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Performance of polydimethylsiloxane membrane contactor process for selective hydrogen sulfide removal from biogas

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ABSTRACT

H_2S in biogas affects the co-generation performance adversely by corroding some critical components within the engine and it has to be removed in order to improve the biogas quality. This work presents the use of polydimethylsiloxane (PDMS) membrane contactor for selective removal of H_2S from the biogas. Experiments were carried out to evaluate the effects of different pH of absorption liquid, biogas flowrate and temperature on the absorption performances. The results revealed that at the lowest loading rate (91 mg $H_2S/m^2{\cdot}h$) more than 98% H_2S and 59% CO_2 absorption efficiencies were achieved. The CH_4 content in the treated gas increased from 60 to 80% with nearly 5% CH_4 loss. Increasing the pH (7–10) and loading rate (91–355 mg $H_2S/m^2{\cdot}h$) enhanced the H_2S absorption capacity, and the maximum H_2S/CO_2 and H_2S/CH_4 selectivity factors were 2.5 and 58, respectively. Temperature played a key role in the process and lower temperature was beneficial for intensifying H_2S absorption performance. The highest H_2S fluxes at pH 10 and 7 were 3.4 $g/m^2{\cdot}d$ and 1.8 $g/m^2{\cdot}d$ with overall mass transfer coefficients of 6.91×10^{-6} and 4.99×10^{-6} m/s, respectively. The results showed that moderately high H_2S fluxes with low CH_4 loss may be achieved by using a robust and cost-effective membrane based absorption process for desulfurization of biogas. A tubular PDMS membrane contactor was tested for the first time to remove H_2S from biogas under slightly alkaline conditions and the suggested process could be a promising for real scale applications.

1. Introduction

Biogas is a renewable and sustainable energy source produced by anaerobic fermentation of organic matters. The raw biogas consists mainly, 40–75% of CH_4, 15–60% of CO_2 and minor constituents such as H_2S and NH_3 (Krich et al., 2005). The large volume of CO_2 reduces the heating value of the gas, increasing compression and transportation costs and limiting economic feasibility to use (Marzouk et al., 2012; Poloncarzova et al., 2011). Besides, H_2S is the most common contaminant which restricts the direct use of raw biogas as fuel, because it can accelerate the corrosion of utilities and reduce lifespan of the pipe work and other installations (Syed et al., 2006; Tang et al., 2009). The concentration of H_2S in biogas can range from 0.1 to 2% v/v (1000–20,000 ppmv) (Fortuny et al., 2011), whereas the manufacturers of combined heat and power (CHP) production units recommend limiting values between 0.01 and 0.03% v/v (100–300 ppmv) to control corrosion problem in piping systems and equipment (Ramos and Fdz-Polanco, 2014). Therefore, by applying different technologies H_2S concentration has to be controlled in order to prevent the damage and fulfill the quality standards required according to the final use of the biogas. For the removal of H_2S from the biogas, various processes are in use such as, physical and chemical absorption in aqueous solutions, physical adsorption on solid adsorbents and conversion to low solubility metal sulfides (Horikawa et al., 2004; Osorio and Torres, 2009). Most of the earlier studies were conducted on water scrubbing process (Kapdi et al., 2005; Rasi et al., 2008), which is a simple and cheap process involving the use of pressurized water as an absorbing solution. However, the use of pressurized water as an absorbing solution for CO_2 and H_2S has several drawbacks, such as high energy consumption, large equipment size requirement and high corrosion rate. Compared to water scrubbing process, chemical absorption seems to be a better alternative due to reduced energy consumption as the process can be operated at lower pressure with less water requirement. The

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chemical absorption process runs rapidly, thus the retention time in the reactor becomes shorter and the volume requirement is smaller. Consequently, it has a widespread usage in industrial applications due to the aforementioned advantages (Palmeri et al., 2008). However, the conventional chemical absorption process also has some significant problems such as flooding, foaming, entraining, channeling, high capital and operating costs (Faiz and Al-Marzouqi, 2009), which stimulated the researchers to develop better technology to remove H_2S from the biogas. The other commonly used technology is membrane purification processes, which presents a number of advantages in terms of low energy consumption, low capital investment, simple and easy operation and compact equipment (Baker et al., 1998). Regarding the economic aspects, the membrane gas purification is beneficial at low gas flow rate and high carbon dioxide concentration (Babcock et al., 1988). However, the need to minimize the cost and to enhance the efficiency of biogas treatment leads to a continuous investigation for novel and more effective technologies. Recently developed polymeric membrane separation process seems to be commercially competitive with the conventional chemical H_2S and CO_2 absorbing processes (Dolejš et al., 2014). Till now, various types of membranes such as, microporous and nonporous hydrophobic membranes have been studied for gas to liquid transfer (Attaway et al., 2001). Porous membranes are preferable, due to their excellent mass transfer characteristics, but the performance of membrane declines when it is used for long operational periods, owing to penetration of water through the pores of wetted membranes (Reij and Hartmans, 1996). By selecting non-porous dense polymeric membranes, pore blocking, leaking and pore wetting problems can be eliminated, which makes the dense polymeric membranes popular in biogas purification applications. Although the use of non-porous polymeric membrane has several advantages, more studies are needed because the process performance may be limited by the reduced mass transfer compared to porous membranes. Polymeric membranes can be classified as glassy and rubbery membranes. Solubility often dominates diffusion characteristics for absorption in rubbery polymers, while absorption in glassy polymers is controlled by the size of the molecule and diffusion coefficient. Hence glassy membranes have much higher selectivity for CO_2/CH_4 compared to H_2S/CH_4, because CO_2 is slightly smaller than CH_4 and has strong affinity to the polymeric material. Therefore, a membrane having high H_2S/CH_4 and moderate CO_2/CH_4 selectivity, a rubbery polymer such as PDMS seems more suitable for biogas cleaning. After selective removal of H_2S gas through the membrane, the reaction between H_2S and alkaline solution is given in Eqs. (1)–(3).

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \quad (1)$$

$$H_2S_{aq} + OH^- \leftrightarrow HS^- + H_2O \quad (pKa = 7.0) \quad (2)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (pKa = 12.9) \quad (3)$$

They have both acidic behavior, but the concentration of CO_2 is much higher than that of H_2S in biogas. Therefore, at alkaline conditions along with desulfurization absorption of CO_2 takes place according to Eqs. (4)–(7). The pKa values of Eqs. (2) and (6) are comparable, thus the absorption of H_2S and CO_2 proceeds at similar pH values. H_2S absorption occurs faster than CO_2 absorption because CO_2 goes through a slow hydrolyzing step (Kohl and Nielsen, 1997).

$$CO_{2_{gas}} \leftrightarrow CO_{2_{aq}} \quad (4)$$

$$CO_{2_{aq}} + H_2O \leftrightarrow H_2CO_{3_{aq}} \quad (5)$$

$$CO_{2_{aq}} + OH^- \leftrightarrow HCO_3^- + H_2O \quad (pKa = 6.4) \quad (6)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (pKa = 10.3) \quad (7)$$

In this study, the performance of tubular PDMS gas diffusion membrane contactor was tested for selective removal of H_2S and partially absorption of CO_2 from biogas for the first time under varying operational conditions. In order to increase the mass transfer of H_2S and CO_2 through the membrane and increase their selective removal, a slightly alkaline solution was used as absorbent on the liquid side of the tubular PDMS membrane. From alkaline compounds NaOH had been chosen due to its low cost and rapid reaction rate with the dissolved H_2S. In addition to using a slightly alkaline solution, the process operated at atmospheric pressure (1 bar) and ambient room temperature in order to decrease the operational cost of desulfurization.

2. Materials and methods

2.1. Materials

A synthetic gas mixture (Hat Industrial Gases PLC, KOCAELI) consisting of H_2S (10,000 ppmv, which is 1% of the biogas), CO_2 (39%) and CH_4 (60%) and simulating a typical biogas was used in the experiments. Tap water was used as absorption solution and its pH was adjusted to 7, 8.5 and 10 with 1 M NaOH solution using a pH transmitter and a dosing pump (Seko, PR 40/Q). Commercially available PDMS membrane (Silicone tube) was used in the study. The PDMS membrane was manufactured by (EUROFLEX GmbH, Germany) and its properties is summarized in Table 1.

2.2. Experimental methods

The bench scale experimental setup and the gas–liquid membrane contactor used are shown in Fig. 1.

The absorption vessel is a pyrex glass cylinder of 120 mm wide and 200 mm high, the total volume and the liquid volume of the reactor (i.e., excluding the membrane volume) were 1.69 L and 1.5 L, respectively. In the experiments, the synthetic biogas was continuously fed to the tubular membrane placed folded into the absorption vessel filled with tap water. The inflow biogas was controlled by a gas flow gauge at different flowrates and counted by gas counters (MGC, Ritter) before entering and after exiting the tubular membrane. The absorption solution was continuously stirred with a magnetic stirrer at 550 rpm to achieve complete mixing. During each experiment the vessel was completely filled with liquid to minimize volatilization of sulfur compounds. After closing the vessel, the solution was flushed with N_2 to remove oxygen.

The temperature of the absorption solution was controlled at different levels with an electrical heating blanket wrapped around the glass absorption vessel to evaluate the effect of temperature on removal efficiency and selectivity. The experiments were carried out at different gas flowrates, temperatures and pH values of absorption solution to determine the optimum CO_2 and H_2S fluxes (Table 2). Each test lasted about 4 h and biogas samples were taken from the exit once every hour and analyzed. The average values were used in evaluating the system performance.

Table 1
Characteristics of PDMS membrane.

Number of module	1
Effective length, m	3
Thickness, mm	1
Inner diameter, mm	7
Outer diameter, mm	9
Internal area (A_i), m^2	0.0659
External area (A_e), m^2	0.0848