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Natural gas purification and olefin/paraffin separation using cross-linkable dual-layer hollow fiber membranes comprising β-Cyclodextrin

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ABSTRACT

In this study, thermally cross-linkable co-polyimide dual-layer hollow fiber membranes grafted with β-Cyclodextrin for separation of CO_2/CH_4 and propylene/propane have been fabricated. In order to find the best spinning condition, the performance of hollow fiber membranes at various take-up velocities and outer-layer dope flow rates was investigated. The fiber membranes were thermally cross-linked at different temperatures and the performance of the fibers before and after silicon rubber coating was studied using CH_4, CO_2, propane and propylene. It was observed that permeances of all gases decreased with an increase in take-up velocity and outer-layer dope flow rate. Selectivities of the membrane with respect to the take-up velocity initially increased and after a take-up velocity value of 7.4 m/min started to decrease. This up and down trend was attributed to the influence of elongational draw ratio and change in surface porosity of the membrane. Optimum take-up velocity and outer-layer dope flow rate for as-spun fibers were 7.4 m/min and 0.5 ml/min, respectively. These conditions resulted in CO_2/CH_4 selectivities of 6.22 and 14.3 before and after silicon rubber coating, respectively. The results demonstrated that thermal treatment improves membrane selectivities and decreases membrane permeances. The enhancement of selectivities can be a result of cross-linking and reduction in permeances due to densification of the hollow fiber membranes. Selectivities of thermally treated fiber membranes at 350 °C were slightly higher than those of the precursor fibers and this improvement was more significant for membranes treated at 400 °C. This enhancement demonstrates that cross-linking is more severe at 400 °C. The best separation performance of the annealed and silicone rubber coated hollow fibers in this study has a CO_2 permeance of around 82 GPU with a CO_2/CH_4 ideal selectivity of around 20 and a high C_3H_6 permeance of around 29 GPU with a C_3H_6/C_3H_8 ideal selectivity of 15.3. It can also resist CO_2 induced plasticization until 25 atm. It is believed that, with these gas separation and anti-plasticization properties, the newly developed membranes may have high prospective for natural gas purification and olefin/paraffin separation.

1. Introduction

Natural gas consumption is more than 100 trillion cubic feet per year in the world and is expected to develop to 160 trillion cubic feet per year in 2035 [1]. Carbon dioxide is the most important impurity in many wells and CO_2 removal is an important step in natural gas processing, as they can reduce the heating value of natural gas as well as pipelines corrosion. Amine absorption is broadly used for CO_2 removal, but the capital and operating costs surge with the increasing CO_2 feed pressure and concentration [2–6].

Propylene is the second highest petrochemical feedstock after ethylene. The growth rate of the global propylene demand was estimated to be 5.5% per year and the total propylene consumptions was about 45 million metric tons in 2007 which led to a turnover of about 65 billion US dollars. The 5-year observation shows world propylene demand growth to average slightly less than 5% per year [7]. Propylene is a raw material for a wide variety of products including polypropylene, which is considered as a flexible polymer used in packaging and other important applications such as automotive components, textiles, and laboratory equipment [8–9]. The production of polymers and other special chemicals from olefins such as propylene requires extremely high purity olefins (> 99.9%). Since light olefins are commonly produced together with corresponding paraffins, the olefin/paraffin separation process in the petrochemical industries is crucial [10].

Capital and operating cost of these separation processes can stand for more than 50% of the production cost in chemical and petroleum refining industries. More efficient separation technologies are vital for

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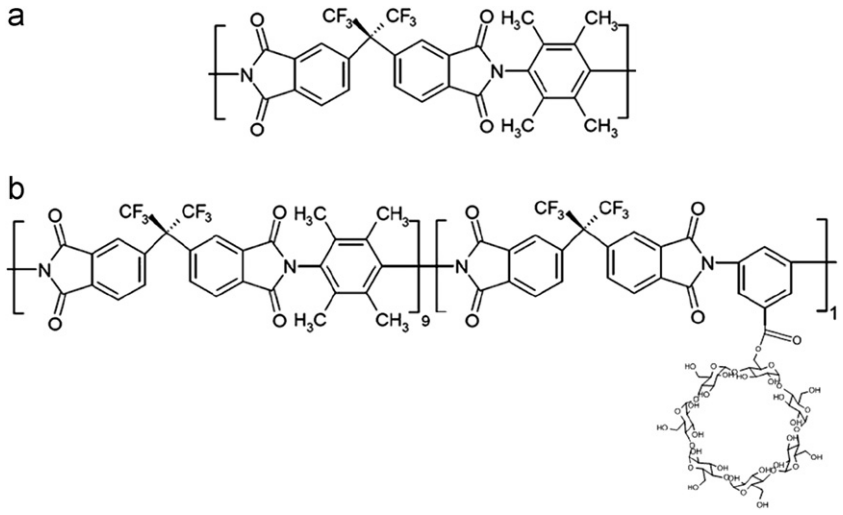

Fig. 1. Chemical structure of (a) 6FDA-Durene and (b) 6FDA-Durene/DABA (9/1) grafted with β-Cyclodextrin.

improving energy efficiency in industrial process [11,12]. Membrane technologies offer the advantages of lower energy requirements, capital investments, footprint and operational costs. The growing concerns over global energy security have also led to the accelerated development of novel membranes for various applications [13–16].

In natural gas purification and olefin/paraffin separation, 6FDA-based polyimides have received particular interest because of their excellent intrinsic CO_2/CH_4 and olefin/paraffin separation properties [17–22]. However, most CO_2/CH_4 and olefin/paraffin studies were investigated on dense films (around 50 μm) at low pressures rather than asymmetric membranes (less than 1 μm) at high pressures which is desirable for industrial applications. The separation performance of 6FDA polyimides generally degrades for separation of highly soluble gases such as CO_2 or hydrocarbons at relatively high pressures. This phenomenon is referred as plasticization [8,17,23–24]. In the occurrence of plasticization, the gas pair selectivity is diminished and the ideal selectivity measured by means of pure gas tests can no longer be used to estimate the mixed gas membrane performance [25]. Cross-linking has been recommended as a way to improve the membrane performance by decreasing plasticization effects and improving the selectivity [23,26].

The current state of gas separation membranes is largely beholden to the notable breakthroughs in both material science and membrane fabrication technology. Majority of gas separation membranes, in early days, were largely fabricated in the form of asymmetric composite flat or hollow fiber membranes with a selective layer made from a neat material [14,27]. The asymmetric structure of hollow fibers not only could considerably reduce the transport resistance of gas species but also offer good mechanical support. The new features offered by the dual-layer hollow fiber membranes, in comparison to the traditional single-layer hollow fibers, created great potentials for material savings through substituting the expensive functional material with inexpensive alternatives in the support layer. Nonetheless, the fabrication of dual-layer hollow fiber membranes with desirable characteristics is still not a trivial task and requires careful considerations from the physicochemical properties of materials throughout the entire chain of dope formulation, spinning and phase inversion process. However, the complexity often arises from the simultaneous co-precipitation of two distinct materials with different formulations. An ideal dual-layer hollow fiber membrane should consist of an ultrathin dense functional layer and a porous substructure. In order to withstand high feed gas pressures, the dual-layer hollow fiber membrane must be free from any delamination at the interfacial region. Literatures indicate that the delamination problems can often be minimized or removed through promoting the integrity of two layers by choosing compatible materials or using spinnerets with modified designs [28,29].

One of the key benefits of the dual-layer hollow fiber technology lies in the great opportunities provided for the exploitation of the wide range of high performance materials for membrane-based separation applications. Liu et al. [30] developed 6FDA-Durene/mPDA (50:50)/polyethersulfone (PES) dual-layer hollow fiber membranes with the enhanced performance for CO_2/CH_4 separation. They found that chemical modification of the outer layer offered membranes with enhanced stability against CO_2 induced plasticization and the ideal CO_2/CH_4 selectivity elevated from 44 to 101 after modification duration of 5 min. As a result, the desirable performance obtained in their hollow fibers promoted the viability of using expensive fluorinated polyimide for gas separation applications. In another work by Li et al. [31], dual-layer hollow fibers membranes were developed by using zeolite-functionalized-PES as the outer layer supported by the P84 co-polyimide. The fabricated hollow fibers exhibited enhanced CO_2/CH_4 selectivity in the order of around 10–20% compared to the PES dense films. Jiang et al. [32] investigated the effect of various spinning parameters on fabrication of defect-free dual-layer hollow fiber membranes using Matrimid and PES materials, and evaluated them for CO_2/CH_4 separations. They observed that a faster inter-layer diffusion occurred when the fibers were spun at elevated spinneret temperatures.

Interestingly, only a few studies have been carried out for olefin/paraffin separation using asymmetric hollow fiber membranes. Lee and Hwang [33] investigated C_3H_6/C_3H_8 separation through an asymmetric hollow fiber membrane made of a 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) based co-polyimide consisting of 4, 4′-oxydianiline (ODA) as the major diamine. They obtained propylene permeance varying from 0.8 to 1.6 GPU (1 GPU$=1\times10^{-6}$ cm^3 (STP)/(cm^2 s cm Hg)$=3.35\times10^{-3}$ kmol/ (m^2 s kPa)) and C_3H_6/C_3H_8 selectivity of about 15 in temperature and pressure ranges of 30–70 °C and 2–6 atm, respectively. They also reported that the performance of mixed gas data was consistent with the theoretical model using the single-gas permeation data. This implies no significant plasticization effect was observed. Krol et al. [34] reported that the asymmetric Matrimid polyimide hollow fiber membrane has quite lower C_3H_6/C_3H_8 separation performance than the BPDA-based polyimide membrane mentioned above. They observed significant plasticization, especially by propylene, whereas the permeance of propane did not