

Removal of hydrogen sulfide from methane using commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes

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Abstract: The performances of commercially available poly (2,6-dimethyl-1,4-phenylene oxide)(PPO) and Cardo-type polyimide (PI) hollow fiber membranes were investigated in removing hydrogen sulfide from methane in a series of bench-scale experiments. It was observed that in the concentration range of 101 to 401 ppm H₂S in methane, the CH₄ permeability decreased in the presence of H₂S for Cardo-type polyimide hollow fiber membranes whereas the PPO membrane performance was not affected. The separation coefficients of H₂S/CH₄ were 6 and 4 for PI and PPO membranes, respectively. Also, the effect of temperature on the performance of PI and PPO membranes was studied. It was observed that the permeabilities of both components of the mixture increased with increasing temperature whereas the selectivities remained constant.

Keywords: Polyphenylene oxide membrane, Polyimide membrane, Gas separation, Natural gas sweetening, Hydrogen sulfide, Hollow fiber

1. INTRODUCTION

Natural gas resources around the world contain different levels of acid gases, mainly hydrogen sulfide and carbon dioxide, as impurities. Samples of Iranian raw natural gas have H₂S contents from 66.2 ppm to 3.27 mol.% in different gas fields. Due to the toxic and corrosive properties of this gas, it should be removed from natural gas to the level of 2 to 4 ppm in order to meet the pipeline specifications. The upper standard for H₂S concentration in the natural gas pipelines in Iran is 4 ppm.

While absorption processes are the main treatment for the removal of acidic gas from natural gas, polymeric membranes have gained momentum during the past few decades. The advantages of membranes compared with the competing processes are their lower energy and capital costs as well as operation simplicity, scalability, and smaller footprint. Commercialization of membranes for natural gas sweetening started around 1979-80 (Baker,2004).

Whereas a significant number of studies have been focused on the removal of carbon dioxide from methane, the permeation behavior of H₂S in membranes has been investigated to a lesser extent. The main reason for this is the high toxic and corrosive properties of this gas. In fact, only a few researches have been carried out on the separation of H₂S from CH₄, notably the studies reported by Stern (1993a,b,1998,2002,1997a,b), Baker (1995,1996), and Klass and Landahl (1985), in which the H₂S/CH₄ selectivities have been reported. Most results presented in these researches were related to cellulose acetate (CA) (Bhide and Stern,1993;Lokhandwala and Baker,1995) polyimide (Stern et al.,1997), polyurethane (Stern et al.,1997,2002) and PEBAX (Stern et al.,1997; Lokhandwala and Baker, 1995) membranes.

Among the glassy polymers, Cardo-type polyimide (PI) and polyphenylene oxide (PPO) possess excellent separation properties that make them suitable candidates for gas separation. The polyimide hollow fiber membranes that were developed for CO₂/N₂ separation by "Research Institute of Innovative Technology for the Earth" (RITE,

Japan) were proved to be good candidates for CO₂/CH₄ separation as well due to their high selectivities in comparison with other glassy membranes (Pourafshari Chenar,2006).

PPO has also been proven a suitable candidate for a wide range of industrial gas separation applications. PPO is a linear amorphous thermoplastic with glass transition temperature (T_g) ranging from 212 to 218 °C. Because of the presence of the phenyl rings, PPO is hydrophobic in nature and has excellent resistance to water, acids, alcohols, steam and bases. It has been reported that, amongst all glassy polymers, PPO shows one of the highest permeabilities to gases (Story and Koros,1992; Mortazavi,2004, Aguilar-Vega and Paul,1993; Matsuura, 2001; Plate and Yampolskii,1994). The high permeability has been attributed to the absence of polar groups in the main chain of PPO (Plate and Yampolskii,1994). An important factor governing the separation properties of any industrial application of membrane is the presence of other contaminants in the stream.

Bhide and Stern (1993) presented the effect of H₂S on the performance of CA membranes in removing acid gases from methane. They indicated that, at concentrations greater than 1% H₂S in a tertiary mixture of CH₄-CO₂-H₂S, not only CO₂, but also H₂S shows plasticization effects. The group showed that the combined effects of the two gases reduced the selectivities of the membranes.

Lee et al. (1995) studied the effect of H₂S impurity on the performance of the CA membrane and observed that in the presence of water vapor the plasticization effect of hydrogen sulfide is magnified mainly in terms of permeation velocity. They proposed that membrane treatment of gases containing both H₂S and water vapor should be avoided especially at relatively high concentrations of H₂S.

Cooley and Coady (Cooley and Coady,1978) also reached a similar conclusion by suggesting that for an effective removal of H₂S from natural gas using CA membranes, the feed should already be free of water vapor.

In the case of (PI) membranes, it is reported that unlike their higher CO₂/CH₄ selectivity compared with CA membranes, their H₂S/CH₄ selectivity is relatively low. For this reason, these membranes are not capable of economically removing H₂S from natural gas in an industrial application. Stern et al.(1997), studied the separation properties of PI membrane based on 6FDA (hexafluoropropane dianhydride). They tried to remove CO₂ from a tertiary mixture of CH₄-CO₂-H₂S at high H₂S concentrations (2.8 to 8%). The group concluded that the selectivity of membranes improved in the presence of H₂S. While they pointed out that this phenomenon was unpredictable, they did not offer any explanation for their observations.

Klass and Landahl (1985) studied the separation of H₂S and CO₂ from CH₄ with membranes such as Nylon 6, Nylon 6.6 (polyimide), polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) and also rubbery membranes. Although they achieved H₂S/CH₄ selectivities in the vicinity of 200, the permeabilities of these membranes were very low.

Chatterjee et al. (1997) studied the permeation properties of the membranes made of a group of polyurethanes (PU) and polyurethane-ureas (PUU). According to their findings, there were direct correlation between permeabilities of the experimental gases and their critical temperatures. Furthermore, because critical temperature directly affects solubility of gases into rubbery polymers, they concluded that the permeation of the experimental gases was controlled by their solubilities. It was also shown that PUU had better H₂S/CH₄ selectivity than PU.

Bhide and Stern (1993a,b) and Bhide et al. (1998) showed that H₂S removal by membranes is an important constraint in system selection affecting the economics of the process. The above authors and Lee et al. (1995) pointed out that most existing commercial membranes are not capable of economically reducing concentration of H₂S from 5000 ppm or more to 4 ppm, and that a hybrid system including absorption would be the preferred process. It should be mentioned that the cost of the hybrid process is independent of concentration of H₂S and perhaps for the same reason the studies were mainly carried out without taking into account the separation of H₂S from CH₄ by membranes. At lower feed concentrations of H₂S where the concentration of H₂S in the product can be reduced easily by absorption, concentration of H₂S in the feed is not a determining parameter in the process design. However, as mentioned before, care must be taken where the presence of small amount of H₂S along with other components could have a negative effect on the performance of membranes for separation of other gases.

In most studies it is assumed that the plasticization effects and permeabilities of H₂S and CO₂ in gas mixtures are the same. For example, Kaldis et al. (2000) substituted CO₂ for H₂S in a series of experiments using commercial Ube polyimide membrane assuming similar permeabilities of these two gases. It should be mentioned that in a few studies this assumption has been confirmed using a gas mixture containing 1% H₂S. For example, Bhide et al. (1998) reported a selectivity of 19 for H₂S/CH₄ and 21 for CO₂/CH₄.

Lokhandwala and Baker (1995) studied H₂S and CO₂ separation from CH₄ by membrane. They proposed a two-step membrane process in which the first step contains a H₂S selective module and the other a CO₂-selective one. For instance, if the natural gas contains water vapor, it is better to feed it first to the H₂S-selective module because such membrane would not be damaged by water vapor and the moisture would be transported along with H₂S to the permeate side. After examining a number of different membrane materials for CO₂ removal they recommended

cellulose acetate and its derivatives as the preferred material for this application. They also recommended copolymers of polyimide polyether as the most suitable membrane material for H₂S removal. The latter polymers are currently marketed under PEBAX and Vestamid trade names by Atochem Inc. and Noudex Inc., respectively. The CA membrane used in the study showed a CO₂/CH₄ selectivity of 20 and H₂S/CH₄ selectivity of 25. The research group (Lokhandwala and Baker) examined three membrane configurations in the study: single-membrane system with high H₂S/CH₄ selectivity, single-membrane system with high CO₂/CH₄ selectivity, and double membrane system as explained above.

In the present study, the removal of H₂S from methane was studied using Cardo-type polyimide and PPO membranes under different experimental conditions.

2. MATERIALS & METHODS

2.1. Materials

The Cardo-type polyimide hollow fiber module was generously supplied by RITE, Japan. The inside and outside diameters of fibers were 370 and 500 μm, respectively. The PPO hollow fibers were generously supplied by Aquilo Gas Separation B.V., the Netherlands (Parker Filtration and Separation B.V., The Netherlands). The inside and outside diameters of hollow fibers were 370 and 520 μm, respectively. The chemical structures of the polymers and the specifications of the membrane modules are shown in Figure 1 and Table 1, respectively.

The PPO module was assembled by loading a bundle of 10 fibers in a shell and tube structure. Although the dense selective layer of PPO hollow fibers was on the shell side, in this study, the feed gas was introduced inside the fibers and permeate was collected from the shell. The permeance was calculated based on the outer surface area of the hollow fibers. Ultrahigh purity CH₄ and H₂S/CH₄ gas mixtures with 101, 198 and 401 ppm of H₂S in CH₄ were purchased from Praxair Distribution Inc., Canada.

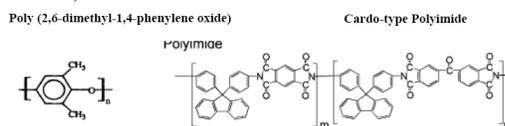


Figure 1. Chemical structure of polyphenylene oxide (PPO) and Cardo-type polyimide membranes [10].

Table 1. Cardo-type polyimide and PPO modules and hollow fibers specifications

Module Name	Membrane Type	Hollow fiber parameters		Module specifications	
		Inside diameter (μm)	Outside diameter (μm)	Number of fibers	Permeation area (cm ²)
RITE-A	Cardo-type PI (PI-BT)	370	500	135	416
PPO#1	PPO	370	520	10	49

2.2. Gas permeation experiments

The experimental gas separation system is illustrated schematically in Figure 2. The separation experiments were carried out at 50, 75 and 100 psig and room temperature (23 C) for each membrane. One set of experiments was also conducted at 100 psig and 40 C in order to understand the effect of temperature on the performance of the membranes.

The H₂S-rich permeate, was collected at atmospheric pressure and the CH₄-rich retentate was collected at a pressure approximately equal to that of the feed. Pure methane or H₂S/CH₄ gas mixture was supplied from a cylinder to the bore side of the hollow fibers. The entire system was placed in a temperature-controlled chamber with air circulation.

The permeation rate was measured by a bubble-flow-meter and the retentate flow rate was measured by a wet-test-meter. The stage-cut was controlled by a metering valve installed at the retentate side. The compositions of the retentate and permeate streams were determined by a gas chromatograph (Varian 3400) equipped with a thermal conductivity detector (TCD) and a “HayeSep T” column. The compositions were corrected using thermal response factors, TRFs. The TRF values were carefully calculated for each gas following Dietz’s method (1967).

The effects of H₂S concentration, pressure, temperature, and stage cut on the performance of the membranes were studied. At each operating conditions the experiments were conducted in the following order: pure CH₄, CH₄/H₂S mixtures at 101, 198, 401 ppm, H₂S contents, and repeat of pure CH₄. Each experiment was repeated three times to ensure the reproducibility of the results.

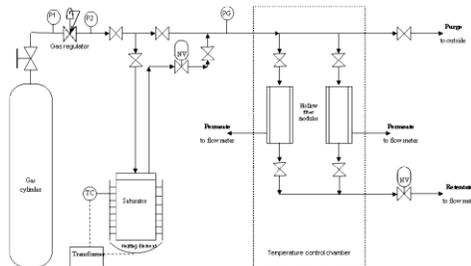


Figure 2. Schematic diagram of the constant pressure membrane testing system.

3. THEORY

The theoretical aspect of permeance, ideal selectivity, separation factor and stage-cut is based on Pourafshari Chenar (2006).

4. RESULTS & DISCUSSIONS

The results of permeability experiments with CH₄/H₂S mixtures at room temperature and different pressures of 50, 75 and 100 psig are shown in Figures 3 and 4. The results for the same set of operating pressures but at 40 °C are shown in Figures 5 to 8.

Figure 3 shows the H₂S permeance at various pressures and different concentrations of H₂S for the RITE-A module (Cardo type PI). This figure shows that the permeance of H₂S increased as the feed pressure (except for H₂S concentration of 401 ppm) and the concentration of H₂S increased. This can be explained by the higher driving force for the higher partial pressure difference across the membrane. These results were obtained at a stage cut of 5%. Figure 4 shows a similar observation for PPO membrane.

The effect of temperature on the permeability of CH₄ and H₂S are shown in Figures 5 and 6. It is shown that an increase in the temperature from 23 °C to 40 °C results in 60-70% increase in permeabilities of both CH₄ and H₂S for RITE-A module and 35-40% for PPO module at the feed concentrations of 101 to 401 ppm. Because the permeability of both components increased at the same rate with increasing temperature, the ideal selectivity and the separation factor for both modules remained constant (Figures 7 and 8). The selectivities of membranes at lower temperature were slightly higher than those at high temperature.

It has been mentioned before that H₂S plasticizes the membranes which seems to be more pronounced at higher temperatures. To study the plasticization effect of H₂S pure CH₄ permeation experiments were performed before and after each series of gas mixture tests. The results, as presented in Figures 9 and 10, indicated that the permeation rate of pure methane slightly declined in the tests done after the gas mixture experiments compared with that before. The effect of H₂S on CH₄ permeation flux and permeance is shown graphically in Figures 11 and 12. Figure 11 compares the permeability and permeance of pure methane with the permeation flux and permeance of methane in the presence of hydrogen sulfide through PI membrane. An obvious decreasing trend in the permeation flux and permeance of methane in the presence of H₂S can be observed from this figure. This observation is contrary to the expectation of higher methane permeation flux and permeance due to the plasticization effect of hydrogen sulfide. The very low concentration of H₂S might play a role in this observation as it might not be enough for an effective plasticization of the membrane. In such case, the decline in methane permeation flux and permeance should only be considered as a random process. This explanation is supported by the trend observed from PPO membrane, as shown in Figure 12. The latter figure indicates a consistent permeation flux and permeance of methane gas in the presence or absence of hydrogen sulfide, emphasizing that the concentration of H₂S is not large enough to plasticize the membrane and increase the methane permeation flux and permeance.

Table 2 shows the concentration of H₂S in feed, retentate and permeate along with the separation factors of H₂S/CH₄ at different feed pressures and three levels of feed concentrations of H₂S. These results indicate that the separation factors of the applied PPO and Cardo-type PI membranes are higher at high feed concentrations of H₂S and therefore it is expected that the performance of these membranes to be better at higher feed H₂S concentrations.

Table 2. Composition of feed, permeate and retentate at different feed pressures.
Separation of H₂S/CH₄ with RITE and PPO module.

Feed pressure psig	RITE-A								
	101 ppm (vol.%, 0.0101)			Feed H ₂ S concentration 198 ppm (vol.%, 0.0198)			401 ppm (vol.%, 0.0401)		
	Retentate H ₂ S (vol.%)	Permeate H ₂ S (vol.%)	Separation factor (H ₂ S / CH ₄)	Retentate H ₂ S (Vol.%)	Permeate H ₂ S (Vol.%)	Separation factor (H ₂ S / CH ₄)	Retentate H ₂ S (Vol.%)	Permeate H ₂ S (Vol.%)	Separation factor (H ₂ S / CH ₄)
50	0.0090	0.0315	3.3	0.0174	0.065	3.5	0.0349	0.141	3.8
75	0.0084	0.043	4.7	0.0162	0.087	4.9	0.0324	0.184	5.1
100	0.0080	0.051	5.7	0.0153	0.104	5.9	0.0309	0.216	6.1
100 [†]	0.0079	0.051	5.7	0.0153	0.104	5.9	0.0306	0.219	6.2
PPO-I									
50	0.0093	0.0255	2.6	0.0180	0.053	2.8	0.0359	0.118	3.1
75	0.0090	0.0317	3.3	0.0174	0.065	3.5	0.0350	0.139	3.7
100	0.0088	0.0353	3.8	0.0169	0.074	4.0	0.0342	0.154	4.1
100 [†]	0.0088	0.0358	3.8	0.0171	0.072	3.9	0.0342	0.152	4.1

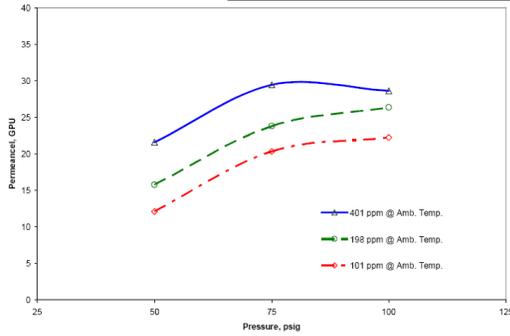


Figure 3. H₂S permeance vs. feed pressure in separation of H₂S/CH₄ mixtures at room temperature for RITE-A module.

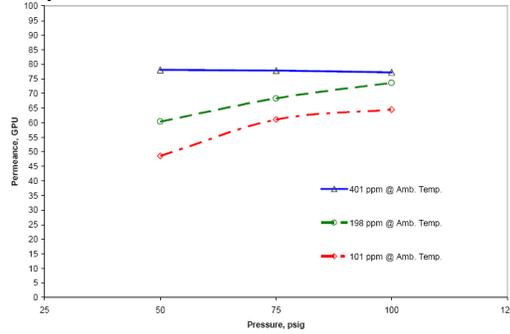


Figure 4. H₂S permeance vs. feed pressure in separation of H₂S/CH₄ mixtures at room temperature for PPO module.

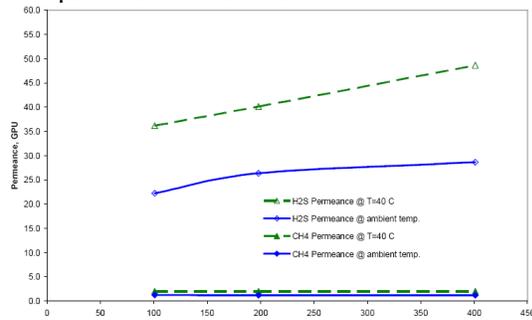


Figure 5. CH₄ and H₂S permeabilities vs. H₂S feed concentration at different temperatures for RITE-A module.

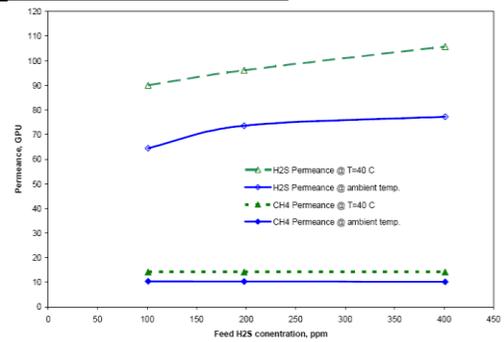


Figure 6. CH₄ and H₂S permeabilities vs. H₂S feed concentration for PPO module.

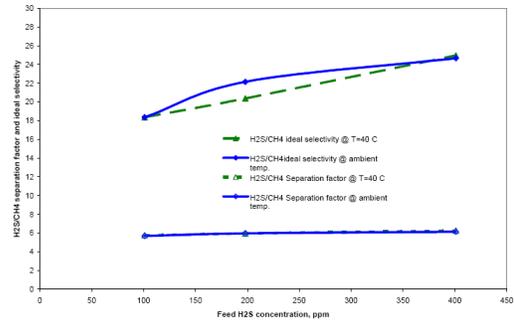


Figure 7. The effect of temperature on the ideal selectivity and separation factor of RITE module for H₂S/CH₄ mixtures.

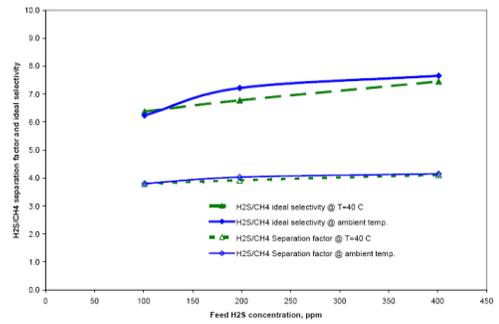


Figure 8. The effect of temperature on the ideal selectivity and separation factor of PPO module for H₂S/CH₄ mixtures.

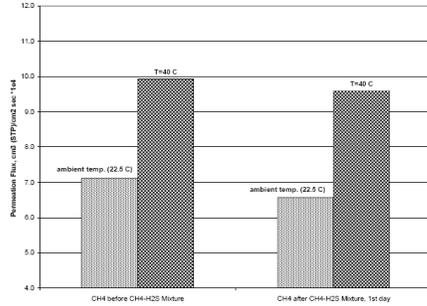


Figure 9. The effect of temperature on permeation flux of CH₄ before and after experiments with H₂S mixtures for RITE module.

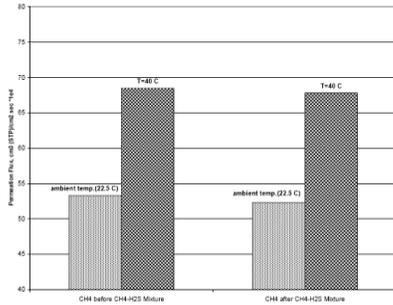


Figure 10. The effect of temperature on permeation flux of CH₄ before and after experiments with H₂S mixtures for PPO module.

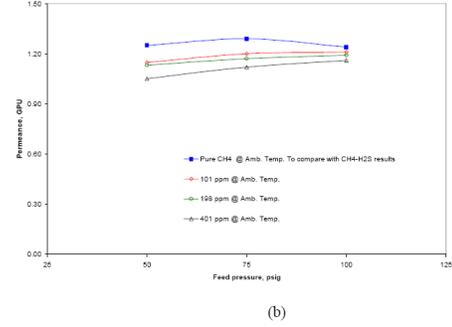
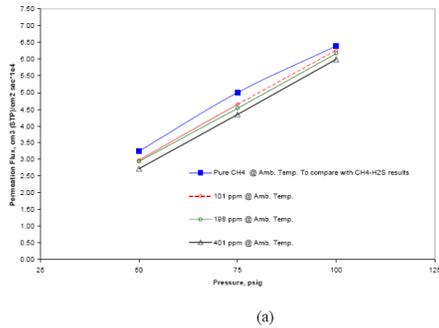


Figure 11.(a) CH₄ permeation flux and (b) permeance of pure CH₄ and CH₄/H₂S mixtures for RITE module.

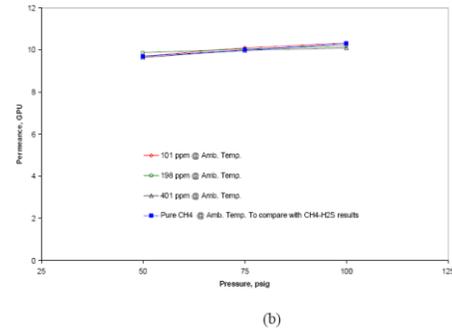
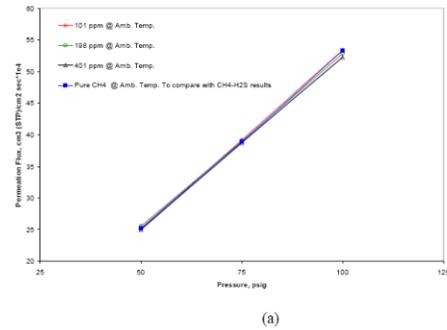


Figure 12. (a) CH₄ permeability and (b) permeance of pure CH₄ and CH₄/H₂S mixtures for PPO module.

5. CONCLUSIONS

Separation of H₂S/CH₄ mixtures at various concentrations of H₂S was investigated for two commercially available hollow fiber membranes including Cardo-type polyimide and polyphenylene oxide (PPO) membranes at different operating pressures and temperatures. It was shown that in the presence of H₂S the permeance of CH₄ declined for the Cardotype polyimide membranes whereas for the PPO membranes it remained relatively unchanged. The separation factors of H₂S/CH₄ were 6 and 4 for Cardo-type polyimide and PPO membranes, respectively. It was also observed that the component permeabilities increased with temperature, but separation factor remained the same.

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