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Facilitated transport hollow fiber membrane prepared by t-Bu CoSalen for O_2/N_2 separation

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ABSTRACT

This study looks at air separation through a facilitated transport hollow fiber membrane using a CoSalen and PDMS coated composite membrane. The facilitated transport membranes were prepared using different CoSalen contents in the coating solution. The effects of the physicochemical properties such as composite membrane thickness were studied by SEM; the effect of cobalt content in the coating layer was studied by EDX; the effect of thermal decomposition and weight loss of the composite membranes were studied by TGA; and functional group analysis of the PDMS and CoSalen coated membranes were studied by ATR-FT-IR analysis to determine the performance of the composite membranes. The facilitated transport membrane made with the cobalt complex presented a 7.7 value of ideal gas selectivity for O_2/N_2; in addition, there was a good separation factor (4.5) for air separation, which showed at low pressure (0.1 bar) in the operating pressure range.

1. Introduction

Various studies have been previously reported on the technologies for air separation. Oxygen and nitrogen enriched air are applied in various industry fields. The storage of gas and oil in fuel tanks, and the food industry use nitrogen enriched air (NEA) and, particularly [1], oxygen enriched air (OEA); not only the steel industry, which is concerned with combustion efficiency [2], but also power plants require oxygen to be widely applied. Furthermore, most power plants have used such things as fossil fuels. The use of these fossil fuels is causing global warming. Among the many types of power plant, Oxy-flue combustion power plants also need an air separation unit for CO_2 capture [3]. On the environmental and economic sides, the OEA process applied in combustion has a diversity of advantages such as increasing the burning rate and the heat utilization, and reducing the smoke rate, ignition point, and burnout time of the fuel [4].

Among the many types of air separation unit, the membrane process for air separation, compared with the other processes, has many advantage such as low energy consumption, low operating cost and flexible design [5,6]. Last two decades researchers are focusing on hollow fiber membranes because, its having a good mechanical property, high packing density, and easy to scale up. Therefore, these membranes have been applied in many industries [7]. Generally, polymeric membranes show a trade-off trend between high permeability and low selectivity or low permeability and high selectivity, as shown in Robeson's chart [8]. Therefore, the way to overcome that relationship of permeability and selectivity has been to use advance materials such as polymer blends and crosslinked matrices, metal complexes, mixed matrix membranes, and magnetic membranes [1]. Facilitated transport membranes are the most capable substitute in the membrane development technology for O_2/N_2 separation. From 1938 researchers found that the Schiff-base/cobalt complexes to reversibly bind molecular oxygen. Since then, lot of compounds have been studied and employed as oxygen carriers. In the case of gas membranes among various permeation theories of membranes, a solution diffusion model is used. The highly reverse-selective gas membrane separation more appears diffusivity-selectivity by transport carriers. Facilitated transport membrane has a high energy efficiency from thermodynamic point of view and overcome trade-off effect [9]. Among all materials, facilitated transport membranes using metal complexes such as Ag^+ for Olefins [10] and Zn for CO_2 [11] have been applied for air separation. Facilitated mediated transport of cobalt base containing various materials such as CoPc [12], CoFPP [13], CoTPP [14], CoBPC [15], and picket-fence cobaltporphyrin [16,17] have been loaded into a flat sheet membranes.

In this study, we demonstrate a CoSalen and cobalt Schift based oxygen carrier mixed with polydimethylsiloxane (PDMS) as a coating materials for hollow fiber membranes coating for O_2/N_2 separation. Generally, PDMS, as a rubbery polymer has a high permeability and very low glass transition temperature; it is applied effectively in the caulking of larger size defects in hollow fiber membranes. A mixed CoSalen and PDMS coating solution was coated on a PES hollow fiber membrane surface to apply a physical coating to make a thin-film composite membrane. The coating on the hollow fiber membranes for air

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

Dope solution composition	
PES	18.0 wt.%
NMP	77.0 wt.%
LiCl	5.0 wt.%
Spinning conditions	
Air gap	0 cm
Spinneret ID/OD	0.16/0.9 mm
Internal coagulant	D. I water
Injection rate of dope solution	5.5 ml/min
Injection rate of internal coagulant	2.5 ml/min
Winding speed	18 m/min

Table 2
Composition of PDMS and CoSalen coating solutions and ratios.

Entry	Material compositions			PDMS:CoSalen (Ratio)
	PDMS (%w/w)	CoSalen (%w/w)	BIm (%w/w)	
M 1	3.0	–	–	100:0
M 2	3.0	0.3	0.075	100:10
M 3	3.0	0.75	0.186	100:25

separation was confirmed using the results of various methods of characterization such as FT-IR, SEM, EDX, and TGA. The O_2 and N_2 pure gas permeance, selectivity and air (mixture gas) separation are presented for each concentration of the coating solution and for each operating parameter for the facilitated transport membrane using CoSalen as a facilitated, mediated transport.

2. Materials and experiments

2.1. Fabrication of PES hollow fiber membrane

The hollow fiber membrane spinning process used a commercial polymer of PES (Ultrason® E6020P, BASF, Germany) prepared using the wet phase method. PES is dimensionally and thermally stable, and it has a highly rigid chain due to the regularity and polarity of its backbone [6,18]. The composition of the dope solution was made by mixing PES (18.0 wt.%, used after drying for 3 days at 80 °C) in *N*-methylpyrrolidone (NMP, Merck) and lithium chloride (LiCl, 5.0 wt.%, Sigma Aldrich, USA). NMP and LiCl were used as the solvent and additive, respectively, to make the porous membrane. The method of fabrication of the hollow fiber membrane, and the dope solution conditions for the preparation of the PES substrate, are listed in Table 1. The dope solution and internal coagulant (D. I. water) were passed through a double pipe spinneret (0.12/0.5 mm inner and outer diameter) with an air gap maintained at 0 cm. The fibers were washed in a bath of continually flowing (50 cm^3/min) hot water (313 K) for six days to remove the excess solvent after spinning. The washed fibers were post-treated with methanol for 2 h to improve membrane performance, and dried for 6 days under ambient conditions. The conditions of the dope solution are shown in Table 1 and a schematic diagram of the hollow fiber spinning process was given in previous work [6]. The dried hollow fiber membranes were prepared cylindrical module for the coating and gas permeability experiment. Each module consist 20 fiber of number and effective length of 30 cm.

2.2. Preparation of PDMS-CoSalen composite membrane

The thin composite hollow fiber membranes were prepared by coating mixed PDMS (Dow Corning, Sylgard 184) and CoSalen ((*R*, *R*)-(−)-*N*, *N*′-Bis (3, 5-ditert-butylsalicylidene)-1, 2-cyclohexanediaminocobalt(II)) coordinated with imidazole(1-benzylimidazole) in toluene (as solvent) on the surface of the PES substrate according to the different concentrations of CoSalen. The CoSalen concentrations used for the hollow fiber coating is in the range of, 0 to 25 ratio % (with respect to PDMS) mixed with PDMS ratio. High concentration of metal complex in coating solution, results high gas selectivity. However, over the 25% of CoSalen concentration with PDMS ratio in coating solution showed not fully dissolved and found the agglomeration. More detailed conditions of the coating solutions used to make the active layer on the PES substrate are shown in Table 2. The inner coating of the composite hollow fiber membrane was used by the injector for 1 min; after that, the wetted membrane was dried at 60 °C in an oven for 1 h.

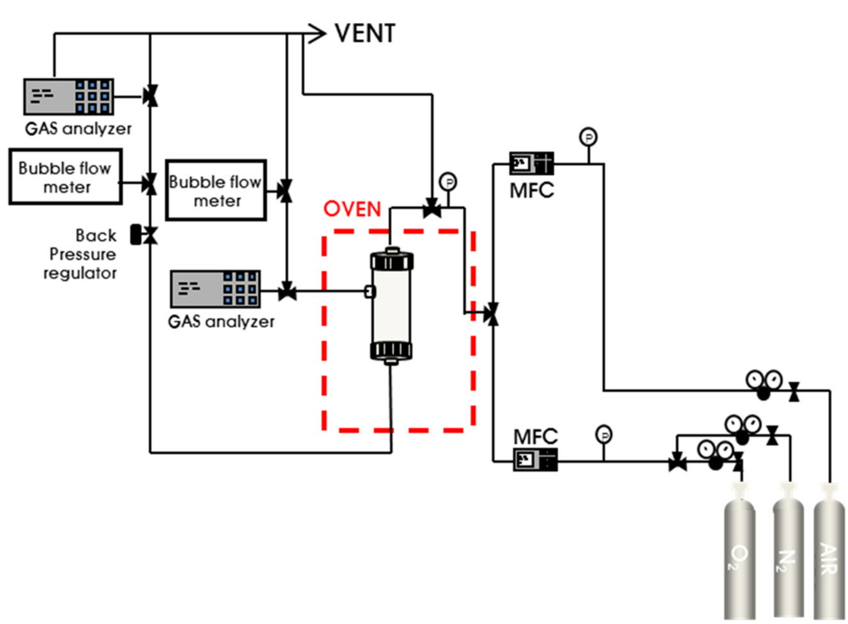

Fig. 1. Schematic diagram of gas permeation experiment apparatus.