Biogas desulfurization using a gas-liquid PDMS membrane contactor under slightly alkaline conditions: Optimization of Operational Parameters

E. Tilahun[1], E. Sahinkaya[2,] B. Calli[1]

[1]Marmara University, Environmental Engineering Department, Istanbul, Kadikoy, 34722, Turkey
[2]Istanbul Medeniyet University, Bioengineering Department, Istanbul, Uskudar, 34700, Turkey
Corresponding author email: ebroti@mail.com

Abstract

Biogas is a suitable alternative renewable energy source if unwanted impurities are removed to avoid corrosion of the engine. This work presents the selective removal of H_2S from biogas using a poly-dimethyl siloxane (PDMS) membrane contactor and a liquid media containing 1 N sodium hydroxide solution. Effects of the gas retention time (gas flow rate), liquid pH and membrane thickness on the extent of H_2S removal and the selectivity were investigated. The experimental results indicated that increasing the gas retention time or decreasing the membrane thickness linearly increases the permeation of the compounds. An efficiency of 99.3% H_2S removal and 56% CO_2 removal was achieved at gas retention time greater than 10 min and membrane thickness of 1 mm. The biogas was enriched up to 87% CH_4. The results also revealed that the PDMS membrane contactor used was very efficient for the selective removal of H_2S particularly at low retention times (5.7 min). When the membrane thickness increased from 1.0 to 2.0 mm, the removal of both CO_2 and H_2S decreased, but the decrease in CO_2 removal was more severe and therefore the H_2S selectivity boosted. The maximum selectivity observed was 2.6 and 40 for H_2S/CO_2 and H_2S/CH_4, respectively. Finally, the gas-liquid PDMS membrane contactor used in this study is concluded as a cheap and easy-to-operate system for desulfurization of biogas.

Keywords: Biogas, desulfurization, gas retention time, membrane thickness.

1. INTRODUCTION

Biogas produced from anaerobic digestion is one of the most favorable bioenergy sources that plays a vital role in the emerging market of renewable energy, because of its great substrate flexibility and energy yields per acreage [1]. Biogas composition mainly depends on the used organic substance and the digestion conditions and it largely consists of methane (CH_4) and carbon dioxide (CO_2) together with other minor components, such as hydrogen sulfide (H_2S), ammonia (NH_3). Generally, biogas can be used directly to generate power and heat, but the high CO_2 content reduces its calorific value and also increases the compression and transportation costs which can limits its use at the point of production [2]. Whereas, the presence of H_2S can cause critical problems such as; toxicity, offensive stench, corrosion of engine components and can have adverse environmental effects due to the sulfur oxides generated during combustion [2-4]. Thus, reducing H_2S contents in the biogas is obligatory to increase the quality of the gas and protect combustion equipment from corrosion. Numerous technologies for biogas cleaning have been developed to date that includes: physical and chemical absorption, adsorption, membrane separation and biological methods [5-6]. However, studies that focused on the combined and continuous operation are limited. Hence, researches on biogas cleaning to further improve the overall efficiency, reducing investment and operation costs are needed. Recently, a combined membrane absorption processes have received much attention due to its advantage in energy efficiency, simple construction, easy scale up, operational flexibility, and reduced environmental impact [7-8]. In the earlier studies semipermeable hydrophobic and microporous membranes type have been studied for gas to liquid transfer [9-10]. The advantage of porous membranes is their excellent mass transfer characteristics, while its performance decreased when the membrane used for long operational period, due to wetting problem [11]. This drawback can be eliminated by selecting non-porous membranes, which is highly permeable to acid gases and fully impermeable to the liquid phase. Furthermore, the nonporous membrane, particularly rubbery polymers, can enhance selectivity for H_2S over CO_2 and CH_4, since separation is mediated by diffusion through the polymeric membrane substrate. However, some studies described nonporous polymeric membrane cannot provide high amount of mass transfer compared to microporous membranes [12]. The motivation of this study is the selective absorption of H_2S from biogas to an aqueous hydroxide solution through PDMS membrane contactor. The principle of gas permeation in PDMS membrane is solubility and diffusivity differences of gas constituents. Here, H_2S is preferably diffused across the membrane and subsequently absorbed into a caustic solution. The reaction of H_2S is instantaneous, whereas CO_2 reacts at a finite rate. Thus, a selective removal of H_2S over CO_2 absorption is achieved, which would lead to the decreased consumption of the base. In the present study, optimal operating parameters such as retention time, membrane thickness, liquid pH and H_2S inlet loading were investigated.

2. MATERIALS and METHODS

2.1. Experimental set-up and operation

The experimental set-up was similar to that used by Tilahun et al. [13] (Fig. 1). The reactor was made of cylindrical Plexiglas (diameter 120 mm, height 200 mm) with a working volume of 1.5 L and it was totally filled with tap water to minimize the volatilization of the sulfur compounds, after closing the vessel the absorbing liquid was flushed with N_2 gas to remove the dissolved oxygen. A simulated gas mixture of methane (CH_4, 60%), carbon dioxide (CO_2, 39%) and hydrogen sulfide (H_2S, 1%) was used (Hat Industrial Gases PLC, Kocaeli, Turkey). The biogas flowrate was regulated by using mass flow controllers at the outlet of the gas cylinder and the cumulative volume of the gas measured by a milligas counters (MGC, Ritter). Subsequently, the gas was passed through the tubular membrane placed folded into the absorption liquid. The nonporous tubular polydimethylsiloxane (PDMS) membrane with 1mm thickness (7mm ID, 3m length) was purchased from EUROFLEX (GmbH, Germany) while the PDMS having thickness of 1.5mm and 2mm (7mm ID, 3m length) were bought from DEUTSCH & NEUMANN (GmbH, Berlin, Germany). Tap water was used as absorption liquid and its pH was adjusted to 10 with 1 N NaOH solution using a pH transmitter and a dosing pump (Seko, PR 40/Q). The absorption liquid was mixed with a magnetic stirrer at 550 rpm. The temperature of the liquid in the reactor was controlled at 20±1 using an electrical heating blanket externally wrapped around the glass vessel.

2.2. Analytical methods

The Sulfide concentration in the liquid media, i.e. permeate side of the membrane, was determined spectrometrically (WTW PhotoLab 6100VIS) following the method described by Cord-Ruwisch [14]. Samples were taken from the inlet and outlet of the membrane contactor to determine the concentrations of the biogas components (H_2S, CO_2 and CH_4) using a GC equipped with thermal conductivity detector and a stainless steel column (Restek MS-13X 45/60, 2.74 m length internal diameter of 2 mm). The temperatures of injection, column and detector were 150 ^oC, 40 ^oC and 150 ^oC, respectively. All samples were analyzed in triplicate and the averages were reported. When the H_2S concentration in the biogas was below the detection limit of the GC-TCD, a 2nd scrubber filled with 0.5% NaOH solution was used to absorb the H_2S before measuring the sulfide concentration spectrometrically as mentioned above. The detail of this system was described in our former paper [15]. During the operation, the concentration of dissolved oxygen (DO), conductivity and oxidation reduction potential (ORP) in the liquid phase were monitored online using a digital multimeter, (Multi 9430, WTW GmbH, Germany).

2.3. Calculations

In this study, the CO_2 or H_2S removal efficiencies (R) and CH_4 loss were calculated according to Eq. (1).

$$\mathrm{R}\ (\%) = \frac{\mathrm{Cin-Cout}}{\mathrm{Cin}} * 100 \qquad (1)$$

where, R - removal efficiency of CO_2 or H_2S, and CH_4 loss, C_{in} - the concentrations of biogas components entering into the tubular membrane, C_{out} - the concentrations of biogas components exiting from the tubular membrane. In gas purification processes the performance of the system can be indicated also by computing the selectivity factor. Selectivity of the polydimethylsiloxane (PDMS) membrane for H_2S may be defined as the tendency for the ratio of H_2S over CO_2 concentrations to be greater in the liquid phase than in the gas phase (Eq. 2). Likewise, the selectivity of H_2S over CH_4 was calculated according to Eq. (3).

$$\mathrm{S(H_2S/CO_2) = (xH_2S/xCO_2)/(yH_2S/yCO_2)} \qquad (2)$$

$$\mathrm{S(H_2S/CH_4) = (xH_2S/xCH_4)/(yH_2S/}y\mathrm{CH_4)} \qquad (3)$$

where, S is dimensionless which represents the selectivity factor, x - denotes the mole fraction of the biogas components absorbed in the liquid phase and y - denotes the mole fraction of the biogas components in the feed gas.

3. RESULTS and DISCUSSIONS

According to the experimental results the membrane contactor performance is quite good for the removal of both acid gases, particularly at high gas retention time. The influence of retention time and membrane thickness on the removal efficiency of the biogas components is shown in Table 1. Under all tested membrane thickness, almost complete H_2S removal had been found particularly at the highest retention time tested (19 min), which is safe to use in cogeneration units [16]. Whereas, decreasing the gas retention time to 5.7 min decreased the H_2S removal efficiency gradually to 62, 56 and 51% at membrane thickness of 1 mm, 1.5 mm and 2 mm, respectively. This indicates that reducing the retention time increases the amount of H_2S concentration in the retentate stream, thus resulting in lower efficiencies.

Table 1. The effects of operational parameters on the performance of the membrane contactor

Thickness (mm)	Retention time (min)	Gas removal (%)			Selectivity factor	
		H_2S	CO_2	CH_4	H_2S/CH_4	H_2S/CO_2
1.0	19.0	100	79.3	4.7	21.4	1.26
	10.4	99.3	56.4	3.4	28.8	1.76
	5.7	61.94	34.91	2.04	30.4	1.77
1.5	19.0	99.9	70.7	4.3	23.1	1.41
	10.4	98.8	45.0	2.9	34.5	2.20
	5.7	55.6	24.8	1.6	35.6	2.24
2.0	19.0	99.78	62.49	3.58	27.8	1.60
	10.4	98.34	37.81	2.5	39.3	2.50
	5.7	50.9	20.02	1.33	40.2	2.60

It should also be noted that decreasing the biogas retention time decreased the removal efficiency of the thickest membrane (2 mm), which was due to the limited diffusion rate of the gas and increased membrane resistance. Our result is in consistent with the findings of Marzouk et al. [2] and Al-Marzouqi et al. [12]. They reported that the H_2S removal efficiency decreased as the gas pressure and flow rate are increased. Similarly, for all thicknesses tested, the CO_2 removal efficiencies declined as the retention time decreased. For instance, when 1 mm thick tubing was used, the CO_2 removal efficiency dropped from 79 to 58% when the retention time decreased from 19 to 10.4 min, and further dropped to 35% when the retention time was 5.7 min (Table 1). Relatively the CH_4 permeance through dense non porous polymeric layers was the lowest because of its considerably low diffusivity through PDMS membrane and low solubility in the liquid media. Stern and Bhide [17] pointed out that H_2S is more permeable than CO_2 through PDMS by approximately a factor of 1.8, which is in consistent with our study. Thus the CH_4 content in the effluent stream increased along with the retention time and reached up to maximum 87% with only 5% loss when 1mm thick PDMS membrane was used. Karaszova et al. [18] reported the enrichment of CH_4 up to 95% when a thin hydrophilic composite membrane with a 33-µm thick membrane layer was used. As a conclusion, the H_2S removal increases when the thickness of the PDMS layer decreases. Upon further optimization, separation of H_2S from the biogas using PDMS membrane may offer a cheaper alternative in comparison with conventional methods.

As formerly reported, a reduction in gas retention time significantly decreased the CO_2 and CH_4 removal, while it has a marginal effect on the removal of H_2S up to the retention time of 10.4 min (Table 1). The H_2S removal efficiency decreased dramatically when the gas retention time dropped below 10.4 min, although its selectivity increased. This result is supported by other studies [19-21]. The higher the H_2S selectivity in the PDMS membrane contactor is due to the instantaneous reaction of H_2S with slightly alkaline aqueous solution and high solubility of sulfide in the slightly alkaline liquid media [22]. Freeman and Pinnau [23] noted that the gas selectivity in PDMS membrane is governed by the penetrant solubility. Chatterjee et al. [24] used cellulose acetate membrane to clean the biogas consisting of H_2S (6%), CO_2 (29%) and CH_4 (65%) at 10.1 bar pressure and reported that the H_2S/CH_4 selectivity factor was 19. This value was significantly lower than the value we found in this study which was about 40, especially at low gas retention times. Table 1 also reveals that, increasing the membrane thickness enhances the selectivity of H_2S, because the H_2S can diffuse relatively faster than the other gases as the membrane thickness increases. This finding is also supported by other studies [25-28]. The drawback of the PDMS membrane contactor we tested is that the gas removal efficiency is inversely proportional with the selectivity factor. Therefore, optimizing the system is crucial to have acceptable amount of H_2S in the effluent stream with minimal absorption of both CO_2 and CH_4.

Conclusions

Both the gas retention time and membrane thickness were found to be very effective on the process performance of PDMS membrane contactor tested for biogas desulfurization. Increased gas retention times resulted in higher H_2S removal efficiencies whereas increased membrane thicknesses decreased the efficiency. H_2S removal efficiencies higher than 99% were obtained when a gas retention time higher than 10 min and a membrane thickness of 1 mm were used. Low gas retention time (less than 10 min) and high membrane thickness increased the mass transfer resistance against CO_2, but showed a marginal influence on H_2S removal, hence resulted in a higher selectivity for H_2S removal. In addition, it was shown that the PDMS membrane submerged in slightly alkaline solution removed the H_2S from biogas without resulting in any noticeable CH_4 loss. The results indicated that the PDMS membrane contactor can be a promising alternative for selective removal of H_2S from biogas. However, further studies should be performed to address the influence of pH on the process performance and to optimize the operating conditions to reduce mass transfer resistance and alkaline consumption particularly at low gas retention times.

Acknowledgments

This study was financially supported by YTB (Presidency for Turks Abroad and Related Communities) and Marmara
University Scientific Research Committee BAPKO (Project No. FEN-C-DRP-070317-0109).

References

[1] Holm-Nielsen, J., Seadi, T.A., Oleskowicz-Popiel, P.: The future of anaerobic digestion and biogas utilization. Biores. Technol. 100 (22), 5478-5484 (2009)

[2] Marzouk, S.A.M., Al-Marzouqi, M.H., Teramoto, M., Abdullatif, N., Ismail, Z.M.: Simultaneous removal of CO_2 and H_2S from pressurized CO_2-H_2S-CH_4 gas mixture using hollow fiber membrane contactors. Sep. Purif. Technol. 86, 88–97 (2012)

[3] Syed, M., Soreanu, G., Falletta, P., Béland, M.: Removal of hydrogen sulfide from gas streams using biological processes - a review. Can. Biosyst. Eng. 48, 2.1–2.14 (2006)

[4] Poloncarzova, M., Vejrazka, J., Vesely, V., Izak, P.: Effective purification of biogas by a condensing-liquid membrane. Angew. Chem. Int. Ed. 50, 669–671 (2011)

[5] Ryckebosch, E., Drouillon, M., Vervaeren, H.: Review Techniques for transformation of biogas to biomethane. Biomass and Bioenerrgy 35, 1633-1645 (2011)

[6] Kasikamphaiboon, P., Chungsiriporn, J., Bunyakan, C., Wiyaratn, W.: Simultaneous removal of CO2 and H2S using MEA solution in a packed column absorber for biogas upgrading. Songklanakarin J. Sci. Technol. 35 (6), 683-691 (2013)

[7] Bhide, B.D., Voskericyan, A., Stern, S.A.: Hybrid processes for the removal of acid gases from natural gas. J. Membr. Sci. 140, 27–49 (1998)

[8] Sun, Q., Yan, H.J., Liu, L., Yu, Z., Yu, X.: Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilization. Renew. and Sustain. Ener. Rev. 51, 521–532 (2015)

[9] Freitos dos Santos, L.M., Hömmerich, U., Livingston, A.G.: Dichloroethane removal from gas streams by an extractive membrane bioreactor. Biotechnol. Prog. 11, 194 (1995)

[10] Attaway, H., Gooding, C.H., Schmidt, M.G.: Biodegradation of BTEX vapors in a silicone membrane bioreactor system. J. Ind. Microbiol. Biotechnol. 26, 316 (2001)

[11] Reij, M.W., Hartmans, S.: Propene removal from synthetic waste gas using a hollow-fibre membrane bioreactor. Appl. Microbiol. Biotechnol. 45, 730 (1996)

[12] Al-Marzouqi, M.H., Marzouk, S.A.M., El-Naas, M.H., Abdullatif, N.: CO_2 removal from CO_2-CH_4 gas mixture using different solvents and hollow fiber membranes. Ind. & Eng. Chem. Res. 48 (7), 3600–3605 (2009)

[13] Tilahun E., Bayrakdar A., Şahinkaya E., Çalli B.: Performance of polydimethylsiloxane membrane contactor process for selective hydrogen sulfide removal from biogas. Waste Manag. 61, 250-257 (2017)

[14] Cord-Ruwisch, R.: A quick method for the determination of dissolved and precipitated sulfides in cultures of sulfate-reducing bacteria. J. Microbiol. Meth. 4, 33-36 (1985)

[15] Bayrakdar, A., Tilahun, E., Calli, B.: Biogas desulfurization using autotrophic denitrification process. Appl. Microbiol. and biotechnol. 100, 939-948 (2016)

[16] Lens, P., Lens, P.N.L., Pol, L.H.: Environmental Technologies to Treat Sulfur Pollution: Principles and Engineering, IWA Publishing, (2000)

[17] Stern, S., Bhide, B.: Permeability of silicone polymers to ammonia and hydrogen sulfide. J. Appl. Polym. Sci. 38, 2131-2147 (1989)

[18] Karaszova, M., Vejrazˇka, J., Vesely´, V., Friess, K., Randova, A., Hejtmanek, V., Brabec, L., Izak, P.: A water-swollen thin film composite membrane for effective upgrading of raw biogas by methane. Sep. Purif. Technol. 89, 212–216 (2012)

[19] Bontozoglou, V., Karabelas, A.J.: Simultaneous absorption of hydrogen sulfide and carbon dioxide in sodium hydroxide solutions: experimental and numerical study of the performance of a short-time contactor. Ind. Eng. Chem. Res. 32, 165–172 (1993)

[20] Lu, J.G., Zheng, Y.F., He, D.L.: Selective absorption of H_2S from gas mixtures into aqueous solutions of blended amines of methyl diethanol amine and 2-tertiarybutylamino-2-ethoxyethanol in a packed column. Sep. Purif. Technol. 52, 209-217 (2006)

[21] Mandal, B.P., Biswas, A., Bandy opadhyay, S.: Selective absorption of H_2S from gas streams containing H_2S and CO_2 into aqueous solutions of N methyl diethanolamine and 2-amino-2-methyl-1-propanol. Sep. Purif. Technol. 35, 191-202 (2004)

[22] Keshavarz, P., Fathikalajahi, J., Ayatollahi, S.: Mathematical modeling of the simultaneous absorption of carbon dioxide and hydrogen sulfide in a hollow fiber membrane contactor. Sep. Purif. Technol. 63, 145-155 (2008)

[23] Freeman, B.D., Pinnau, I.: Separation of gases using solubility-selective polymer. Trends Polym. Sci. 5, 167 (1997)

[24] Chatterjee, G., Houde, A.A., Stern, S.A.: Poly (ether urethane) and poly (ether urethane urea) membranes with high H_2S/CH_4 selectivity. J. Membr. Sci. 135, 99-106 (1997)

[25] Nii, S., Takeuchi, H.: Gas absorption with membrane permeation – acid gas removal from flue gases by perm absorption method. Trans. I. Chem. E. 72, 21–26 (1994)

[26] Al-Saffar, H.B., Ozturk, B., Hughes, R.: A comparison of porous and nonporous gas–liquid membrane contactors for gas separation, Inst. Chem. Eng. 75, 685–692 (1997)

[27] Nguyen, P.T., Lasseuguette, E., Medina-Gonzalez, Y., Remigy, J.C., Roizard, D., Favre, E.: A dense membrane contactor for intensified CO_2 gas/liquid absorption in post-combustion capture. J. Membr. Sci. 377, 261-272 (2011)

[28] Cookney, J., Cartmell, E., Jefferson, B., Mc Adam, E.J.: Recovery of methane from anaerobic process effluent using polydimethylsiloxane membrane contactors. Water Sci.Technol. 65, 604–610 (2012)