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Hollow fiber membrane process for the pretreatment of methane hydrate from landfill gas

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ABSTRACT

Landfill gas is major source of green house effect because it is mainly composed of CH_4 and CO_2. Especially, the separation of CH_4 from landfill gas was studied actively due to its high heating value which can be used for energy resource. In this study, polymeric hollow fiber membrane was produced by dry–wet phase inversion method to separate CH_4 from the landfill gas. The morphology of the membranes was examined by scanning electron microscopy (SEM) to understand and correlate the morphology with the performance of the membrane. Firstly, single gas permeation and mixed gas separation were performed in lab-scale. After then, a pilot scale membrane process was designed using a simulation program. The manufactured process settled in Gyeong-ju landfill site and operated at various conditions. As a result, CH_4 was concentrated to 88 vol.% and also CO_2 removal efficiency increases up to 86.7%.

1. Introduction

The control of green house gas is one of the most challenging environmental issues since the Kyoto protocol. Moreover, the recent substantial increase in the price of the crude oil in the international market has a negative impact on the economy worldwide and environmental effects associated with its usages. Thus, the international society is interested in research about non-fossil renewable and substantial energy resource [1].

Landfill gas was produced as a result of organic waste decomposition, which was comprised of 55–65 vol.% CH_4 and 35–40 vol.% CO_2 with some amount of trace gasses [2]. Landfill gas is a flammable and potentially harmful mixture and also, it contributed to global warming effect. Especially, CH_4 significantly influenced global warming because it is estimated to have 21 times higher global warming potential (GWP). In addition, a total of 40–60 tons of CH_4 emitted from landfills and old deposits worldwide, accounts for approximately 12% of global anthropogenic CH_4 emissions [3]. However, from the landfill gas, only CH_4 is a desirable component for an automotive fuel as well as for other energy uses. Other compounds (CO_2, N_2) reduce its energy content and have adverse effects on engine performance [4]. Owing to the potentially large supplies of CH_4 from landfill gas recovery, development of technology as an alternative energy source is of commercial interest [5].

One of the methods is gas hydrate for CH_4 recovery from landfill gas. Gas hydrate is a complex in which gas molecules were encaged within the hydrogen-bonded lattice network formed by the water molecule. CH_4 was collected by hydrate form for the use of abandoned energy from landfill sites [6]. However, impurities in landfill gas affect hydration efficiency. Lee et al. investigated gas storage capacity according to the composition of landfill gas [7]. The results show the amount of gas storage in the hydrate decreased with the decrease of CH_4 composition in the initial gas. A number of papers researched for the upgrading of landfill gas by adsorption, absorption and membrane process [8–10]. A membrane is defined as a selective barrier between two fluid phases [11]. Gas separation process became a major industrial application of membrane technology only during the one and half decades, but the study of gas separation actually began long before that period [12]. Membrane process has some advantages that have lower power usage and costs, simplicity in operation and its compactness and portability. Also, it doesn't need an additive for the separation and it easily combines with other processes [13].

In this study, membrane process was applied to the removal of CO_2 and purified CH_4 from the landfill gas. Hollow fiber membrane was fabricated by dry/wet phase inversion method using polyethersulfone (PES) as a polymer material. Asymmetric membranes that are suitable for gas separation should have thin and dense skin layers supported by thick porous sub-layers [14–16]. Fibers are characterized from SEM and single gas permeation test. Based on the experiment results, membrane area was estimated to be modulated using the pilot scale membrane process. Then, the hollow fiber membrane module was utilized,

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and the pilot scale membrane process designed was applied to the Gyeong-ju landfill site.

2. Experimental

2.1. Manufacturing of hollow fiber membrane

The production of durable resilient materials is the main focus of industrial applications and it is a challenge for the researchers. The new generation of membranes must be able to maintain its durability in rigorous environments, e.g. high resistance to plasticization and good mechanical stability at high feed pressure/temperature, to ensure a long-term stable operation. Moreover, a highly permeable membrane with high selectivity is required so that it can process large volumes of the feed gas.

Hollow fiber membrane was produced by a dry/wet phase inversion method. In this process an extruded fiber first passes through an air gap where a controlled evaporation takes place. Due to the evaporation locally a high polymer concentration is created near the outer surface, which is necessary to form a dense membrane at the top layer. After the air gap, the nascent fiber enters a coagulation bath where phase inversion occurs and the membrane structure is arrested. This procedure should result in membranes with an asymmetric structure [17].

Commercially available PES (Ultrason® E6020P, BASF, Germany) was used as membrane material. N-methylpyrrolidone (NMP, Merck, Germany) and distilled water were used as the solvent and non-solvent, respectively. Distilled water was used as internal coagulant [18]. Hollow fiber membranes were spun using the set-up schematically shown in Fig. 1. Dope solution has high viscosity and was maintained at 25 °C for easy transfer and fast phase inversion.

It was mixed by a mechanical stirrer after removing the moisture in the PES at 80 °C over a tree-days period. In order to remove bubbles that occurred in the mixing process, the dope solution was left in a vacuum tank for one day. After that, the viscosity was measured with a viscometer (LVDV-II PRO, BK instrument, Denmark) at 25 °C. The dope solution and internal coagulant were supplied by using a gear pump and HPLC pump (Series II pump, Lab Alliance, USA), respectively. The dope solution and internal coagulant were passed through a double pipe spinneret with a 0.12/0.6 mm inner/outer diameter. In this study, the air gap (the distance from the spinneret to the first coagulation bath) was maintained at 2.0 cm. The composition of the dope solution and spinning are shown in Table 1.

Hollow fibers were passed through the first coagulation bath where phase inversion occurred rapidly. Then, the hollow fiber moved to the second coagulation bath where it was washed out and coiled around the winder. After this process, the fibers were washed in a bath of continually flowing water (40 °C) for six days to remove the remaining solvent. The manufactured hollow fiber (KM1) was dried at 40 °C in the dryer for six days. Some of the washed fibers (KM2) were post-treated with methanol for 2 h to improve flux and dried at atmosphere for six days [19].

Table 1
Composition of dope solution and spinning condition for the preparation of PES hollow fiber membrane.

Composition	
PES	27.0 wt.%
NMP	68.5 wt.%
Distilled water	4.5 wt.%
Spinning condition	
Air gap	2.0 cm
Internal coagulant	Distilled water
Injection rate of dope solution	3.2 ml/min
Injection rate of internal coagulant	1 ml/min
Winding speed	11 m/min

The membrane was examined by scanning electron microscopy (SEM, S-4700, Hitachi). Based on this observation, the fiber was deposited in distilled water and refrigerated with liquid nitrogen so that it could be maintained with the original cross section after being cut off. After being dried off completely, the membrane was coated with Polydimethylsiloxane (PDMS) to remove surface defects and pin-holes

2.2. Single gas permeation experiment

The basic apparatus used here is shown schematically in Fig. 2. To determine the single gas permeance, the module was permeated with pure gas CO_2 (99.5 vol.%, SAFETY GAS, Korea) and CH_4 (99.999 vol.%, SAFETY GAS, Korea) with pressure and temperature difference, respectively. The physical properties of the experimental gasses are listed in Table 2.

The permeate side was maintained at atmospheric pressure. Moreover, the direction of the permeate flow was counter-current for the maximized efficiency. Gas permeation rates were measured with bubble flow meter. Permeance can be described universally as Eq. (1).

$$P = \frac{Q_P}{A \cdot \Delta p} \tag{1}$$

where Q_P is the permeate flow rate through the membrane, Δp is the gas pressure difference across the membrane, and A is the effective membrane area. In the SI system, the permeance is expressed in the following units: P = mol/(m^2·s·Pa) or cm^3(STP)/cm^2·cmHg·s. However, a more widely used and accepted unit for P is expressed in gas permeation units (GPU), where 1 GPU = 1×10^{-6} cm^3(STP)/cm^2·cmHg·s [20]. The pure gas selectivity was determined by taking the ratio of the pure gas permeances:

$$\alpha_{i/j} = P_i/P_j \tag{2}$$

Because gas mixtures show non-ideal effects, the individual permeances were calculated using the trans-membrane fugacity difference (f) instead of the trans-membrane partial pressure difference (p)

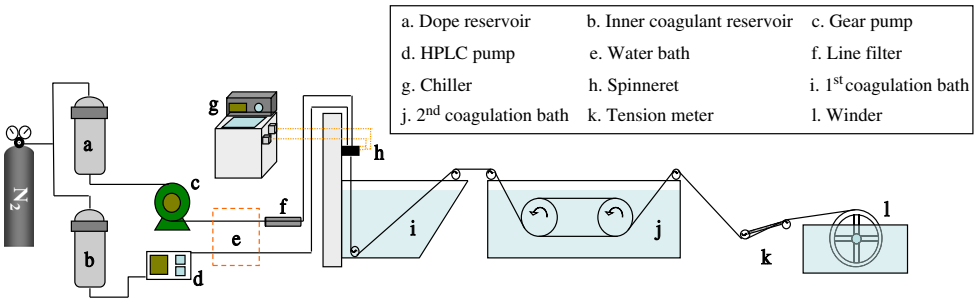

Fig. 1. Schematic diagram of hollow fiber membrane spinning system.