Chemical Engineering Science 155 (2016) 239–247

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Practical designs of membrane contactors and their performances in CO_2/CH_4 separation

Seong-Joong Kim [a,b], Ahrumi Park [a], Seung-Eun Nam [a], You-In Park [a,b,*], Pyung Soo Lee [a,*]

[a] Advanced Materials Division, Center for Membranes, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong-gu, Daejeon 305-606, Republic of Korea

[b] University of Science & Technology (UST), 176 Gajung-dong, Yuseong-gu, Daejeon 305-350, Republic of Korea

HIGHLIGHTS

- A hollow fiber membrane contactor was studied for CO_2/CH_4 separation.
- Water was used as a physical absorbent.
- Single and combined absorption/desorption processes were compared.
- A CH_4 purity (98%) suitable for use as a fuel for vehicles was achieved.
- The combined processes gave a drop in separation due to incomplete CO_2 desorption.

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
22 June 2016
Accepted 9 August 2016
Available online 10 August 2016

Keywords:
Membrane contactor
Absorption
Desorption
CO_2
CH_4

ABSTRACT

Porous polypropylene (PP) hollow fiber membrane contactors operated by either single absorption processes or combined absorption/desorption processes using water have been investigated for use in the production of biomethane from simulated biogas. To observe the effect of operating parameters on the membrane contactors, the connection of modules, flow rates, and operating pressures were tuned. For CO_2/CH_4 separation, operations using single absorption processes produced a good yield (85%) of high purity CH_4 (97%). Connections in series containing two absorption modules facilitated CO_2 absorption due to an increase in contact area at the liquid–gas interface. In the combined absorption/desorption processes, CH_4 was recovered in 75% yield and 98% purity using two 1″ absorption modules and four 2″ desorption modules connected in series. Although the results were somewhat poorer than those of the single absorption processes due to limits in desorption performance, the combined process provided the potential for producing renewable methane as a fuel for vehicles. Furthermore, for the single absorption processes, the PP hollow fiber membrane contactor was operated continuously, while the membrane used in the combined absorption/desorption processes required periodic maintenance to maintain an acceptable performance.

1. Introduction

Biogas generated by anaerobic digestion typically contains 40–70% methane and 30–60% carbon dioxide, along with traces of hydrogen sulfide (H_2S) and water vapor (Goujard et al., 2009; McLeod et al., 2013). The produced biogas can then be upgraded by separation and subsequent concentration processes, leading to green and renewable biomethane for use in industry, households, and vehicles (Rongwong et al., 2012; Yan et al., 2014). Biomethane with a purity of 81% is also suitable for supply into the natural gas line (Heile et al., 2014), while higher purity biomethane (> 95%) can be directly used in vehicle fuels (Yan et al., 2014). In order to make biomethane economically attractive, efficient separation systems delivering high CH_4 recovery from biogas are greatly needed, which also are beneficial for global warming since CH_4 is a strong greenhouse gas. CO_2 capture and storage from biogas through the separation systems also contribute to negative CO_2 emission although CO_2 emission from biogas does not increase the CO_2 concentration in the atmosphere. Furthermore, natural gas is

Abbreviations: AMP, 2-amino-2-methyl-1-propanol; BPR, back pressure regulator; CP, circulation pump; DEA, diethanolamine; GCP, geared circulation pump; MDEA, *N*-methyldiethanolamine; MEA, monoethanolamine; MFC, mass flow controller; PP, polypropylene; RM, rotameter; VP, vacuum pump

* Corresponding authors.
E-mail addresses: yipark@krict.re.kr (Y.-I. Park), zeolite@krict.re.kr (P.S. Lee).

http://dx.doi.org/10.1016/j.ces.2016.08.018
0009-2509/

used to generate the energy at decentralized sites, and capture of CO_2 there is not still economically favorable. Upgrading of biogas can solve this problem by capture of carbon dioxide at biogas production cite, even though the major necessity to upgrade biogas is to meet the requirements for gas grids and fuel.

A number of methods have been investigated for the separation of CO_2 and CH_4, including chemical and physical absorption, adsorption, cryogenic refrigeration, and membrane technology (Al-Marzouqi et al., 2009; Jeon and Lee, 2015; Mansourizadeh et al., 2010; Shannon et al., 2011; Yuan et al., 2013). Among these, chemical absorption using monoethanolamine (MEA) has been widely studied as a proven and commercialized approach (Faiz et al., 2011; Paul et al., 2007; Rongwong et al., 2013; Shirazian et al., 2012). However, the extensive use of this process in industry has been limited by its high energy consumption, large system spaces, and operational limitations, such as flooding, entrainment, and foaming (Atchariyawut et al., 2007; Ghasem et al., 2012). Recently, membrane-based separations have become popular alternative methods as they have the potential to greatly improve process energy efficiency. However, low gas flux and CH_4 loss must still be overcome for the application of such processes in biogas separation (Simons et al., 2009). Furthermore, additional treatments to remove impurities present in biogas must be performed before contact with the membranes. However, employing a membrane contactor is beneficial for both the absorption process and the membrane technology. The use of a porous or dense membrane in the membrane contactor serves as a boundary to separate the liquid and gas phases, with the differences in absorption between gas mixtures and liquid absorbents determining the separation performance. This separation method has a number of advantages over conventional absorption processes because it provides high contact areas, compact configuration, and easy scale-up. Furthermore, this technique can work effectively using a biogas feed without pretreatment, which is a prerequisite of most membrane technologies (Boributh et al., 2012; Lu et al., 2009; Lv et al., 2010).

Since the chemical and physical absorbents in membrane contractors play an important role in the separation performances of gaseous mixtures, a number of studies have been carried out focusing on these factors. In the case of chemical absorbents, alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and mixed aqueous solvents were demonstrated to exhibit high CO_2 absorption capacities and absorption rates (Sema et al., 2012). CO_2 absorption in polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) hollow fiber membranes using MEA as a single absorbent has also been reported, with MDEA, AMP, and DEA being used individually for CO_2 removal (Lu et al., 2009). An absorbent mixture of piperazine and 2-amino-2-methyl-1-propanol (AMP) has also been tested for CO_2 removal (Lin et al., 2009), along with physical absorbents such as water, propylene carbonate, and methanol. Boributh et al. (2011) built a mathematical model for CO_2 absorption using water as a physical absorbent, and reported its wetting ratio, absorption flux, and mass transfer coefficient. Marzouk et al. later demonstrated that physical absorbents worked attractively at high gas pressure (50 bar g) (Marzouk et al., 2010). In addition, Yan et al. (2014) compared the CO_2 absorption efficiency of a physical absorbent (i.e., water) with chemical absorbents (TEA, DEA, MEA, and potassium arginate) using a 2D mass transfer model, while Rangwala (1996) carried out a similar study using water, sodium hydroxide, and DEA as absorbents. Both studies concluded that other chemical absorbents exhibit superior performance over water because of the enhanced mass-transfer rate for CO_2 absorption; however, the majority of studies have not considered subsequent desorption processes. Such desorption processes are necessary to refresh and recycle absorbents into the absorption section of the membrane contactor system. However, using chemical absorbents, desorption results in a high energy consumption through heating, accompanied by a loss of absorbents through evaporation. In contrast, physical absorbents allow facile desorption and low capital costs, although their CO_2 absorption efficiency is low. For example, the inexpensive polypropylene (PP) can be selected as a membrane material, which would not be possible for many chemical absorbents due to reactivity of their amine solutions (Li and Chen, 2005). Considering that both types of absorbent have their individual pros and cons, the choice of an appropriate absorbent based on the targeted application is important for the construction of membrane contactor setups.

For biogas separation, both chemical and physical absorbents have been studied and their feasibility examined. Atchariyawut et al. (2007) investigated the potential of CO_2/CH_4 separation using a membrane contactor with chemical absorbents, and found that there was no significant CH_4 loss during the operation, which resulted in a CH_4 recovery of $\sim$100%. Moreover, Vogler et al. (2013) reported CO_2/CH_4 separation using a Liqui-Cel® membrane with water as the absorbent, purifying biogas to a methane purity of $>$98 vol%. However, the majority of studies focused on CO_2 flux and CO_2 rejection, with results related to CH_4 retention and purity being generally ignored. Indeed, results obtained from single absorption processes using membrane contactors were often discussed, but details regarding performance changes in the desorption process were generally lacking. We believe that such studies are also essential to evaluate the potential of a membrane contactor for biogas upgrading.

Motivated by this, we developed a PP hollow fiber membrane contactor equipped with both absorption and desorption modules for biogas upgrading, with the ultimate goal of application in vehicle fuel production (CH_4 purity $>$95%). We selected water as the physical absorbent, as it is capable of desorbing CO_2 simply by depressurizationa. Other physical absorbents such as methanol(Rectisol process), proprylene carbonate (Fluor solvent), and polyethylene glycol(Selexol) were not considered in this study since they have either high vapor pressure causing evaporation loss or low surface tension resulting in membrane wetting (Dindore et al., 2004). The effects of membrane modules (the number of modules and their connections) and operating conditions (pressure, flow rate, and operation stability) on the membrane contactor will be investigated. In particular, CH_4 recovery and CH_4 purity in the retentate will be carefully measured along with CO_2 flux to evaluate the applicability for renewable fuel processing. Operation stabilities in membrane contactors are also presented and discussed.

2. Experimental

2.1. Hollow fiber membranes and modules

Polypropylene (PP) hollow fiber membrane modules for absorption (1″) and desorption (2″) were provided by SepraTek Inc. (Daejeon, Korea). The specifications of the membrane and module are summarized in Table 1. The outer and inner diameters of the membrane were 880 μm and 450 μm, respectively, and the thickness was 215 μm. The absorption and desorption modules were composed of 200 and 600 fibers per module, respectively.

2.2. Membrane characterization

Single gas permeation tests were carried out to investigate the permeation properties of the PP hollow membrane on the membrane contactor. Pure CH_4 and CO_2 gases were used and were flowed into the bore side of the membrane. With a pressure difference of 0.3 bar, the permeation flow was measured using a bubble flow meter at 25 °C. The CO_2/CH_4 permselectivity was calculated from the ratio of the CO_2 and CH_4 permeances.