Impact of heavy hydrocarbon impurities on polytetrafluoroethylene (PTFE) membrane stability

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Abstract. Membrane contactor technology has attained considerable attention as a promising technology to reduce CO2 content in natural gas. In this study, the main objective is to investigate the effect of heavy hydrocarbons impurities, often present in natural gas, on polytetrafluoroethylene (PTFE) hollow fibre membrane. The membranes were immersed for months in n-heptane, 1-decene, benzene and toluene, and analysed periodically through its surface morphology, composition, functional groups, hydrophobicity, and thermal stability. The characteristics of PTFE fibres remained unchanged even after long term exposure with heavy hydrocarbons. This study provides a better understanding of the robustness of using PTFE membrane fibre for CO2 removal in membrane contactor system.

Keywords: Polytetrafluoroethylene (PTFE), membrane, heavy hydrocarbon

1. Introduction

In the recent decades, removal of impurities, especially CO2, from natural gas has become a concerning issue. High CO2 content would cause severe corrosion issues, decrease the value of natural gas as a fossil fuel and reduces pipeline capacity [1]. Membrane contactor is a potential technology that can be developed further to reduce CO2 content in natural gas. Membrane contactor uses microporous hollow fiber membrane (HFM) as phase barrier allowing gas and liquid to flow on different sides of the membrane; hence more efficient mass transfer without two phases dispersing into each other. It offers modularity, larger contact area and advantageous as it has no flooding, channelling, or foaming issues. Gas selectivity is dependent on the absorbent of choice.

As in other membrane-based CO2 removal technologies, membrane material selection is crucial in determining the stability of membrane from plasticization and wetting effect during CO2 removal process. Polyimide, polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are the common polymeric membrane materials for CO2 capture. Previous studies reported the challenges in membrane based gas separation includes plasticization, conditioning and physical aging due to the interaction between impurities from feed stream and membrane [2-5]. A review from Suleman, Lau and Yeong indicated that destruction of the polymer structure could occur due to plasticization from dissolution of different penetrants in the polymer matrix [6].

Fluoropolymer such as polytetrafluoroethylene (PTFE) has drawn attention due to its high physical and chemical stabilities [7]. Its outstanding chemical stability and resistance to plasticization, in presence of condensable organics, is due to its carbon backbone, and strong C-F and C-C bonds. It is protected
by the electron cloud of the large fluorine atoms which are tightly bonded with monomer unit [8], shown in figure 1. For long-term operation of over 180 days, it is reported that PTFE HFM indicated no apparent deterioration of CO₂ removal performance during operation. PTFE polymer also maintained good stability in absorbent solutions over 24 weeks [3][6]. In a study by deMontigny et al., membrane contactor with PTFE showed better resistance towards wetting from aminomethyl propanol (AMP) and monoethanolamine (MEA), and higher CO₂ transfer coefficient; whilst polypropylene (PP) was easily wetted [9].

![Figure 1. Molecular arrangement of PTFE polymer [10].](image)

Natural gas commonly contains heavy hydrocarbons which includes benzene, toluene, ethylbenzene and xylene (BTEX) ranged in 200 – 3000 ppm [11]. These heavy hydrocarbons may act as plasticizer which can cause swelling of most polymeric membranes. The larger pores, caused by swelling, will then allow other gas species to pass through and result in significant drop of CO₂ permeability [12-13]. For membrane contactor, enlargement of membrane pores would result in dramatic reduction of critical entry pressure and eventual membrane wetting [13].

Encouragingly, Scholes et al. showed that CO₂ and CH₄ separation with Teflon AF1600 and Hyflon AD60 membrane films in the presence of hexane and toluene showed minor performance reduction [12]. There have been several research studies carried out to determine the effect of heavy hydrocarbons such as pentane, heptane, and toluene on membrane materials such as PP, PE, polyimide and polyamide in CO₂ removal. However, research studies on PTFE HFM for longer duration remain limited due to the toxicity and volatility of liquid heavy hydrocarbons, and high cost of PTFE membrane fabrication compared to other polymeric membranes [9].

Therefore, the purpose of this study is to examine the impact of long-term exposure of heavy hydrocarbons on the characteristics of PTFE HFM. Often lab test on CO₂ performance is limited to using binary gas for testing and are of short duration; hence this study shall provide indication on what to be expected for continuous exposure to heavy hydrocarbons present in actual natural gas. This study is conducted through immersion of PTFE HFM into heavy hydrocarbons and analysing its surface morphology, hydrophobicity, chemical and thermal stability. The result from this study shall serve as valuable reference on the long-term stability of PTFE membrane for application in actual natural gas fields.

2. Experimental Methodology

2.1. Materials

The PTFE hollow fibre membranes were supplied by Dalian Institute of Chemical Physics (DICP) for testing. The characteristics of PTFE membrane used in this study are listed in Table 1. The heavy hydrocarbons used for the immersion of membrane were n-heptane, 1-decene, benzene and toluene, and were all purchased from Merck KGaA, Germany. Distilled water and amine solvent (mixture of methyldiethanolamine, MDEA and piperazine at concentration of 35 wt. %) were used for the contact angle measurement; the amines were purchased from Sigma-Aldrich.
Table 1. Characteristics of the PTFE HFM.

| Characteristics      | Value       |
|----------------------|-------------|
| Outer diameter (cm)  | 0.08949     |
| Inner diameter (cm)  | 0.04344     |
| Wall thickness (cm)  | 0.02225     |
| Porosity (%)         | 47.3092     |

2.2. Membrane Immersion
As shown in figure 2, roughly about 10 cm of PTFE HFMs were immersed in vials containing n-heptane, 1-decene, benzene and toluene, respectively. The PTFE HFMs were fully immersed in every vial at ambient condition over 4 months. At the end of each month, samples were taken, rinsed with deionised water and vacuum dried at 900 mbar and 70 °C for 24 hours to remove traces of heavy hydrocarbon from membrane surfaces, before proceeding with further characterisation.

![Figure 2. Immersion of PTFE HFM in heavy hydrocarbons.](image)

2.3. Characterisation
The characterisation of the initial and immersed membrane samples includes the analyses on surface morphology, porosity, hydrophobicity, and chemical and thermal stability.

2.3.1. Field-Emission Scanning Electron Microscope (FESEM). The membrane fibres were fractured using liquid nitrogen to obtain a smooth cross-sectional area. The fractures were then coated with gold using ion sputtering device (Quorum, Q150RS). The morphologies of inner, outer, and cross-sectional surfaces of PTFE HFM were examined by FESEM (EVO (Hitachi, Model SU7000). The membrane thickness, inner and outer diameters were also measured through FESEM.

2.3.2. Porosity Test. The effect of heavy hydrocarbons towards the overall porosity, $\varepsilon$ of the PTFE HFM was determined from the average outer diameter (OD) (in mm), and inner diameter (ID)(in mm) obtained from FESEM analysis, and the weight of 1 metre long of PTFE fiber (W) (in gram) using analytical balance. This measures on the porosity for CO$_2$ permeability. The porosity, $\varepsilon$ of the PTFE HFM is determined by the following equation:

$$\varepsilon (%) = [1 - W/2.17/\pi*(OD*OD - ID*ID)/4*100]$$  (1)
2.3.3. **Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy.** ATR-FTIR was used to determine chemical stability of the immersed membrane fibres. The spectra were obtained using spectrophotometer (Perkin Elmer, Spectrum 100 FTIR). The fibre was pressed against ATR crystal in transmittance mode from 450 to 4000 cm$^{-1}$ using 4 scans at ambient temperature to determine the composition, structure, and the functional groups in the sample. Additionally, the heavy hydrocarbons that were used for immersion were also measured with ATR-FTIR as to compare their spectra with the immersed PTFE HFM spectra respectively to identify the presence of hydrocarbon in the membrane matrix during the immersion. This is in case traces are still present even after high temperature (70 °C) vacuum drying method has been applied on the membrane.

2.3.4. **Contact Angle Measurement.** Tensiometer (Model T200, Biolin Scientific) was used to perform contact angle measurements. Sessile drop method was done, using 35 wt. % amine solvent to conduct the analysis, to determine the variation of hydrophobicity of PTFE HFM after the immersion. The volume of liquid drop was controlled manually at the range of 0.5 – 2.0 μL through a syringe and measured by tensiometer software. Minimum of eight readings were taken and averaged, similar to other researchers in membrane study [7][14-15].

2.3.5. **Thermogravimetric Analysis (TGA).** Thermogravimetric analysis (TGA) of the membrane fibres was completed using a Mettler Toledo Thermogravimetric Analyzer. 10 mg of PTFE HFM is analysed at the heating rate of 10 °C/min, from 30 to 800 °C and a nitrogen flow of 50 mL/min. Thermogravimetric loss of the PTFE HFMs were compared to determine the effect of heavy hydrocarbons immersion on the membrane thermal stability. The decomposition temperature of PTFE HFM and existence of heavy hydrocarbon in membrane after the immersion were determined through the thermogravimetric curve.

3. **Results and Discussions**

3.1. **Membrane Surface Morphology and Porosity**

figure 3(a) shows the surface morphologies of the initial membrane fibres. The structure of PTFE HFM has microstructures of nodes interconnected by fibrils; where node is the solid agglomerates of particles and fibrils bridged the two adjoining nodes together. The size of pores on the inner surface of PTFE membrane are commonly larger than those on the outer surface, due to higher reduction ratio and higher extrusion pressure on the outer surface [14]. The cross-section of the non-immersed PTFE HFM (figure 3(a)iii) shows a continuous porous layer from inner to outer surface.

After immersion, the morphology of PTFE HFM has no significant change. The structures at 5000 of magnification (in figure 3(b) to 3(e)) show no displacement of fibrils and the surface area of nodes remained at almost the same even after long term in contact with heavy hydrocarbons. PTFE HFM does not suffer plasticization as its microstructure of C-F bonds in the polymer matrix and extra-electronegative protective layer from fluorine atoms inhibited the penetration of heavy hydrocarbons molecules into the membrane matrix [16–18]. Other polymer, such as polyimide membrane has its small pores closed and large pores enlarged just after 4 days in contact with gas plasticizing agent [5].

Porosity, ε of the PTFE HFM is determined from measurement of the inner and outer diameters, and weight of the membrane, and through calculation using equation (1). Result in figure 4 shows the porosity of the PTFE HFM throughout the four months’ immersion. Based on t-test done, there is no significant change observed where the overall porosity calculated, for before and after immersion, is about 47 %. Membrane porosity is important to maintain CO₂ flux whilst preventing membrane wetting phenomenon; higher porosity would lead to lower breakthrough pressure and ease the amine solvent to enter the membrane pores. Consistent porosity of membrane in long term membrane contactor operation shall allow stable CO₂ absorption performance and prevent unnecessary wetting [19-20].
Figure 3. FESEM images of PTFE HFMs. (a) Initial; (b) to (e): Immersed PTFE HFM. (i): outer surface, (ii): inner surface, (iii): cross-sectional surface.
3.2. Compositional and Functional Group Analysis

ATR - FTIR spectroscopy is used to identify the composition and functional groups of the sample. Figure 5(a) shows the IR spectra of results of initial membrane; whilst figure 5(b) shows the overlapped IR bands for the immersed PTFE HFM samples.

Peaks of C−F bonds could be detected within range of 1000-1400 cm⁻¹. In figure 5, C-F bonds are observed clearly at 1204 cm⁻¹ and 1149 cm⁻¹. These peaks remain practically unchanged in their respective intensities over the periods of immersion as shown in figure 5(b), since there is no active reaction happening during the immersion that may deteriorate the composition of the PTFE functional groups. The consistent intensity of functional peaks indicate that PTFE polymer is inert towards organic solvent [3][12].

If there was any degradation and defluorination were to occur, it would have been detected by presence of C=C bond within the range of 665 – 995 cm⁻¹, and presence of any C-H and O-H bonds at the range 2840 – 3000 cm⁻¹ and 1330 – 1420 cm⁻¹, respectively [21-22]. The absence of those peaks indicate again that no reaction has taken place on the PTFE even after 4 months of immersion.

This stability is due to PTFE polymer microstructure where the (−CF₂−CF₂−) has the spiral molecular structure. Its carbon backbone is totally covered and protected by extremely high electronegative F atoms which are tightly connected. The size of the F atoms resulted in close contact among each other and allowed continuous coverage around the C−C bonds which protects them from attack. Both C−C bonds and C−F bonds are extremely strong (C−C, 607 kJ/mol; C−F, 552 kJ/mol). Hence this lead to chemical resistance and stability to the molecule [3]. In addition, the PTFE polymer is highly crystalline which contributes to its insolubility in most solvents, even at higher temperature [23]. Only a few chemicals, such as molten alkali metals, can attack PTFE molecules [3]. Therefore, it is very difficult for the heavy hydrocarbon molecules to disrupt the PTFE membrane matrix and cause swelling.

Hence, the IR analysis indicated that PTFE polymer exhibited strong chemical stability for long term contact with the heavy hydrocarbons. This is important for minimising membrane damage and the need to put the membrane offline for rejuvenation. The good chemical stability also helps to lengthen the membrane module lifespan and to cut cost from having to change membrane module too frequently.
3.3. Contact Angle Measurement

After the PTFE membrane fibres have undergone 4 months of immersion in heavy hydrocarbons, contact angle measurements for each of the PTFE HFM (figure 6) were still able to maintain its high value. Contact angle readings of immersed PTFE HFM remained in non-wetting mode (i.e. >90°) with minimum value averaged at 96.97° after 4 months of immersion. Furthermore, based on t-test between the initial and immersed PTFE HFM in table 2, there was no significant difference between the results. Hence, it can be concluded that the heavy hydrocarbons immersion does not cause deterioration on the hydrophobicity of the PTFE HFM. This is important because it is critical for the membrane to maintain high hydrophobicity in membrane contactor operation, in order to prevent the liquid phase from easily going into the membrane. Reduction in hydrophobicity could result in increase of membrane wetting, which would lead to reduction in performance.

Figure 5. Comparison of IR spectra between (a) initial fresh membrane and (b) the immersed PTFE HFM.
**3.4. Thermal Stability Analysis**

The thermal stability of membrane was investigated by TGA to determine the decomposition temperature and weight loss of the PTFE HFM samples as a function of temperature. Figure 7(a) displays the TGA curves of the initial PTFE membrane fibres, whilst figure 7(b) shows those after 4-months immersed in heavy hydrocarbons.

The results indicate no weight loss identified below 400°C for all the samples. Boiling temperature of heavy hydrocarbons and water are all below 400°C. This indicates that there were no heavy hydrocarbons trapped in the matrix and pores of membranes [24].

As temperature increased, the weight loss transition of PTFE HFM samples began after 460°C and was noticeably complete after 610°C. Decomposition of the immersed PTFE HFM remained the same as the initial PTFE, where the membrane began to lose weight at temperature of 460°C. This indicated that tetrafluoroethylene (TFE) began to dissociate from the membrane matrix and decomposed. Most of the weight loss occurred at around 600°C, and this is observed from the steep slope in the TGA graph. The result is consistent with the works by R. Wang, Xu & He [22] and Zhu et al. [7].
Therefore, the membrane exhibited good thermal stability even after long exposure to heavy hydrocarbon.

![Thermogravimetric curve of (a) initial membrane and (b) immersed PTFE HFM.](image)

**Figure 7.** Thermogravimetric curve of (a) initial membrane and (b) immersed PTFE HFM.

4. Conclusion
In this study, the impact of heavy hydrocarbons towards PTFE HFM was investigated. PTFE hollow fibre membranes were immersed for months in n-heptane, 1-decene, benzene and toluene, and analysed periodically through its surface morphology, composition, functional groups, hydrophobicity, and thermal stability. The results indicate that there is no significant change in the characteristics of PTFE HFM. This study serves as a good reference on the robustness of PTFE membrane for application in membrane contactor process for natural gas sweetening.

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