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Comparison of biogas upgrading performances of different mixed matrix membranes

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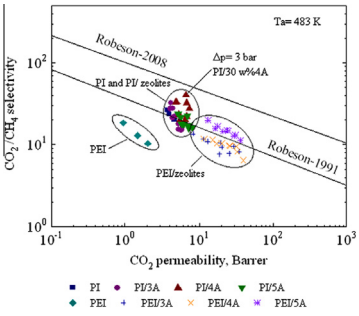
HIGHLIGHTS

- Annealing of membranes above solvent boiling point improves their performances.
- The effect of zeolite loadings on gas permeabilities differs for polymers.
- Partial relation exists between gas permeability and sorption capacity of membranes.
- Second component like H_2O in feed gas mixture reduce the CO_2 permeabilities.
- It is possible to separate CO_2 from the biogas in the purity of 95% using MMMs.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study composite membranes were manufactured by introducing zeolite 3A, 4A and 5A within polyimide (PI) and polyetherimide (PEI) in order to increase their separation performances for the gaseous mixture of CO_2 and CH_4 which are main components of the biogas. The effects of annealing temperatures, zeolite loadings, feed pressures and mixed gas and biogas feedings on the separation of CO_2–CH_4 by membranes were investigated. It has also investigated that whether there is a relation between gas sorption capacity and separation performances of membranes manufactured. Membranes were characterised DSC, TGA and SEM analysis. The pure gas permeation and the mixed gas or biogas separation experiments indicated that the mixed matrix membranes (MMMs) prepared by introducing zeolite 4A into PI is a suitable candidate for CO_2/CH_4 separation and/or methane enrichment from biogas. Zeolite loading into PEI increased the CO_2 and CH_4 permeabilities more than PI/zeolite-MMMs showed. But, the higher the zeolite loadings caused the lower the ideal CO_2/CH_4 selectivities for PEI/zeolite-MMMs at all the feed pressures applied. The results also showed that there is a partial relation between gas permeability and sorption capacity of membranes used.

The results of biogas separation experiments showed that the CO_2 content in the permeated gas increased as much as 95% at 3 bar feed pressure. The highest CO_2 content in the permeated gas was obtained when PI/4A-MMM was used, and followed by PI/3A, pure PI, PI/5A, pure PEI, PEI/5A, PEI/4A and PEI/3A.

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1. Introduction

Biogas is a gaseous mixture produced from microbial digestion of organic materials in the absence of oxygen. Raw biogas, depending on organic materials, digestion time and process conditions, contains about 40–70% methane (CH_4), 30–60% carbon dioxide (CO_2), traces of hydrogen sulfide (H_2S), moisture and some other organic compounds. Constituents of biogas, except the methane, are called energy diluting components which reduce its calorific value and make it uneconomical. Depending on the amount of energy diluting components, lower heating value of biogas changes

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Table 1
Summary of CO_2/CH_4 separation by mixed matrix membranes.

Membrane material	Filler	Effect of fillers on CO_2/CH_4 separation	Reference
Rubber	Silicalite-1	Improved	[12]
	13X and KY	Improved	
	Carbon molecular sieve	Not improved	
Polyimide	Silica	Improved	[13]
Aluminosilicate gel	T-type zeolite	Improved	[14]
Polyvinyl acetate	Zeolite 4A	Improved	[15]
Polyethersulfone	Zeolite NaA	Improved	[16]
	Zeolite AgA	Improved	
Matrimid® 5218	Carbon molecular sieve	Improved	[17]
Ultem® 1000		Improved	
Acrylonitrile–butadiene–styrene	Activated carbon	Improved	[18]
Matrimid	Carbon aerogel	Improved	[19]
Polyethersulfone	2-Hydroxy 5-methyl aniline (HMA)	Improved	[20]
	SAPO 34	Improved	
	SAPO 34/HMA	Improved	
Polyethersulfone	Carbon nanotube	Improved	[21]
Aromatic poly (amide-imide)	TiO_2	Improved	[22]
Matrimid 5218	TiO_2	Improved	[23]
Matrimid	MgO	Improved	[24]
Polysulfone	Metal organic frameworks	Improved	[25]
	(HKUST-1, ZIF-8) Silicalite-1	Improved	
6FDA-ODA polyimide	MOFs (UiO-66, NH_2-UiO-66, UiO-67, MOF-199, NH_2-MOF-199	Improved	[26]

between 13,720 and 27,440 kJ/m^3 while pure methane has a lower heating value of 34,300 kJ/m^3 at standard pressure and temperature [1].

Biogas is used generally where it is produced, and it has to be upgraded in order to increase its heating value, inject into natural gas grid, bottle into cylinders, make it transportable to long distances and use as a vehicle fuel. Upgrading techniques vary from simple physical techniques to complex hybrid multi-step processes, depending on the nature and concentration of impurities as well as on the treated gas specifications. The removal of energy diluting components from biogas can be performed by one or more ways considering energy requirements, additional chemicals, gas quality, methane loss, maintenance, and space and weight demands [2]. For instance, water vapor and H_2S can be removed from biogas efficiently using a condenser and an iron-sponge filter or an absorber, respectively [3,4]. But, application of current industrial techniques for the removal of CO_2 from biogas is so difficult at the farmyard. Therefore, biogas upgrading means separating the methane from its primary diluent, carbon dioxide [5–8].

The removal of CO_2 from biogas can be performed by applying adsorption, absorption, cryogenic method, and membrane gas separation. The first three methods are more traditional compared to the membrane separation which has some advantages such as low cost, high energy efficiency, ease of operation and modular state.

Since the first application of cellulose acetate membrane to the CO_2 separation in 1980s [9,10], various polymeric membrane materials such as cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide have been used for the removal of CO_2 from gaseous mixtures. But, cellulose acetate, polyimides and perfluoropolymers have become commercially available for CO_2 removal [11]. Although polymeric membranes have been commonly used in last few decades for gas separation applications, researchers seek continuously new membrane materials or modify the existing ones to overcome their shortcomings such as poor performance stability at high temperatures and pressures and low selectivity and permeation rate, and to improve productivity, selectivity and mechanical strength. One method is to insert a nano-sized material into polymeric phase. Membranes include nano-sized particles such as zeolites, called as mixed matrix membrane (MMM), have attracted in last two decades for their potential use in gas separation and purification. Apart from zeolite, MMMs can also be manufactured using carbon molecular sieves, MgO, TiO_2, metal organic frameworks (MOFs) and conductive polymers. In a MMM structure, polymer is the continuous phase and nano-particles are the fillers or dispersed phase. Separation by MMMs follows mechanisms based on molecular sieving, preferential adsorption and diffusion effects. Depending on the temperature, one or a combination of the mechanisms can govern the selective transport of one gaseous constituent over others.

Many researchers have manufactured MMMs using different polymers and fillers to achieve better CO_2/CH_4 separation in all over the World. They also studied different polymer: filler ratios, annealing temperatures, gas concentrations, feed gas pressures, etc. in order to determine better preparation and operation conditions. Table 1 summarizes the pioneer studies conducted about CO_2/CH_4 separation by MMMs.

In this study, the separation characteristics of different membranes for CO_2 and CH_4 gases which are two main components of biogas were investigated. Permeation measurements were done for pure polyimide (PI) and polyetherimide (PEI) nonporous dense membranes and their mixtures with zeolite 3A, 4A and 5A. The effect of annealing temperature (423, 483 and 523 K for PI and 423, 453 and 483 K for PEI), feed gas pressure (3, 5 and 8 bar) and zeolite content (10, 20 and 30 wt%) of mixed matrix membranes (MMMs) on gas permeation and selectivity were investigated. The membranes were characterized by differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA) and scanning electron microscopy (SEM). Gas sorption capacities of membranes manufactured for CO_2 and CH_4 gas pairs and the effect of impurities, such as water, on the CO_2/CH_4 selectivity were also investigated. All membranes manufactured were also used for the enrichment of CH_4 in biogas. All gas separation experiments were performed at room temperature, 298 ± 2 K.

2. Experimental methods

Gas permeation experiments were carried out using nonporous polyimide (PI) and polyetherimide (PEI) membranes and their mix-

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