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High-performance ester-crosslinked hollow fiber membranes for natural gas separations

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ABSTRACT

A significantly improved defect-free ester-crosslinkable hollow fiber membrane was developed through simultaneous optimization of the spinning solution and dry-jet/wet-quench spinning process variables. The resultant ester-crosslinked hollow fibers show extremely high separation productivity and efficacy with CO_2 plasticization resistance under aggressive feed conditions. The CO_2 permeance was improved from 50 GPU to 117 GPU with a CO_2/CH_4 selectivity of 37 in testing at 200 psi with 50/50 CO_2/CH_4 feed, 35 °C. Moreover, the crosslinked hollow fibers maintain a high CO_2 permeance under highly aggressive feed pressures up to 800 psi of 50/50 CO_2/CH_4 feed without CO_2 plasticization. A lower operating temperature can improve the CO_2/CH_4 selectivity significantly without apparent loss of CO_2 permeance. The mixed gas permeation with high CO_2 feed pressure demonstrates that ester-crosslinked hollow fiber membranes provide a significant advance in the state of the art for CO_2/CH_4 separations.

1. Introduction

As one of the most important fuel sources worldwide, raw natural gas often contains an unacceptably high level of carbon dioxide (CO_2), which must be reduced to a level of $<2\%$ to avoid problems caused by CO_2 induced pipeline corrosion, compression cost and a reduction of heating value [1]. The main technologies currently used to separate CO_2 from natural gas include cryogenic distillation, amine absorption and membranes [1–3]. Cryogenic distillation is highly energy intensive because gases must be cooled down to realize the CO_2/CH_4 separation [4]. While amine absorption removes CO_2 almost completely, high capital cost, complex operation, expensive maintenance and corrosion makes this technology problematic [3]. Membrane separation technology described here can overcome the key operational problems associated with cryogenic distillation and amine absorption processes [5,6].

Many materials can be used to produce membranes, including polymers, carbon molecular sieves (CMS), zeolites and ceramics [3]; however, polymers are the dominant membrane materials used for natural gas separations. Polymeric hollow fiber membrane devices were developed as an alternative to flat sheet and spiral wound membrane devices and were first commercialized by Monsanto in 1977[7]. Asymmetric hollow fiber membranes are industrially preferred to improve the productivity and reduce the cost of membranes in gas separation technology due to the high surface area to volume ratios up to 10,000 m^2/m^3[8]. The cylindrical structure of the hollow fibers can withstand high transmembrane pressure difference up to 1000 psi [9]. Despite its excellent separation performance, high CO_2 partial pressure induced plasticization tends to cause polymeric membranes to show lower CO_2/CH_4 separation efficiency and loss of CH_4 into the permeate. To mitigate this problem, covalent ester crosslinking has been investigated and shown to stabilize polymer membranes against CO_2 plasticization by suppressing the degree of swelling and segmental chain mobility in the polymer [10–13]. This study focuses upon extending the success of crosslinking to even more productive hollow fibers with enhanced CO_2 plasticization resistance to meet the industrial application requirements.

2. Background and theory

2.1. Gas transport mechanism in membranes

Several mechanisms have been proposed for gas transport in polymeric membranes [5,6,9]; however, the so-called sorption–diffusion is the most preferred. The sorption–diffusion model first qualitatively described by Graham in 1831 is the most widely accepted description of gas molecule transport in nonporous polymeric membranes [5,14]. In this model, the permeants first sorb in the membrane material and then diffuse through the membrane under a partial pressure difference. The differences in the solubility of gas in the membrane and the rate of permeants

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diffusion through the membrane cause the different gases to be separated. In this case, the permeability coefficient, P, of a polymer membrane can be described by the product of the diffusion coefficient, D, and sorption coefficients, S, as shown in the following equation [5]:

$$P = D \cdot S \tag{1}$$

2.2. Characterization of membrane performance

To characterize the performance of a membrane, two key factors are commonly studied: permeability and selectivity. The permeability represents the intrinsic productivity of a membrane and is defined by the flux of penetrant i, normalized by the membrane thickness and the partial pressure difference across the membrane, as shown in the following equation [5]:

$$P_i = \frac{n_i \cdot l}{\Delta p_i} \tag{2}$$

In Eq. (2), n_i represents the flux of penetrant i through the membrane; l refers to the membrane thickness, and Δp describes the partial pressure or fugacity difference of each penetrant across the membrane. The common unit of membrane permeability is the Barrer, shown as

$$\mathrm{Barrer} = 10^{-10}\left(\frac{\mathrm{cc(STP)cm}}{\mathrm{cm^2\ s\ cm\ Hg}}\right) \tag{3}$$

In an asymmetric hollow fiber membrane, the actual membrane thickness is difficult to define unambiguously; therefore, the productivity of a hollow fiber membrane is usually described by the permeance, P_i/l, which is the flux of penetrant i normalized by partial pressure or fugacity difference, as shown in the following equation:

$$\frac{P_i}{l} = \frac{n_i}{\Delta p_i} \tag{4}$$

The common unit of permeance is the GPU [15], which is defined as

$$\mathrm{GPU} = 10^{-6}\left(\frac{\mathrm{cc(STP)}}{\mathrm{cm^2\ s\ cm\ Hg}}\right) \tag{5}$$

The ideal selectivity measures the intrinsic membrane separation efficacy. For a given pure gas pair, if the total upstream pressure is much larger than the total downstream pressure, the ideal selectivity, α_{ij}, is defined by the ratio of the fast gas (i) permeability or permeance to the slow gas (j), as shown in the following equation:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{P_i/l}{P_j/l} \tag{6}$$

Practically, complications including plasticization, non-infinite pressure ratio and competition among gas molecules may occur for mixed gas permeation. Therefore, the separation factor, $(S.F.)_{ij}$, is commonly used to evaluate the separation performance, as shown in the following equation [15]:

$$(S.F.)_{ij} = \frac{y_i/y_j}{x_i/x_j} \tag{7}$$

In Eq. 7, x and y represent the mole fraction of the penetrants in the upstream and downstream of the membrane, respectively; and i and j means the different penetrants in the mixed gases. The α_{ij} and $(S.F.)_{ij}$ become equal when the ratio of upstream pressure to downstream pressure is very high. The relative permeance ratio is preferred to measure a membrane's intrinsic separation performance, since the $(S.F.)_{ij}$ is affected by the ratio of feed to permeate pressure, which complicates polymer separation properties.

2.3. Plasticization and crosslinking

The plasticization of a polymeric membrane is often observed when a high CO_2 partial pressure is fed on the upstream, which increases the permeance and reduces selectivity significantly. In the presence of plasticization, the penetrant–polymer interaction increases the segmental mobility of polymer chains and causes an increase of diffusion coefficients of penetrants, thereby increasing the permeance [16–18]. When the plasticization pressure is reached, the selectivity decreases with the pressure. The loss of selectivity is due to the relatively larger increase of permeance for the slow CH_4 than the fast CO_2. To develop a practical membrane with sufficient separation performance, the plasticization must be suppressed to achieve a high permeance without a loss of selectivity.

Different strategies can be utilized to stabilize polymer membranes against CO_2 induced plasticization, including polymer thermal annealing [19,20], blending [21,22] and crosslinking [11,17,23–25]. A highly effective approach, covalent ester-crosslinking, has been shown to improve the CO_2 plasticization resistance by reducing the degree of swelling and segmental chain mobility in the polymer. The crosslinking mechanism can be explained by Fig. 1.

Notwithstanding the advantages in stabilizing polymeric membrane against plasticization, crosslinking can cause a loss of CO_2 permeance, which undermines the separation productivity for crosslinked hollow fibers [15]. In such a case, crosslinking is believed to also cause a densification of transition layer of hollow fibers, thereby increasing the transport resistance and essentially reducing the permeance. Therefore, this research is focusing on development of the most productive asymmetric hollow fiber membranes with the thinnest skin layer thickness to achieve the desirable highest separation performance potential of crosslinked hollow fibers.

2.4. Asymmetric hollow fiber membranes

Typically, asymmetric hollow fiber membranes can be spun using a dry-jet/wet-quench hollow fiber formation process [6]. The homogeneous polymer solution (called dope) is co-extruded with bore fluid through an annular die, called a spinneret, into an aqueous quench bath. During the dry-jet period, the volatile components evaporate from the dope and increase the polymer concentration in the outer layer of nascent fibers. When the fiber enters the quench bath, phase separation occurs rapidly and the dope demixes into a polymer rich phase and a polymer lean

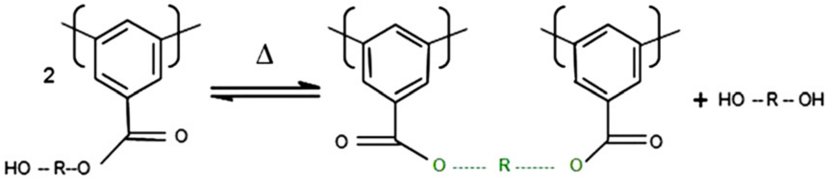

Fig. 1. Ester-crosslinking mechanism showing the formation of new ester bonds between polymer chains.