Separation and Purification Technology 98 (2012) 472–480

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Effect of different additives on the physical and chemical CO_2 absorption in polyetherimide hollow fiber membrane contactor system

M. Rahbari-Sisakht [a,b,c], A.F. Ismail [a,b,*], D. Rana [d], T. Matsuura [d]

[a] Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[b] Gas Engineering Department, Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[c] Department of Chemical Engineering, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran
[d] Department of Chemical and Biological Engineering, Industrial Membrane Research Institute, University of Ottawa, 161 Louis Pasteur St., Ontario, Canada K1N 6N5

ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form 20 June 2012
Accepted 25 June 2012
Available online 4 July 2012

Keywords:
Polyetherimide
Hollow fiber membrane contactor
CO_2 capture
Additives

ABSTRACT

Porous asymmetric polyetherimide (PEI) hollow fiber membranes were fabricated via a phase-inversion method using ethanol, glycerol and acetone as the additives in the spinning dope. Also, hollow fiber PEI membrane without additives was fabricated. An aqueous solution of 1-methyl-2-pyrrolidone (80 wt.%) was used as bore fluid to prevent forming of an inner dense skin layer. The precipitation rate of the polymer dopes with the different additives was studied using cloud point measurement. The effect of the additives on the resulting membrane structure, surface porosity, pore size, critical water entry pressure, collapsing pressure and physical and chemical CO_2 absorption performance by distilled water and NaOH (1 M) solution in a gas–liquid membrane contactor system were investigated and compared. Cloud point diagrams indicated that the precipitation rate of the polymer dopes increased following the trend of ethanol > acetone > glycerol. Results of gas permeation tests showed that ethanol and glycerol as additives provided the membranes with the largest and smallest pore size, respectively. Moreover, all the additives resulted in an increase in the effective surface porosity. The cross-section of the membranes was examined via a scanning electron microscopy. Ethanol in the spinning dope provided the membrane structure with a sublayer with finger-like macrovoids, originating from the inner and outer surfaces of the hollow fiber and extending to the middle section of the hollow fiber wall, which resulted in a larger pore size and higher CO_2 absorption rate than the other PEI hollow fiber membranes.

1. Introduction

The enhancement of carbon dioxide (CO_2) concentration in atmosphere due to fossil fuel usage in industries and domestic usages, and its implications on global warming, are now commonly admitted [1]. CO_2 concentration is expected to double at around 2050, if no special actions are taken [2]. Industry and petroleum refineries are among the largest contributors to anthropogenic CO_2 emissions. Beside energy efficiency improvement, renewables and nuclear energy, CO_2 capture and storage (CCS) is considered a promising option to achieve significant reduction in CO_2 emissions. CCS has a large potential in industry and petroleum refineries not only because of its large CO_2 emissions but also because there are many industrial processes that generate gas streams rich in CO_2, or in some cases pure CO_2, which could reduce the costs of CCS [3].

CO_2 absorption using amines (e.g., using monoethylamine, MEA) has been widely employed due to the high selectivity of amines towards CO_2. The system is include two main stages: an absorber where the CO_2 is removed and a regenerator where the CO_2 is released in a concentrated form and the original solvent is recovered [4]. Some of the solvent is lost during the process due to physical losses, entrainment, vaporization and chemical degradation, involving a MEA makeup of 0.5–3.1 (1.5 as nominal value) kg MEA/tonne CO_2 [5]. A large amount of heat is required to regenerate the solvent and it has a major impact on the overall efficiency of the power plant [2]. This heat is typically drawn from the steam cycle and significantly reduces the net efficiency of the power plant [5]. Therefore, this technology demonstrates operating limitations such as the interdependence of the two fluid phases to be contacted that may produce emulsions, foaming, unloading and flooding [6]. As well, amines are very toxic compounds and the use of equipment like scrubbers involves solvent emissions due to the gas–liquid contact and liquid volatilization (1–4 ppm of MEA lost in the exhaust gas) [5]. Also, this technology is costly and energy intensive, expecting an increase of 50–90% in the cost of electricity

---

[*] Corresponding author at: Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia. Tel.: +60 7 5535592; fax: +60 7 5535925.
E-mail addresses: afauzi@utm.my, fauzi@petroleum.utm.my (A.F. Ismail).

1383-5866/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seppur.2012.06.033

Nomenclature

A	surface area (m^2)
C	concentration (mol/m^3)
d	diameter (m)
D	diffusion coefficient (m^2/s), shell side diameter (m)
E	enhancement factor
Gz	Graetz number
H	Henry's law constant
$\overline{P}$	gas permeance (mol/m^2 s Pa)
k	mass transfer coefficient (m/s)
K	overall mass transfer coefficient (m/s)
A_o	intersept of J vs. $\overline{P}$ plot
L	hollow fiber length (m), pore length (m)
m	distribution coefficient
M	molecular weight (kg/mol)
n	number of fibers
K_o	overall mass transfer coefficient
$\bar{p}$	mean pressure (Pa)
B_o	slope of J vs. $\overline{P}$ plot
Q	flow rate (m^3/s)
r	radius (m)
R	gas constant (J/mol K)
T	temperature (K)
U	velocity (m/s)
x	fraction of pore filled with liquid
$1/K_o$	overall mass transfer resistance (s/m)

Subscripts

A	component
b	bulk
e	equivalent
f	fiber
g	gas
i	inner, interface
l	liquid
lm	log mean
m	membrane
o	outer, overall, outlet
p	polymer, pore
w	water

Greek letters

δ	pore length (m)
ε	surface porosity
ε_m	membrane overall porosity
μ	gas viscosity (kg/ms)
ρ	density (kg/m^3)
τ	tortuosity

in power plants if an amine system is used to remove 90% of CO_2 from the flue gas [7,8].

Non-dispersive absorption using a gas–liquid contactor showed interesting advantages compared to the conventional absorption towers and also, they may be strong rivals to the use of dense membranes and supported liquid membranes [4]. Regarding the traditional absorption performed in scrubbers, the use of membrane-based absorption has more operational flexibility because of the independent control of gas and liquid flow rates, a controlled and known interfacial area, a linear scale-up thanks to the modularity of membrane contactors. The mass transfer of CO_2 from the gas to the liquid phase does not have a significant impact on the gas flow because of the low concentration of CO_2 in the gas stream [9]. In addition, compared to other membrane systems, the membrane pores are filled (in theory) with gas and the mass transfer through the membrane should be favoured in comparison to using dense membranes or membranes with pores filled by liquid (supported liquid membranes). The pore size and porosity of the membrane are key factors to consider since the contact between the gas and liquid phase occurs in the pores of the membrane and higher membrane porosity leads to a better performance [10–13].

Recently, acid gases captured by using porous hollow fiber membranes have attracted considerable attention [2–20]. The high permeability, low mass transfer resistance and excellent chemical resistance to various chemical-feed streams are the essential properties of these kinds of membranes.

In a gas–liquid membrane contactor, fluids can be contacted on opposite sides of the membrane and the gas–liquid interface is formed at the mouth of each membrane pore. Mass transfer occurs by diffusion across the interface.

The structure of a membrane is influenced by the rate of the phase inversion process. The thermodynamic stability of the polymer solution and the diffusion rate of coagulant into polymer solution are two important parameters that determine the rate of phase inversion process, which further depends on the composition of the spinning dope and coagulation media [21]. A rapid phase inversion process forms finger-like macrovoids in the structure of the membrane and a slow phase inversion makes a sponge-like structure [22,23]. One method to alter the rate of the phase inversion process is blending additives to the spinning dope and/or coagulant. Polymers [24–26], nonsolvents [27–29] and salts [30] are additives for spinning dope whereas solvents [31] and weaker nonsolvents [32,33] are used as additive for coagulant. The structure of the membrane also depends on the polymer concentration at the cloud point. Furthermore, highly water soluble phase inversion promoters of low molecular weight can be washed out during the phase inversion process, which in turn increases the porosity of the membrane [21].

Mansourizadeh and Ismail [34] studied the effects of different additives such as polyethylene glycol of average molecular weight 200 Daltons (PEG200), glycerol, acetic acid and ethanol on the polysulfone (PSf) membrane morphology. Their results showed that adding glycerol into the spinning dope provided the membrane structure with a thin finger-like and a thick sponge-like layer, which resulted in a higher critical water entry pressure (CEPw) and CO_2 absorption rate than the other PSf hollow fiber membranes. Bakeri et al. [21] added low molecular weight organic compounds to the spinning dope as phase inversion promoters and studied their effects on the structure of polyetherimide (PEI) hollow fibers. They employed water, methanol, ethanol, glycerol and acetic acid as additives in the spinning dope and fabricated hollow fiber membranes via wet spinning method. Their results showed the solution containing water as the additive had the lowest thermodynamic stability and highest viscosity, which yielded a hollow fiber with a thin skin layer of high porosity and a sublayer with sponge-like structure. The four other polymer solutions were more stable thermodynamically and less viscous. Among all their fellow fiber membranes, adding methanol resulted in the highest absorption flux.

PEI is a polymer with good thermal and chemical stability which makes it a suitable candidate for contactor applications. In addition, the low viscosity and hydrophobicity of PEI solution promotes the formation of finger-like macrovoids in the structure of PEI membranes which decreases the membrane mass transfer