membrane pores. Similar to the previous results, the operating time has similar effect on both hydrophobic and superhydrophobic PP membrane, where the CO$_2$ concentration increases as the increase of operating time due to the accumulation of CO$_2$ in the solution.
3.3. The effect of membrane material

In this work, the performance of PP and PSf ultrafiltration hollow fiber membranes as membrane diffuser was studied. Figure 4 shows the comparison of CO$_2$ concentration by PP and PSf membranes. In PP membrane, the CO$_2$ concentration significantly increases after 13 minutes. Meanwhile, the CO$_2$ absorption by PSf membrane is relatively low. It is due to the different pore structure between PP and PSf membrane. PP membrane was produced by stretching method, thus resulted in symmetric pore structure. Meanwhile, PSf membrane has asymmetric pore structure due to the solvent/non-solvent exchange during its production by phase inversion method.

4. Conclusion

In this work, PP and PSf ultrafiltration hollow fiber membranes were used as membrane diffuser. The results showed that membrane diffuser has great potential for wet-free CO$_2$ absorption. The CO$_2$ concentration increased by increasing the operating pressure. Superhydrophobic polypropylene
membrane exhibits higher CO$_2$ transfer than the hydrophobic membrane. Meanwhile, the CO$_2$ absorption by PSf membrane is relatively low.

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