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Effects of hydrocarbon and water impurities on CO_2/CH_4 separation performance of ester-crosslinked hollow fiber membranes

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ABSTRACT

High-performance ester-crosslinked hollow fiber membranes were evaluated for sensitivity to aggressive hydrocarbon and water impurities. The hollow fiber samples show improved separation productivity and hydrocarbon-induced antiplasticization resistance under extremely challenging feed conditions in comparison to previously reported cases. The CO_2 permeance was improved from 10 GPU to 50 GPU with a CO_2/CH_4 selectivity of 28 in testing at an 800 psi 50/50 CO_2/CH_4 feed with 1000 ppm (molar) toluene, 35 °C. Moreover, membrane samples with different skin layer thicknesses show significantly different sensitivities to toluene. The thinner skinned samples are hypothesized to have higher fractional free volume (*FFV*) and hence show more tendency to antiplasticize when exposed to impurities as compared to thicker skinned samples. The high separation performance of crosslinked hollow fibers was fully recovered after removing the high-level contaminants, including toluene and heptane, and showed negligible changes over 100 h exposure to a 600 psi 50/50 CO_2/CH_4 feed with 750 ppm toluene, indicating a strong stability against contaminants. Furthermore, exposure to 101 ppm (molar) water impurity did not cause an apparent subsequent change in the separation properties. The excellent properties in the presence of hydrocarbon and water contaminants demonstrate that ester-crosslinked hollow fiber membranes are attractive for natural gas purification, even under more aggressive operating conditions.

1. Introduction

Our previous work has shown that the skin layer thickness and separation performance of hollow fibers can be engineered by spinning solution reformulation and spinning process optimization [1,2]. The significantly improved CO_2 separation productivity and plasticization resistance of the ester-crosslinked hollow fibers were characterized previously using a model natural gas feed consisting of only CO_2 and CH_4. Since some raw natural gas contains heavier hydrocarbons, which may be detrimental to the membrane performance [3–5], we have now characterized the ester-crosslinked hollow fiber membranes in the presence of high-level hydrocarbon impurities. This paper focuses on separation performance under such challenging operation conditions.

The presence of a relatively low level hydrocarbon impurity, generally called an antiplasticizer [6–8], can cause so-called antiplasticization of glassy membranes, leading to a decrease in the glass transition temperature of polymer and increase in the local segmental stiffness of glassy polymers [9–11]. The presence of such miscible diluents can cause increased modulus and strength, with corresponding losses in elongation at break [6]. Some excess polymer free volume is believed to be occupied by the antiplasticizer, causing a loss of fractional free volume with a resultant reduction of permeate flux and complicated effects on separation selectivity [11]. Such hydrocarbon-induced antiplasticization can significantly reduce the CO_2 permeance and even cause loss of CO_2/CH_4 selectivity [3–5,12,13]. The effect of toluene was investigated by previous researchers [3,5,12–15] who found that Matrimid® hollow fibers showed a decreased permeance at a lower toluene concentration due to the antiplasticization effect [16]. On the other hand, the Matrimid® fibers showed increased permeance after reaching a critical toluene content, indicative of conventional plasticization induced by the higher-level toluene. Omole used ester-crosslinking to stabilize hollow fibers against plasticization [5,12]; however, the CO_2 permeance of the crosslinked hollow fibers decreased from 50 GPU to 10 GPU with 1000 ppm toluene in the feed. Besides the antiplasticization effect on mobility, the presence of toluene cause a reduction of permeance due to competitive sorption for unrelaxed volume previously available for CO_2 [16]. The significant reduction of permeance in the presence of toluene suggests that having high permeance hollow fibers *prior to toluene exposure* is useful to achieve desirably highly productive fibers under contaminant-laden feed conditions. Details regarding this optimization process

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to create such higher productivity membranes are presented in our earlier paper [2]. The current paper will discuss effects of different types of contaminants on the performance of ester-crosslinked hollow fibers, including aliphatic, aromatic and water impurities. Effects of contaminant concentrations, recovery of performance after contaminant exposure and stability of hollow fibers under aggressive contaminant feeds will also be addressed in the work.

2. Experimental methods

2.1. Materials

The material used for the hollow fibers is a propane-diol monoesterified crosslinkable polyimide, called PDMC polyimide, which has been investigated in previous research [5,17,18]. The starting material for PDMC polyimide is called 6FDA/DAM:DABA (3:2), which is synthesized via a two step polycondensation and imidization from 4, 4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2, 4, 6-trimethyl-1, 3-diaminobenzene (DAM) and 3, 5-diaminobenzoic acid (DABA), as described in Reference [19]. The DABA units in the polyimide are additionally partially monoesterified with 1, 3-propanediol to form the PDMC polyimide. Details about polymer synthesis and monoesterification can be found in Reference [1]. The carboxylic acid groups and ester groups in the PDMC can react to form new ester bonds, thereby crosslinking the polymer chains and stabilizing the polymer against plasticization. In this paper, the membrane samples were crosslinked by annealing them at 200 °C for 2 h under vacuum. The crosslinking reaction is shown in Fig. 1.

2.2. Hollow fiber spinning

Asymmetric hollow fiber membranes are typically developed through a so-called dry-jet/wet-quench spinning process, as shown in Fig. 2.

The polymer spinning solution, called dope, is co-extruded through a spinneret to form hollow fibers with a bore fluid, consisting of solvents and non-solvents, to avoid bore collapse of nascent hollow fibers during spinning. During the dry-jet air gap step, volatile components evaporate from the dope to increase local polymer concentration in the outmost layer of the fiber. When the fiber enters the water quench bath, the outer layer vitrifies and the dope rapidly demixes into polymer-rich and polymer-lean phases to form an open porous substructure underneath the skin layer [20]. The hollow fibers are then wound on a rotating drum and soaked in water bath to remove residual solvents and non-solvents. Dehydration and post-spinning treatment are finally conducted to prepare the desirable hollow fibers. Details about dope composition and spinning variables are described in Reference [2].

2.3. Gas permeation

2.3.1. Theory background

The diffusion of gas molecules in the polymeric membranes is generally described by the sorption–diffusion model [21,22]. In this model, the gas molecules first sorb in the upstream of a polymer membrane and then diffuse through the membrane

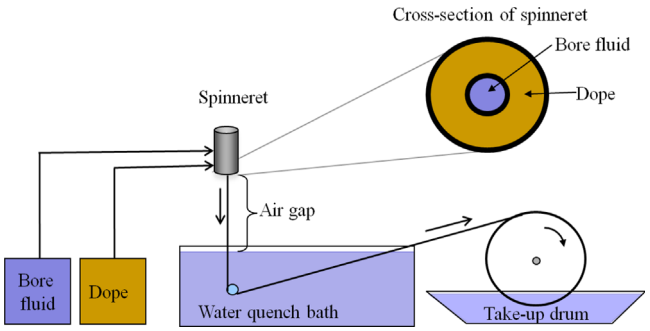

Fig. 2. Dry-jet/wet-quench hollow spinning system to prepare asymmetric hollow fibers [2].

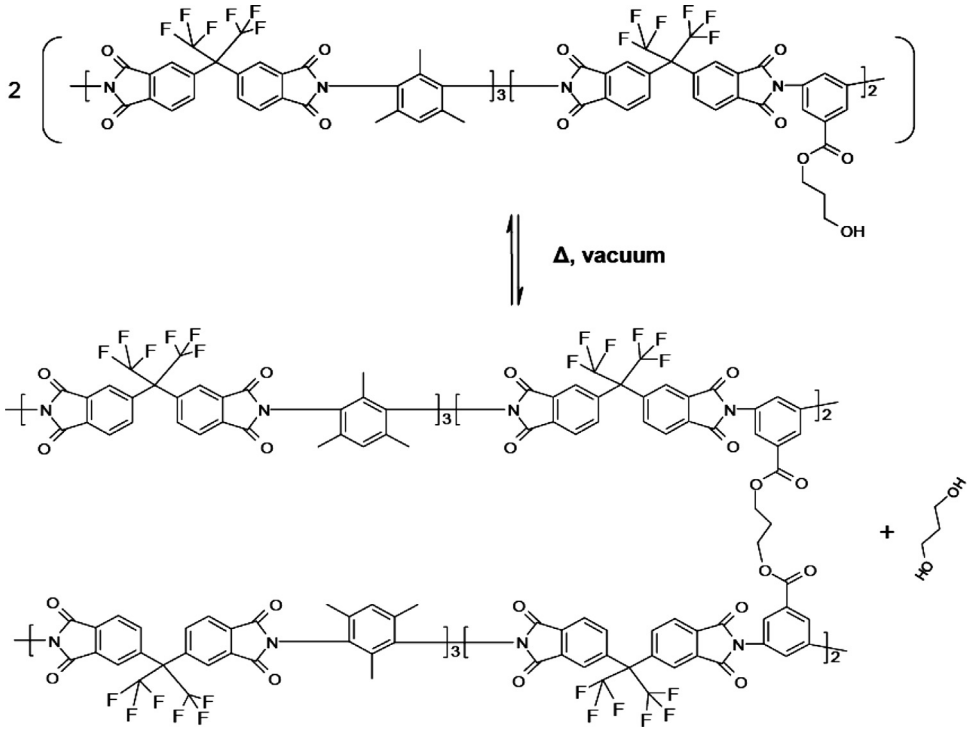

Fig. 1. Schematic showing the structure of PDMC polyimide (top) and crosslinking reaction [5].