

## Membrane Wetting in Membrane Contactor System: A Review

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### ABSTRACT

Chemical absorption is the most developed technology for carbon dioxide (CO<sub>2</sub>) removal in gas processing application. In a long term operation, this conventional method has suffered from significant drawback such as flooding, channelling, entrainment and foaming; therefore membrane contactor is seen as the perfect solution to overcome these problems. In principle, a perfect combination of membrane material and liquid absorbent is vital in membrane contactor system in order to avoid membrane wetting. This review presents the introduction to membrane contactor for CO<sub>2</sub> removal via absorption and stripping process. Details on membrane wetting phenomena were discussed which includes the factors contributing to wetting problem and prevention methods to minimize these issues.

*Keywords:* Membrane contactor, PVDF, hydrophobic, gas-liquid phase, wetting

### 1.0 INTRODUCTION

In industrial and natural gas processing, removal of acid gases (mainly CO<sub>2</sub> and H<sub>2</sub>S) is essential as they could cause corrosion in the gas pipeline and reduce the hydrocarbon content hence resulting in a lower energy content of the fuel. These phenomena incurred economical losses in investment and reduction in the efficiency of the system [1] Several established technologies in gas separation namely chemical absorption (amine), physical absorption, cryogenic distillation and membrane system have been applied to combat the problem and have produced promising results. The removal of CO<sub>2</sub> by absorption-stripping into aqueous solutions using equipment such as packed bed, spray columns and bubble column has been conventionally applied and acknowledged as an effective method to remove CO<sub>2</sub>. However, for a long term operation, this conventional equipment has suffered from significant drawback such as

flooding, channelling, entrainment and foaming [2] Therefore, alternative technology such as gas-liquid membrane contactor has been identified as a promising option that has the potential to replace conventional equipment in CO<sub>2</sub> absorption-stripping process.

Gas-liquid membrane contactor was employed earlier in 1970's by Esato and Eiseman for blood oxygenation which consists of hydrophobic microporous PTFE membrane known as Gore-Tex membranes. These membranes were also used in fuel cell system for United States space program in the late 1960's. Further application of membrane in gas-liquid contactor started to emerge when Feron and Jansen [3] first introduced CORAL solvent with porous polyolefin membranes for the production of carbon dioxide from flue gas. Since then, membrane contactor technology has been applied in wide range applications such as fermentation, pharmaceuticals, water

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treatment [4], beverage carbonation [5] and absorption-stripping process [6].

Polymer membranes such as polyvinylidene fluoride (PVDF), polytetrafluorethylene (PTFE), polypropylene (PP), polyethylene (PE) and polyetherimide (PEI) are among the prominent polymers applied in gas-liquid contactor application. Due to their favorable properties such as being hydrophobic, compatible in organic solvent, resistant to heat and chemical reaction; having a straightforward process in membrane preparation has made these polymers amongst the favourite polymer material chosen for gas-liquid contactor application.

Membrane structure plays an important role in ensuring the efficient flow of gas through the pore structure in mass transfer process. A porous membrane structure with combined finger-like was found suitable for CO<sub>2</sub> absorption in membrane contactor application [7]. This could be done by controlling the spinning variables or adding non-solvent additives to tailor the membrane structure. The existence of finger-like structure can provide an easy channel for the liquid to permeate and this would reduce the liquid entry pressure of the system.

In addition, an ideal liquid absorbent for contactors application should be compatibility with membrane material, non-corrosive or less corrosive, fast absorption/ stripping rates, high surface tension and less regeneration energy. These characteristics reflect the performance and efficiency achieved by the membrane contactor with minimal wetting occurs in the membrane structure. Therefore, a trade-off between membrane material and liquid absorbent properties should be obtained to achieve high CO<sub>2</sub> removal flux and process efficiency in membrane contactor system.

## 2.0 MEMBRANE WETTING

Membrane wetting can be considered as the main problem in membrane contactor application; which in the case of wetting, increasing the membrane mass transfer resistance and reduce the mass transfer efficiency of the system. This occurs when the liquid absorbent enter the membrane pores, over a prolonged period of operation time resulting gradual membrane wetting. The membrane wetting can be classified into three different modes; non-wetted, partially wetted and completely wetted. In the non-wetted modes, the membrane pores are completely filled with gas phase over a period of time. Meanwhile, in the partially or completely wetted mode, the membrane pores are partially filled or completely filled with the liquid absorbent over time.

According to Mavroudi *et al.* [8], when 13% of the membrane pores were liquid-filled, the mass transfer resistance of the membrane can increase up to more than 98%. From simulation study conducted by Wang *et al.* [9], it was estimated that if 5% of the membrane pores were wetted, the overall mass transfer coefficient might be reduced by 20%. It was also claimed that the absorption rate in wetted mode was six times lower than those in non-wetted mode. In order to retain the best performance of membrane in CO<sub>2</sub> absorption and stripping, it is suggested that the maximum acceptable percentage of membrane wetting is about 40% [10].

## 3.0 THE POTENTIAL OF MEMBRANE WETTING

Membrane wetting can occur in several ways in which it varies according to the mutual interaction of the liquid absorbent and the membrane materials.

Dealing with physical absorbent is easier than with chemical absorbent since the problem of wetting is less significant. However, the CO<sub>2</sub> absorption capacity of physical absorbent is lower than that of chemical solvent. Therefore, experimental work has been focusing on the wetting of chemical absorbent on the membrane material. Wang *et al.* [11] experimented Celgard X40-200 and Celgard X50-215 (polypropylene membrane) in aqueous diethanolamine solution for 3, 10 and 30 days. Both fibers were found wetted by the diethanolamine solution which can be observed through the morphology changes via scanning electron microscopy analysis. Pore structure and surface roughness of the membrane was also altered significantly as detected by atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) analysis. It was possible that the chemical reactions between the membrane and diethanolamine solution have decreased the surface hydrophobicity (reduction of contact angle) which leads to the deterioration of membrane matrixes. In addition, a similar study on the Celgard membrane for CO<sub>2</sub> absorption in diethanolamine solution has experiencing the same wetting problem indicated by the reduction of absorption flux, changes in membrane morphology and reduction of the overall mass transfer coefficient [9].

On the other hand, Lv *et al.* [12] studied PP hollow fiber membrane on prolonged contact in various liquid absorbent such as MEA, MDEA and deionized water for 90 days with concentration of chemical absorbent of 3 M. Their findings indicated that the absorbent molecules tend to diffused onto the membrane pores which resulted an alteration of surface properties and reduction the hydrophobicity properties of the

membrane. These in turn enhanced the degree of wetting of the membrane pores thus remarkably reduced the contact angle. It was suggested that an effective ways that could overcome wetting problem in membrane is by improving the membrane surface hydrophobicity, since high surface tension of the absorbent favours small changes in membrane surface morphology.

Study on the effects of membrane porosity in two different modules with porosity of 23% and 40% was performed by Khaisri *et al.* [13] for desorption performance. Although the results showed that the module with high membrane porosity (40%) produced a high desorption rate, the performance dropped when the module was carried out for long hour operation due to the wetting problem. PTFE membrane used in their study is one of the most chemical resistant polymers available in the market. However, it was predicted that the effects of increasing temperature and possible reaction with aqueous MEA solution might contribute to continuous decline of desorption flux. This trend was also supported by Lu *et al.* [14] where a membrane with high porosity promotes pore wetting significantly compares to one with lower porosity.

Although some of the liquid absorbent used are compatible with the membrane material, the harsh operating condition may affect the physical appearance and performance of the membrane. This is even experienced by the commercial membrane where it tends to react with liquid absorbent such as sodium hydroxide and amine solution especially when contacted for long hours and exposed to high temperature condition [15]. By exposing PP membrane in diethanolamine aqueous solution for 3 and 10 days, Wang *et al.* [11] reported that not only the pore structure of the

membrane was altered but the surface roughness of the membrane surface was also increased. This is in agreement with a study reported by Rangwala [16] where it was speculated that partial wetting of PP membranes could be possible when amine aqueous solution was applied. Rangwala [16] studied PP membrane (Hoechst Celanese Corporation) in different module sizes with aqueous NaOH and aqueous DEA as liquid absorbent. The measurement of membrane mass transfer indicated that the polypropylene fiber was partially wetted by both the aqueous solutions despite the fact that the membrane should be non-wetted by any solution.

Barbe *et al.* [17] studied surface morphology of polypropylene membrane (Celgard 2500 and Accurel) and they found that both membranes undergone changes in pore size, porosity and pore length with exposure to water for 72 h. This was made possible by the high lateral forces exerted by the water on the surrounding fibrils in the larger pores which contributed to the enlargement of pores.

#### 4.0 MEMBRANE WETTING PREVENTION

In order to minimise or eliminate membrane from wetting, researchers have recently focused on the screening of liquid absorbents and membrane materials; mixing various type of liquid absorbents [18], surface modifying membrane via grafting [19], incorporation of pore forming agent [20] and inorganic filler on the membrane surface [21]. Polymer with high surface energy is prone to wetting. To avoid this, polymer should have low surface energy and the smallest possible maximum pore size. Wetting pressure is inversely proportional to membrane pore size [22] where higher pressure is

needed for lower pore size (0.1  $\mu\text{m}$ ) compared with lower pressure needed for higher pore size (10  $\mu\text{m}$ ). The surface energy of polymers and contact angles with water are exemplified in Table 1.

**Table 1** Surface energy of polymer materials [22]

Polymer	Critical surface tension (mJ/m <sup>2</sup> )	Water contact angle
Polytetrafluoroethylene	19.4	109.2
Polytrifluoroethylene	23.9	-
Polypropylene	30.5	102.1
Polyvinylidene fluoride	31.6	89
Polyethylene	33.2	-
PDMS	20.1	107.2

In the case of liquid absorbent, various types of aqueous liquid have been employed such as pure water, aqueous solution of NaOH, KOH, amine and amino acid salts. Each of the absorbent has its own specialties which define a proper selective process application. Li and Chen [23] conducted a study on the selection of liquid absorbent in membrane contactor where they highlighted such criteria for choosing chemical solvent to be implemented in membrane contactor; high reactivity with CO<sub>2</sub>, liquids with low surface tension, good chemical compatibility with membrane material, regenerability, low vapour pressure and good thermal stability. Since any liquid having surface tension lower than critical surface tension of polymers may wet the membrane spontaneously, the solvents must have a substantially higher surface tension than the polymer's critical surface tension values. A low critical surface tension means that the surface has a low energy per unit area.

Dindore *et al.* [24] provides an extensive study on membrane-solvent

combination for CO<sub>2</sub> removal in gas-liquid membrane contactors. They highlighted that the possibility of membrane wetting is primarily governed by the membrane pore size, surface tension of the liquid and the mutual interactions of liquid and membrane materials (signify by contact angle). It was concluded that the combination of polypropylene membrane and propylene carbonate as liquid absorbents is the best option for further research. However, the study was only limited to PTFE membrane and no comparison was made with the other types of membranes.

## 5.0 RECOMMENDATIONS

Good combination of membrane-liquid absorbent is critical to ensure an effective mass transfer thus leading to high removal of CO<sub>2</sub> flux. Therefore, new and cheap polymer membranes should be studied to minimize the impact of membrane wetting and reduce the total cost of the membrane contactor system. In addition, surface modification of the polymer membrane is one of the potential options to enhance the performance of membrane in membrane contactor application. This can be achieved by surfactant treatment, coatings to form a new composite formation, chemical grafting of low molecular weight active group, plasma grafting on the membrane polymer material or polymer blending which can improve the chemical properties of the membrane.

An observation of membrane characteristics before and after stripping process should be carried out to have a closer look on the effect of long hour contact with the liquid absorbent. These can be done by performing the morphology analysis via SEM or FESEM, measurement of contact angle and tensile strength

before and after the stripping test. Thus, a correlation of the membrane properties used in the membrane contactor before and after stripping test can be highlighted and structurally defined.

## 6.0 CONCLUSION

From this review, it can be concluded that in membrane contactor system; compatibility of membrane material and liquid absorbent are crucial to ensure the efficient mass transfer process between gas and liquid phase. Increasing membrane resistance due to intrusion of liquid absorbent into membrane pores can be detrimental to the system performance thus reducing of CO<sub>2</sub> flux. Therefore, a thorough study and research should emphasize on the endurance study of membrane materials in liquid absorbent especially when dealing with chemical absorbent at different temperatures, concentrations and contact hours.

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