Journal of Membrane Science 392–393 (2012) 38–47

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

Simultaneous absorption of CO_2 and H_2S from biogas by capillary membrane contactor

Wichitpan Rongwong[a], Somnuk Boributh[a], Suttichai Assabumrungrat[b], Navadol Laosiripojana[c], Ratana Jiraratananon[a,*]

[a] Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[b] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[c] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

ARTICLE INFO

Article history:
Received 9 September 2011
Received in revised form 8 November 2011
Accepted 30 November 2011
Available online 9 December 2011

Keywords:
Carbon dioxide
Hydrogen sulfide
Mass transfer resistance
Membrane contactor
Simultaneous absorption

ABSTRACT

This work presents the study on the simultaneous absorption of H_2S and CO_2 from biogas using a capillary membrane contactor. The synthetic biogas contained 250–1000 ppm H_2S, 20–40% CO_2 and CH_4. The absorbents used were water and monoethanolamine (MEA) solution. The effects of liquid and gas velocities, gas composition, on the absorption performance and selectivity of H_2S were investigated together with the detailed analysis of the mass transfer resistances of the membrane contactor system.

The use of MEA solution gave much higher absorption fluxes of both CO_2 and H_2S compared to water. The absorption flux of H_2S significantly increased with increasing gas flow rate and slightly increased with liquid velocity and MEA concentration, while the absorption flux of CO_2 moderately increased with liquid velocity and was highly enhanced with increasing MEA concentration. The increase in CO_2 concentration obviously decreased the H_2S flux. The results of H_2S selectivity and the mass transfer resistance analysis of the non-wetted mode showed that the gas phase resistance played the important role on the mass transfer of H_2S. The opposite was found for the mass transfer of CO_2, i.e., the liquid phase resistance controlled the mass transfer. For the partially wetted mode, the wetted membrane resistance controlled the CO_2 absorption. On the contrary, for H_2S absorption, the wetted membrane resistance was insignificant and the gas phase resistance controlled the mass transfer. The observation of CO_2 and H_2S flux for a period of 6 h in order to investigate the effect of membrane wetting showed that the CO_2 flux dropped approximately 7.6%, while change of H_2S flux was negligible.

1. Introduction

Nowadays, the development of the alternative energy as well as the environmental friendly processes have been extensively studied, because of the increasing demand for energy and the concerns associated with the use of fossil fuels due to the continuously increase in price and environmental problems. Biogas is one of the alternative energy, which appears to be a potential candidate to replace fossil fuels. The physical and chemical properties of the biogas are similar to those of natural gas. Therefore, biogas can replace natural gas for all applications, especially as the vehicle fuel of which the demand has significantly increased in the past decades. Biogas can be produced during anaerobic degradation of organic materials from many sources such as weeds, woods, animal farm, and sewage or agro-food sludge. The main constituents of biogas are methane (CH_4), carbon dioxide (CO_2) and trace of hydrogen sulfide (H_2S). The constituents depend on the source's compositions. For example, biogas from sewage digesters usually contains 61–65% methane and 36–38% carbon dioxide, trace of hydrogen sulfide and saturated water were also detected [1].

CO_2 is a bulk contaminant in biogas. CO_2 content must be reduced in order to achieve higher heating value of biogas by increasing the volume of methane. Moreover, due to its acidic character, the presence of CO_2 leads to corrosion in equipments. H_2S, which is found in the low range about 10–500 ppm, is one of the most harmful pollutants. It must be removed before the transmission or consumption because it is harmful to health and can severely corrode the equipments. Furthermore, the combustion of H_2S produces sulfur dioxide (SO_2) which can react with water in the atmosphere leading to acid rain problem. Therefore, CO_2 and H_2S in biogas have to be removed before use depending on the applications. In the case of using biogas as the vehicle fuel or NGV (Natural Gas for Vehicle), CO_2 and H_2S must be lower than 4% and 15 ppm, respectively [2].

There are varieties of technologies for H_2S and CO_2 removal from biogas, such as absorption, adsorption, cryogenic process and

* Corresponding author. Tel.: +66 2470 9222; fax: +66 2428 3534.
E-mail address: ratana.jir@kmutt.ac.th (R. Jiraratananon).

0376-7388/$ – see front matter
doi:10.1016/j.memsci.2011.11.050

membrane processes. The most widely common method is chemical absorption in conventional contactors such as packed towers, bubble columns, and spray columns. However, these conventional equipments are not easy to operate because of many drawbacks and operational limitations such as flooding, foaming, entraining, channeling, high capital and operating costs.

An alternative technology which can overcome the disadvantages of the conventional contactors is a membrane contactor. The membrane contactor is a hybrid process that combines the conventional technique of the gas absorption into an absorbent and a membrane separation module as a mass transfer contactor. Membrane contactor has become one of the research focuses for decades because of its several advantages over the conventional processes, such as, the specific surface area of the membrane contactor is typically very high 500–5000 m^2/m^3 compared to 200–500 m^2/m^3 in conventional contactors [3]. The membrane contactor is also flexible to be scaled up, and is easy to operate because of the independent gas and liquid flow rates, resulting in no flooding and foaming [4].

However, the membrane contactor also has its disadvantages. The membrane introduces the resistance which is not found in the mass transfer in the conventional contactors. Moreover, hydrophobic membranes used in the membrane contactor should be kept in a dry mode in order to achieve high flux. In practice, the absorbents could wet the hydrophobic membranes by penetrating into the membrane pores. The topic of membrane wetting has been widely discussed in the literature [5,6]. Wang et al. [7] found that if the membrane pores were only 5% wetted, the reduction of the overall mass transfer coefficient may reach 20%. To prevent the membrane wetting, the operating pressure is kept below the critical value known as the penetration pressure and the high surface tension absorbent is selected.

Most studies on the application of the membrane contactors for gas absorption have focused on separation of CO_2 from flue gases by using N_2 or air as the makeup (CO_2: 15–20%v/v) [6,8] and the separation of CO_2 from synthetic natural gas using CH_4 as the makeup (CO_2: 9.5–20%v/v) [9,10]. The common absorbents used in these studies are water, sodium hydroxide and alkanolamine solutions. There are few published works on simultaneous absorption of CO_2 and H_2S. Mandal and Banyopadhyay [11] and Mandal et al. [12] investigated the simultaneous removal of CO_2 and H_2S by wetted wall column using amine solutions. The selective removal of H_2S from CO_2 and N_2 (CO_2 20–25%v/v and H_2S 1157 ppm) by hollow fiber membrane (HFM) was investigated by Wang et al. [13]. Mathematical models were proposed [14,15] to predict the performance of HFM contactor for simultaneous absorption of CO_2 and H_2S. The developed models were validated with the published data for CO_2 absorption only [7,9,16] due to the lack of the experimental data for H_2S absorption. Recently, Marzouk et al. [17] reported the experimental data on the removal of H_2S from pressurized H_2S–CH_4 gas mixture (2% H_2S) by HFM contactor. These studies [14,15,17] presented the results as the CO_2 and H_2S recovery, the concentration profile, flux and selectivity, but, do not include the analysis of mass transfer of the system. In a more recent work, Hedayat et al. [18] reported the experimental data of simultaneous absorption of CO_2 ad H_2S from natural gas (H_2S: 2400 ppm and CO_2: 6%v/v) by different alkanolamines, using polyvinyledene fluoride (PVDF) and polysulfone HFM contactors. The authors concluded that with the presence of H_2S, the liquid side mass transfer was negligible while the gas phase resistance was substantial. However, the values of the individual mass transfer resistances and the effect of membrane wetting were not reported.

In Thailand, biogas is widely produced throughout the country. It is the interest of the PTT (Thailand) Plc., the only supplier of NGV, to use biogas as another raw material for NGV. In this work, we report the experimental study on the use of capillary membrane contactor for simultaneous removal of CO_2 and H_2S from synthetic biogas using pure water and monoethanolamine (MEA) as absorbents. The effects of important operating parameters, i.e., liquid velocity, gas flow rate, gas composition, and MEA concentration on the absorption performance were investigated. Detailed analysis of the mass transfer resistances of the membrane contactor system based on the resistance-in-series model, for simultaneous absorption of CO_2 and H_2S with MEA, including the membrane wetting are also reported for the first time. The results of this work are expected to provide a better understanding on the simultaneous removal of CO_2 and H_2S.

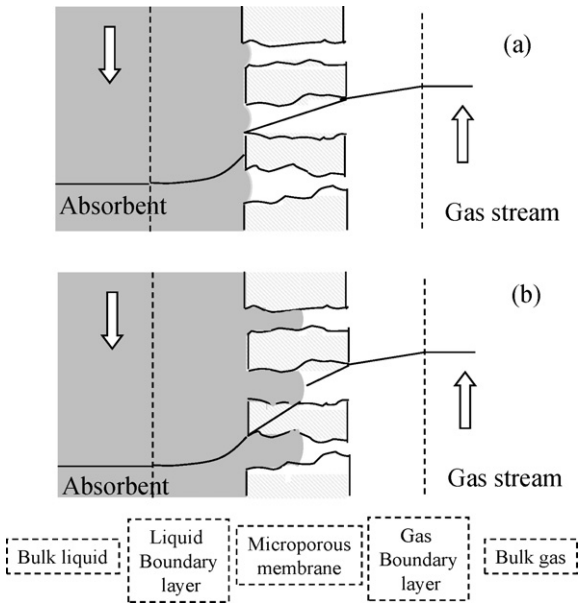

Fig. 1. Schematic drawing of mass transfer regions and resistance-in-series for membrane contactor: (a) non-wetted and (b) partially wetted.

2. Theory

2.1. Mass transfer in capillary gas–liquid membrane contactor

The resistance-in-series model has been widely applied to describe the mass transfer mechanism in the gas–liquid membrane contacting process. Fig. 1a illustrates the mass transport of the interested gas for a non-wetted mode. The mass transfer occurs in 3 steps, i.e., (1) diffusion from the bulk gas phase to the outer surface of the membrane, (2) diffusion through the membrane pores and (3) dissolution into the liquid absorbent. For the liquid flow in the tube side and the gas flow in the shell side, the resistance-in-series model for non-wetted mode including gas, membrane and liquid phase resistances can be expressed as Eq. (1) and for a partially wetted mode in which the wetted membrane resistance is included, the resistance-in-series model can be written as Eq. (2).

$$\frac{1}{K_G d_i} = \frac{1}{HEk_L^0 d_i} + \frac{RT}{k_M d_{\ln}} + \frac{RT}{k_G d_o} \quad (1)$$

$$\frac{1}{K_G d_{\text{int}}} = \frac{1}{HEk_L^0 d_i} + \frac{1}{HEk'_M d'_{\ln}} + \frac{RT}{k_M d_{\ln}} + \frac{RT}{k_G d_o} \quad (2)$$

where K_G is the overall mass transfer coefficient based on gas phase (mol/m^2 s atm), k_G, k_M, k'_M and k_L^0 are the individual mass transfer coefficients of gas, non-wetted membrane, wetted membrane and liquid phase (physical absorption) (m/s), d_i, d_o, $d_{\ln}$, d_{int} are the inner, outer, logarithmic mean and interfacial diameters of the capillaries (m), respectively. H represents Henry's constant (mol/m^3 atm). E is the enhancement factor and R is gas constant (m^3 atm/mol K).