REMOVAL OF HYDROGEN SULPHIDE CONTENT FROM BIOGAS BY ATOMIZING OF ALKALI SOLUTION

ÉVA MOLNÁR[a, *], DÓRA RIPPEL-PETHŐ[a], GÉZA HORVÁTH[a], JANKA BOBEK[a], RÓBERT BOCSI[a], ZOLTÁN HODAI[a]

ABSTRACT. Our energy requirements increased significant in the last decades. For this reason the potential utilization of renewable energy sources come into view. Biogas is a kind of renewable energy sources. Purification of raw biogas is essential prior to use. Mainly the hydrogen sulfide content of gas is very harmful. It can cause corrosion in compressors and engines. Furthermore sulfur dioxide and sulfur trioxide are formed from hydrogen sulfide due to combustion, which similarly corrosive present of water and toxic like hydrogen sulfide. We examined the hydrogen sulfide absorption from biogas model gas mixtures (CO_2, H_2S, N_2) based on alkali competitive chemisorption technology.

Keywords: biogas, chemisorption, sodium hydroxide, hydrogen sulphide, carbon dioxide

INTRODUCTION

Renewable energy produced by biogas technology has a great potential for growth to meet our future energy demands. Furthermore the technology is instrumental in waste management [1-2]. Biogas is generated from organic materials (fats, proteins, carbohydrates) by anaerobic metabolism [1-6]. The character of the used biomass and the applied operational conditions during anaerobic digestion determine the effective composition of the gas [6]. The raw biogas consists of mainly methane (CH_4) and carbon dioxide (CO_2). Additionally small amount of ammonia (NH_3), hydrogen sulfide (H_2S), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), water (H_2O), siloxanes and halogenated volatile organic compounds (VOCs) are present as impurities in biogas [2; 5-8]. Table 1 shows the chemical composition of raw biogas from different sources [7].

[a] *Institute of Chemical and Process Engineering, Department of Chemical Engineering Science, University of Pannonia, H-8200 Veszprém, Hungary.*
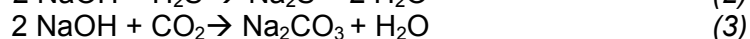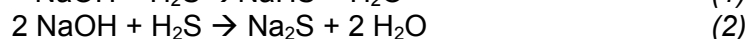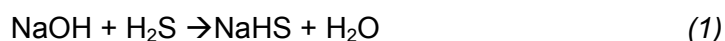[*] *Corresponding author: molnare@almos.uni-pannon.hu*

First of all H_2S content should be removed from the raw gas for many reasons. It can cause corrosion in compressors, gas storage and engines, in addition sulfur di- (SO_2) and trioxide (SO_3) are formed duo to combustion, which are similarly hazardous components like H_2S [1-2; 5-10].

Table 1. Chemical composition of raw biogas from different sources [7]

Component	Biogas factory	Sewer factory	Garbage landfill
CH_4 [% vol.]	60-70	55-65	45-55
CO_2 [% vol.]	30-40	35-45	30-40
N_2 [% vol.]	<1	<1	5-15
H_2S [ppmv]	10-2000	10-40	50-300
NH_3 [ppmv]	Trace		
CO [ppmv]	Trace		
O_2 [ppmv]	Trace		
VOCs [ppmv]	Trace		
H_2O [ppmv]	Trace		
Siloxanes [ppmv]	Trace		

Nowadays desulfurization of biogas can be carried out in many ways, for example biological desulphurization, adsorption on impregnated activated carbon, scrubbing in aqueous sodium hydroxide (NaOH) solution or in water (H_2O), addition of iron chloride ($FeCl_2$) to the bioreactor, membrane separation and so on [1-3; 6-10].

In this paper we deal with H_2S chemisorption in NaOH solution. The reaction time of CO_2 and H_2S with NaOH are different. CO_2 reacts with NaOH solution more slowly than H_2S [11-13]. Based on this fact the chemisorption in NaOH solution is able to work as a selective method for H_2S capture, if the sufficiently short contact time (<1s) is provided. The selectivity is important in order to minimize the consumption of chemicals. Besides it is necessary to ensure the large contact surface and intense contact of gas and absorbent in order that the operation achieves a relatively high efficiency (>50%) [12; 14-16]. During the process stable and undangerous compounds are formed (Equations 1-2-3), such as sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3) [15; 18].

$$NaOH + H_2S \rightarrow NaHS + H_2O \qquad (1)$$
$$2\ NaOH + H_2S \rightarrow Na_2S + 2\ H_2O \qquad (2)$$
$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (3)$$

The mentioned requirement for conditions of operation cannot be achieved by using a classical packed column chemisorber [12-16]. Therefore, spray method was applied for measurements. The objective of

this work was to study the feasibility of technique based on competitive chemisorption of H_2S and CO_2 in NaOH fine spray for biogas purification. If the efficiency of H_2S absorption achieves at least 50% while the alkali excess is less than 10mol NaOH/mol H_2S, we can say that the operation is economic. The primary purpose is to achieve this theoretical limit.

RESULTS AND DISCUSSION

Measurements were performed based on knowledge of general properties of biogas, results of pre-experiments and the application range of experimental apparatus. The experiences of pre-measurements were the follows: the optimal concentration of NaOH solution is influenced by contact time of gas and liquid phases; the molar alkali excess (>1mol NaOH/mol H_2S) must be provided to achieve effective operation; increase of absorbent volumetric flow rate causes improvement of efficiency of H_2S absorption, however it is limited by the quality of atomization (drop and surface formation) and by the difference between contact time and reaction time requirement.

For the measurements 4 different gas mixture were examined. The applied experimental conditions were: 4 bar pressure; 0,4Nm^3/h volumetric gas flow rate; 2% weigh NaOH absorbent concentration; 1-2-3-4-5cm^3/min volumetric flow rate of NaOH solution. The results of experiments are shown in Figures 1-3.
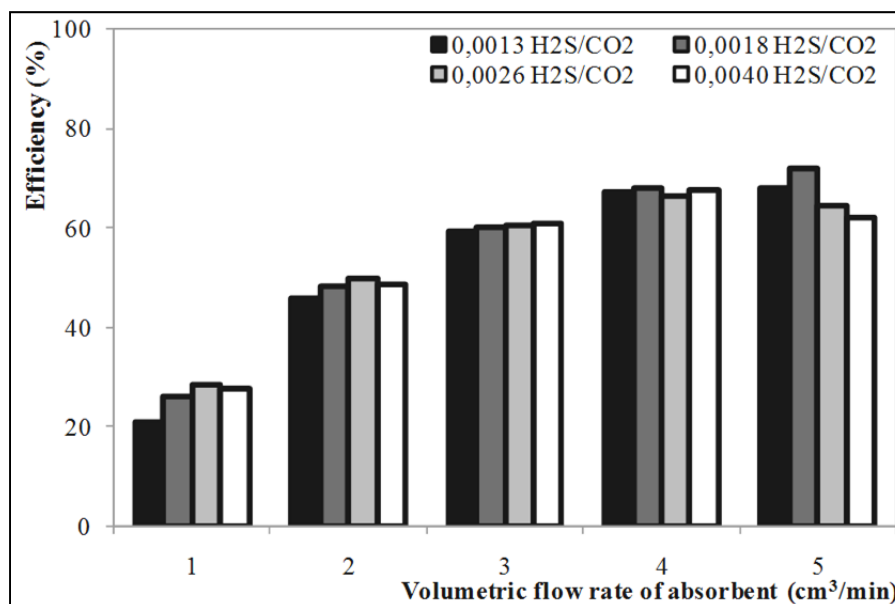

Figure 1. Efficiency of H_2S absorption as a function of absorbent flow rate

The efficiency of absorption system modified between 20 and 72%. Increase of NaOH solution volumetric flow rate caused improvement of efficiency of H_2S absorption, however raising from 4 to 5cm^3/min resulted in clear advance. Striking differences were not observed among the results of test series in Figure 1.

In order to see this process also by economic aspect, efficiency data were represented as a function of molar ratio of NaOH and H_2S (Figure 2).
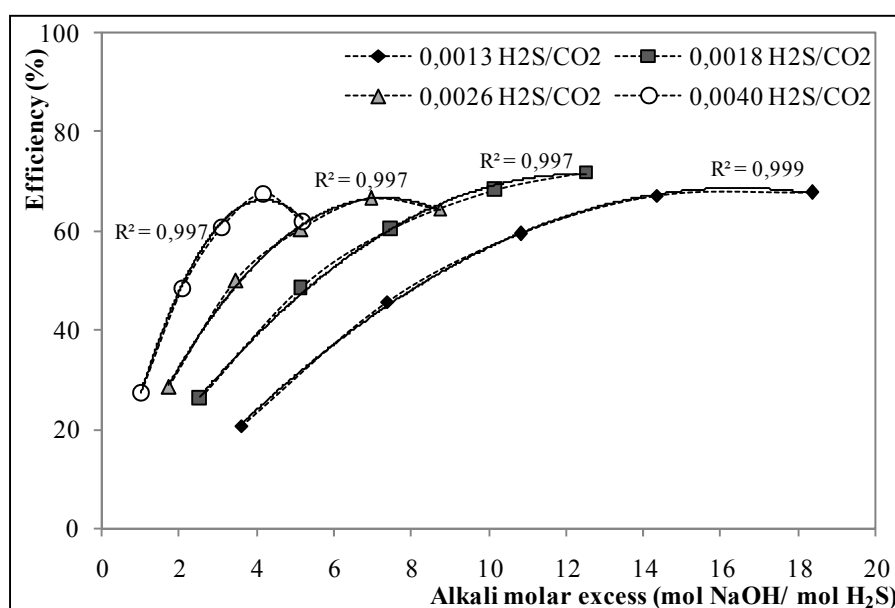

Figure 2. Efficiency of H_2S absorption as a function of alkali molar excess

The system was able to reach 50% efficiency less than 10mol NaOH/mol H_2S alkali excess by using every gas mixture in the tested range. Namely, according to our expectations the operation was economic and efficient. Second-order polynomial curves can fit on the measuring data ($R^2 \geq 0,997$). The efficiency of H_2S absorption improves with increase of H_2S/CO_2 volumetric ratio. This result can be explained by change of degree of competition. If H_2S/CO_2 volumetric ratio increases, in terms of H_2S the competition will be lower. Furthermore, the probability of encounter of H_2S and NaOH will raise with increase of H_2S/CO_2 ratio. In contrast at the same time the probability of encounter of CO_2 and NaOH will decrease.

Investigation of mass transfer as a function of alkali molar excess was performed as well (Figure 3). To calculate the transfer surface we had to determine the average size of droplets. We assumed Nukiyama-Tanasawa

equation (4 Equation) is capable for this task and the formed droplets are spherical. The number of drops is given by ratio of absorbent volumetric rate and volume of average drop. The transfer surface can be defined by multiplication of quantity of drops and surface of average droplet.

$$D_S = \frac{585}{U_r} \left(\frac{\sigma}{\rho_L} \right)^{0.5} + 597 \left[\frac{\mu_L}{(\sigma \rho_L)^{0.5}} \right]^{0.45} \left(1000 \frac{Q_L}{Q_G} \right)^{1.5} \qquad (4)$$

where σ=liquid surface tension (dyne/cm); ρ_L=liquid density (g/cm^3); μ_L=liquid viscosity (poise); Q_L=liquid volume flow rate (cm$_3$/sec); Q_G=gas volume flow rate (cm^3/sec); U_r=relative velocity between liquid and gas (cm/sec) [19].
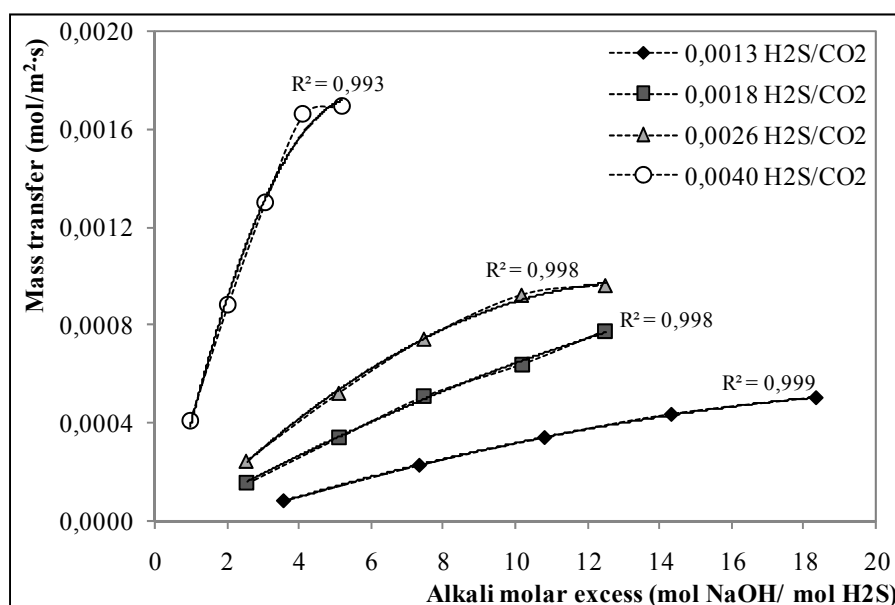

Figure 3. Change of mass transfer as a function of alkali excess

The highest gradient slope of the mass transfer curve was in the case of highest value of H_2S/CO_2 volumetric ratio as a function of NaOH/H_2S molar excess. By using second-order polynomial curves we can follow the change of data series ($R^2 \geq 0,993$). The results can be explained also by the change of degree of competition between H_2S and CO_2.

CONCLUSIONS

The described technique based on competitive chemisorption of H_2S and CO_2 in NaOH fine spray is feasible for biogas purification. The system was able to reach 50% efficiency less than 10mol NaOH/mol H_2S

alkali excess by using every gas mixture in the tested range. The results proves that increase of H_2S/CO_2 volumetric ratio have positive impact on the efficiency of H_2S absorption and the mass transfer of H_2S from gas to liquid phase. This experience can be explained by change of competition degree, and change of probability of encounter of CO_2 and H_2S with NaOH.

EXPERIMENTAL SECTION

Examinations were implemented by use three different compositions of gas mixture (Table 2).

Table 2. Composition of examined gas mixtures

Calculated N_2 content [% vol.]	Measured CO_2 content [% vol.]	Measured H_2S content [ppmv]	Volumetric ratio of H_2S/CO_2 [-]
62,9520	37,0	480	0,0013
60,9310	39,0	690	0,0018
60,9000	39,0	1000	0,0026
57,4304	42,4	1696	0,0040

Table 3 shows the parameters of operation.

Table 3. Experimental conditions

Pressure [bar]	4
Volumetric gas flow rate [Nm³/h]	0,4
Volumetric liquid flow rate [cm³/min[	1-2-3-4-5
Concentration of NaOH absorbent [% weigh]	2
Contact time [s]	0,23

The procedure is operated as follows. The NaOH solution is delivered by chemical feeder pump to the experimental appliance. The pre-mixed gas mixture gets into the apparatus from the gas cylinder. The liquid and gas stream encounter in reaction space immediately after the nozzle (Figure 4).
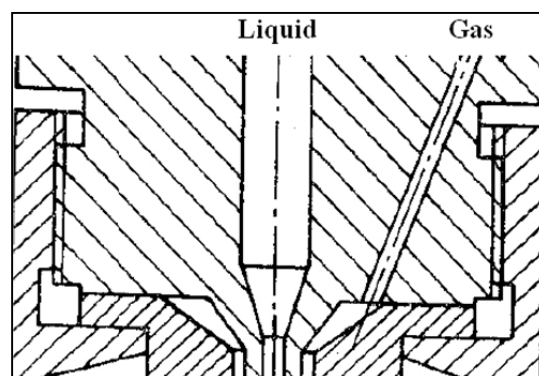

Figure 4. External mixed pneumatic liquid atomizer [20]

The kinetic energy of the gas phase covers the energy required for atomization. After intensive contact of two different phases the phase separation is done by applying mist eliminator. The spent absorbent should be removed periodically from the separation zone by using a tap. The CO_2 (% vol.) and H_2S (ppmv) content of output purified gas is sampled continuous by applying Dräger X-am 7000 gas analyzer [12]. This gas analyzer is able to measure the H_2S level by electrochemical sensor and the CO_2 level by infrared sensor [21].

ACKNOWLEDGMENTS

REFERENCES

1. N. Tippayawong, P. Thanompongchart, *Energy*, **2010**, 35, 4531.
2. L. Grazia, *Journal of Cleaner Production*, **2016**, 131, 364.
3. J. Krischan, A. Makaruk, M. Harasek, *Journal of Hazardous Materials*, **2012**, 215-216, 49.
4. S.S. Kapdi, V.K. Vijay, S.K. Rajesh, R. Prasad, *Renewable Energy*, **2005**, 30(8), 1195.
5. S. Qie, L. Hailong, Y. Jinying, L. Longcheng, Y. Zhixin, Y. Xinhai, *Renewable and Sustainable Energy Reviews*, **2015**, 51, 521.
6. E. Ryckebosh, M. Drouillon, H. Vervaeren, *Biomass and Bioenergy*, **2011**, 35, 1633.
7. J. Lasocki, K. Kolodziejczyk, A. Matuszewska, *Polish Journal of Environmental Studies*, **2015**, 24(3), 1427.
8. L. Dubois, D. Thomas, *Chemical Engineering Technology*, **2010**, 33(10), 1601.
9. D. Panza, V. Belgiorno, *Process Safety and Environmental Protection*, **2010**. 88, 420.
10. M. Pawlowska, M. Zdeb, A. Montusiewicz, M. Lebiocka, *Environmental Protection Engineering*, **2009**, 35(3), 157.
11. K. T. Hsieh, R. C. Aiken, *Chemical Engineering Commuication*, **1988**, 31, 367.
12. Á. Vágó, D. Rippel-Pethő, G. Horváth, I. Tóth, K. Oláh, *Hungarian Journal of Industrial Chemistry*, Veszprém, **2011**, 39 (2), 283.
13. J. B. Siemak, M. Gelbs, *SPE California Regional Meeting*, **1985**, 13650-MS
14. R. G. Heltz, Al L. Rocklin, *U.S. Patent,* US2747962 A, **1956**.
15. V. Srinivasan, R. C. Aiken, *Fuel Processing Technology*, **1988**, 19, 141.
16. É. Molnár, D. Rippel-Pethő, G. Horváth, Z. Hodai, R. Bocsi, J. Bobek, *Periodica Polytechnica Chemical Engineering*, **2016**, 60(2), 74.

17. E. Bendall, R. C. Aiken, F. Mandas, *AIChE Journal*, **1983**, 29(1), 66.
18. A. L. Kohl, R. B. Nilsen, *Gas Purification*, Houston, Gulf Publishing Company, **1997**.
19. D. S. F. Atkinson, W. Strauss, *Journal of the Air Pollution Control Association*, **1978**, 28(11), 1114.
20. J. Turba, *Carburators*, Műszaki Könyvkiadó, Budapest, Hungary, **1976**.
21. http://www.draeger.com