REMOVAL OF H_2S FROM BIOGAS BY IRON (Fe^{3+}) DOPED MGO ON CERAMIC HONEYCOMB CATALYST USING DOUBLE PACKED COLUMNS SYSTEM

Nirattisai Rakmak[1], **Wisitsree Wiyaratn**[2] **and**
Juntima Chungsiriporn[1]*

[1] Department of Chemical Engineering, Faculty of Engineering,
Prince of Songkla University, Songkhla. 90112
[2] Department of Production Technology Educations,
Faculty of Industrial Education and Technology,
King Mongkut's University of Technology, Tonburi. Bangkok, Thailand 10140

E-mail : O_took@yahoo.com[1], wisitsree@gmail.com[2] and juntima.c@psu.ac.th[1]*

ABSTRACT

Biogas, a clean environment fuel, is produced by anaerobic digestion of biological wastes. The presence of hydrogen sulfide (H_2S) in biogas has a toxic and corrosive to most equipment such as piping, boilers, and power-generating machine. H_2S removal from biogas is of crucial importance to guarantee better performances in biogas exploitation processes, and to reduce environmental impact of gaseous emissions. Iron (Fe^{3+}) doped magnesium oxide (MgO) catalyst was synthesized using sol–gel dip coating process on foam ceramic honeycomb for removal of H_2S in biogas. The synthesis catalyst was characterized by XRD and SEM techniques. Double packed columns containing absorption column and catalytic column were used to remove H_2S in biogas in this paper. The absorption column using water absorbent was run with counter current mode to absorb H_2S from biogas. The synthesized catalyst was packed in catalytic column to continuously degrade the H_2S in water absorbent liquid and regenerated by air flow. The results showed that the double packed columns system was effectively performed in H_2S removal from biogas. The L/G ratio of 0.6, biogas flow rate of 1 l/min and 10 pieces of catalyst were optimum operating condition of the double packed columns system to get the highest H_2S removal efficiency of 72% without any loss of CH_4 in the biogas.

KEYWORDS

hydrogen sulfide (H_2S), double packed columns, Fe^{3+}doped magnesium oxide, sol–gel, dip coating doi:10.4186/ej.2010.14.1.15

I . Introduction

Biogas originates from bacteria in the process of bio-degradation of organic material under anaerobic (without air) conditions. In principle, all organic materials can be digested to produce biogas. However, only homogenous and liquid substrates can be considered for simple biogas production: wastes and urine from cattle, pigs and possibly from poultry and the wastewater from toilets. Raw biogas contains about 55–80% methane (CH_4) and 20–45% carbon dioxide (CO_2) with small amounts of water vapor, trace amount of hydrogen sulfide (0-1% H_2S), and other impurities [1]. H_2S itself has an offensive odor of "rotten eggs". The H_2S levels in biogas have range between 200-5000 ppmv from municipal facilities to over 30,000 ppmv from industrial wastewater treatments [1]. In industries, a trace amount of H_2S in gas stream is extremely corrosive to most equipment such as boilers and piping, and can ruin power-generating equipment. This corrosion may be prevented by separating and removing H_2S from the biogas.

There are multiple technologies available to remove H_2S such as the gas-gas membrane, alkaline/amine scrubbing, chemical oxidation, adsorption, bio-filtration, and catalytic wet oxidation [2]. However, all the methods have similar disadvantages, such as the cost implication being, a huge investment cost, or a costly operation. Another method employable to destroy H_2S is through H_2S oxidation in the solution using Fe supporting on MgO normal size surface (Fe/MgO) catalyst at room temperature [2-4]. Fe^{3+} catalyst in heterogeneous catalytic system has potential in decomposition of H_2S because it can be regenerated by contacting with oxygen. Mechanism of H_2S oxidation on Fe^{3+} catalyst and the regeneration can be shown in Eqs.(1)-(3). The overall reaction of H_2S degradation and elemental sulfur (S) formation can be written as Eq.(4) [5].

$$H_2S(g) \leftrightarrow S^{2-} + H^+ \tag{1}$$
$$2Fe^{3+} + S^{2-} \rightarrow S + 2Fe^{2+} \tag{2}$$
$$4Fe^{2+} + 2O_2 + 4\,H^+ \rightarrow 4Fe^{3+} + 2\,H_2O \tag{3}$$

Overall Reaction

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \tag{4}$$

Since MgO a typical basic metal oxide was often used as supporting material and has strong basic-property. The MgO can associate with the base-catalysis in many organic reactions. In additional, a pH control system of the reaction media is not needed. However, studies on the characteristics and application of the Fe^{3+}-doped MgO on supporting media for increasing in efficiency of H_2S degradation system have not been elaborated. Foam ceramic honeycomb typically possess a high void fraction of 75–85% (v/v), highly porous structure, and the pore size of foam ceramic honeycomb, quoted in pores per inch (ppi) is available between 5 and 100 ppi. They are well established as filters and catalyst supports with low flow resistance for several industrial applications [6]. Current developments have concentrated on coating methods of the catalyst on foam ceramic honeycomb that lead to coating layers with a large surface area and a good adhesion to support of the coating layer. One of these methods is the dip-coating of a suspension containing the desirable catalyst material onto structure of the supporting media [7]. Sol–gel method is effective for surface design, especially it has high potential for homogeneously mixed oxides, and highly dispersed metal–metal oxide composites. Sol-gel process allows the use of commercially available catalysts with high catalytic activity, none of the expensive precursors, and commonly used for dip-coating.

Packed columns are most frequently used to remove H_2S contaminants from a biogas stream by absorption technique. The contacting between the water absorbent solution and H_2S was performed as a high solubility property of H_2S in water. However, the absorbent solution was unable to eliminate and recover to absorb more H_2S so the catalytic column was added to the system for eliminate H_2S in the absorbent solution. As a consequent, the double columns containing absorption column and catalytic column were used in this paper.

The aims of this research were to prepare Fe^{3+}-doped MgO catalyst supporting on foam ceramic honeycomb by sol-gel dip-coating technique for remove H_2S in biogas using double packed columns system**.** XRD, SEM and EDX were used to investigate for the characterization of synthesis catalyst. The catalytic activity, effect of parameters (amount of catalyst, L/G ratio, and gas flow rate) and the composition of the biogas before and after treatment on double columns system was studies to find for the optimum condition of this system.

II. Materials and Methods

2.1 Reagents and chemicals

Magnesiumnitrate hexahydrate ($Mg(NO_3)_2.6H_2O$, 99.5%) with analytical grade was purchased from QREC. Oxalic acid ($(COOH)_2.2H_2O$, 99.5%), ferric nitrate ($Fe(NO_3)_3.9H_2O$, 98.0%), ethanol 99.9% with analytical grade were purchased from AJAX. Foam ceramic honeycomb (20ppi) purchased from Assab steels (Thailand) public company limited. The biogas stream obtained from the fixed-dome digesters of a pig farm.

2.2 Catalyst preparation

A schematic flow chart of the Fe^{3+}-doped MgO prepared by sol–gel dip coating on foam ceramic honeycomb is shown in Fig. 1. The “A” solution was made by dissolving 0.1 M of $Mg(NO_3)_2.6H_2O$ in 80 ml ethanol. The “B” solution was made by dissolving 0.1 M of $(COOH)_2.2H_2O$ in 80 ml ethanol. The “C” solution was prepared by dissolving 0.1 M of $Fe(NO_3)_3{\cdot}9H_2O$ in 80 ml ethanol. The Fe^{3+}-doped MgO sol–gel was prepared by premixing the “B” solution into the “A” solution and stirring at room temperature for 10 min to form solution (sol). Then catalyst solution as adding the solution “C” into the prepared sol was formed by stirring at room temperature for 12 h [6] - [8].

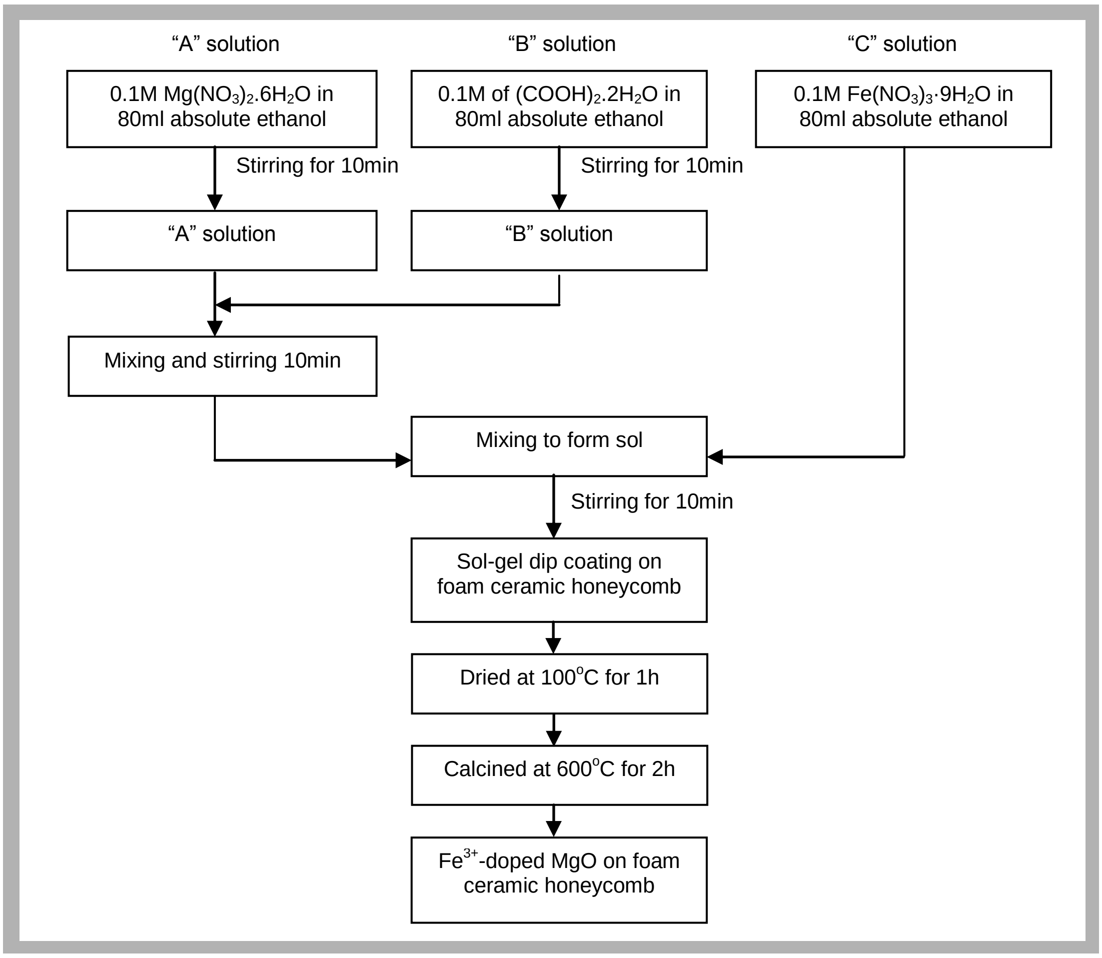

Figure 1
Schematic diagram of the Fe^{3+}-doped MgO on foam ceramic honeycomb synthesis by sol-gel dip coating technique.

Before dip coating, foam ceramic honeycombs were degreased by cleaning thoroughly and drying in an oven at 100°C for 30 min. The circular foam ceramic honeycomb was dipped into the catalyst solution. Subsequently the films were dried at 100°C for 1h, calcined at 600°C for 2 h, and cooled at 10°C/min. Finally, the Fe^{3+}-doped MgO on ceramic honeycomb were obtained. The synthesized catalysts were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), and Energy Dispersive X-ray Spectrometer (EDX).

2.3 Catalytic activity and operating parameter on H_2S degradation

The catalytic activity and effect of operating parameters on H_2S degradation were tested by gas scrubbing in double packed columns system over room temperature (30 ± 1°C).

2.3.1 Double packed columns system

Fig. 2 shows schematic diagram of the laboratory scale double packed columns consisting of absorption and catalytic column for H_2S removal from biogas producing from pig farm. The absorption column (5 cm in diameter) contained raschig rings (0.5 cm in diameter) packing media for H_2S scrubbing from biogas using deionized water as absorbent liquid. The biogas containing H_2S was continuously introduced to the bottom of absorption column and exit on the top. The catalytic column (8 cm in diameter) was packed with bed of the honeycomb catalyst (10x2 cm, 20 ppi) for degradation of absorbed H_2S in scrubbing water. The bed of honeycomb catalyst was regenerated by O_2 in compressed air flow.

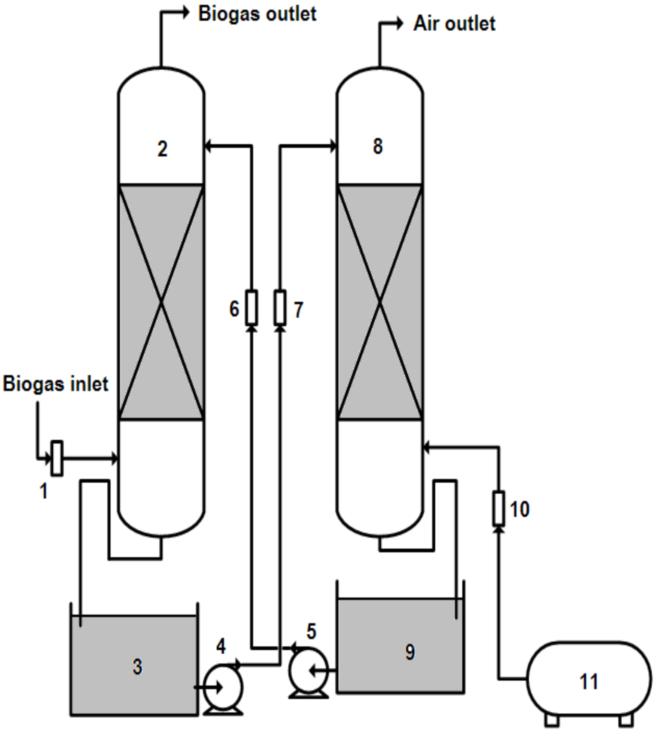

Figure 2
Schematic diagram of laboratory scale double packed columns for H_2S removal from biogas.

The biogas containing 1,300-1,500 ppm of H_2S concentration was introduced to the absorption column. The deionization water (DI) was pumped and sprayed to top of the absorption column by counter current flow with the gas phase. The solution draining from H_2S scrubbing was pumped to catalytic column for H_2S oxidation and accompanied regeneration the catalyst by counter current flow with an excess O_2 in air stream (40 l/min).

2.3.2 System performance analysis

During experiment, the inlet and outlet H_2S concentration was measured by extracting gas volume from sampling port with air sampling pump and a series of the impingers containing a solution of cadmium sulfate ($CdSO_4$). The H_2S in biogas sample was drawn into $CdSO_4$ solution which turns to cadmium sulfide (CdS) as contacted with H_2S. The concentration of H_2S was then measured from amount of CdS formed by iodometric method [9]. The H_2S removal efficiency can be determined by equation (5) through concentrations of H_2S inlet and outlet. CH_4 and CO_2 in biogas were determined by gas chromatography using ShinCarbon ST 100/120 micropacked column, expressed as a mass percentage.

doi:10.4186/ej.2010.14.1.15

$$\% \ H_2S \ Removal = \frac{H_2S\,inlet - H_2S\,outlet}{H_2S\,inlet} \times 100 \qquad (5)$$

Where *% H_2S Removal* is percentage H_2S removal efficiency, *H_2S inlet* is inlet H_2S concentration in biogas or absorbent solution and *H_2S outlet* is H_2S concentration in biogas or absorbent solution after treated.

III. Results and Discussions

3.1 Characteristic of Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst

The Fe^{3+}-doped MgO on ceramic honeycomb were obtained as shown in Fig. 3. The catalyst surface has brown color with smooth thin film of the Fe^{3+}-doped MgO

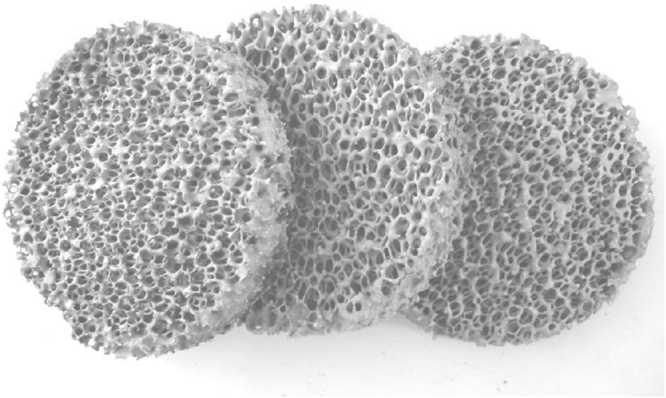

Figure 3
Fe^{3+}-doped MgO on foam ceramic honeycomb catalysts with a pore size of 20ppi.

The X-ray diffraction pattern of Fe^{3+}-doped MgO on foam ceramic honeycomb product obtained by calcination at 600 ◦C for 2 h is presented in Fig. 4. This diffractogram agree with those of standard MgO samples available in the literature. This result also shows that the crystals have cubic phase and matches well with the lattice parameters a=4.2198A^0, b=4.2198A^0, c=4.2198A^0, α = 90.0000A^0, β=90.0000A^0, γ=90.0000A^0 and Z=4.00. From the characteristic peaks, no other diffraction peaks corresponding to Fe^{3+} species are found such as α-Fe_2O_3. The EDX spectra from X-ray Spectrometer showed elemental of Mg, O and Fe on the analysis of Fe^{3+}-doped MgO. The result indicated that Fe^{3+} can be present in groups of ionic on the MgO surface.

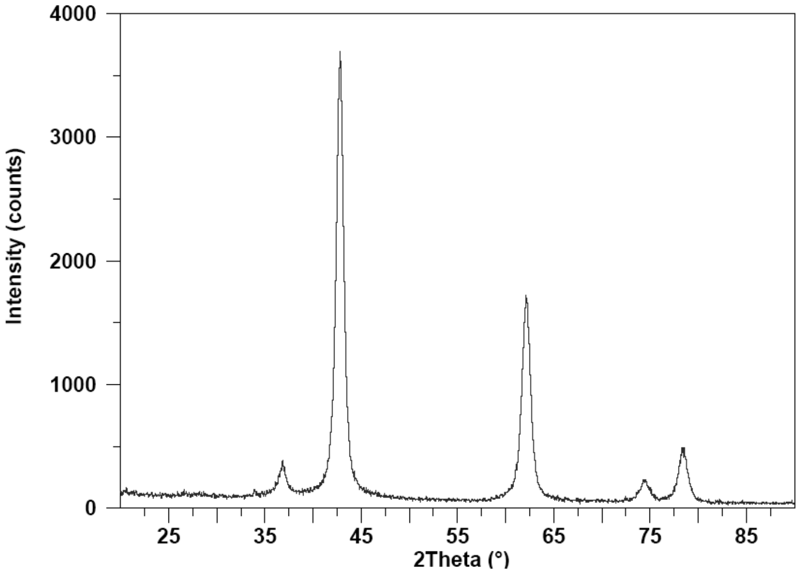

Figure 4
XRD profiles of Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst synthesis.

Fig. 5 shows surface morphology of Fe^{3+}-doped MgO on foam ceramic honeycomb contents carried out scanning electron microscope (SEM). Fig. 5(a) illustrates Fe^{3+}-doped MgO on foam ceramic honeycomb. It is observed that the films are homogeneous containing little of agglomerates without cracks compared with the surface morphology of original foam ceramic honeycomb in Fig. 5(b).

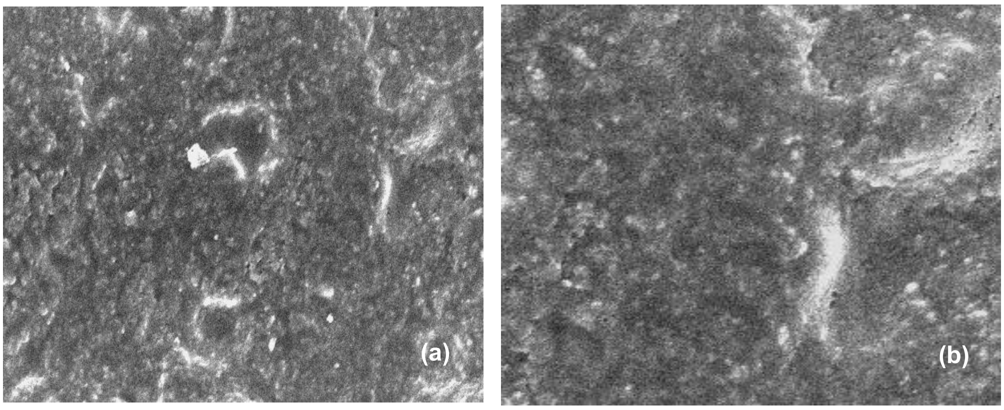

Figure 5
Surface morphology of Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst (a), and original foam ceramic honeycomb (b).

3.2 Catalytic activity on H_2S degradation

Catalytic activity of the Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst in H_2S degradation was tested in double packed columns. H_2S was removed from biogas by absorbing to ionized scrubbing water in the absorption column. Oxidation of H_2S to elemental sulfur, S, was carried out in catalytic columns by using prepared catalyst of the Fe^{3+}-doped MgO on foam ceramic honeycomb. Fig. 6 shows the comparison result of double packed columns (EXP#1) with catalyst and single column of absorption column (EXP#2) in H_2S degradation. The absorption column was controlled by liquid circulated mode at 1.5 l/min of solution, 2 l/min of inlet biogas flow rate containing 1,500 ppm of H_2S concentration (0.75 liquid to gas flow ratio) for biogas scrubbing. For the EXP#1, 1.5 l/min of solution collecting from the absorption column was introduced to catalytic column for H_2S in liquid degradation. The catalyst column containing 10 pieces of catalyst was constantly fed the air flow up at 40 l/min. It was found that the EXP#1 gave 60% H_2S removal efficiency from biogas over the experiment. While the test in EXP#2 of single absorption column without the catalytic column (Fig. 6 (EXP#2)) initially gave 100% removal efficiency, and then decreased continuously to 0% at 20 minute. Fig. 7 presents for H_2S concentration in absorbent solution collecting in circulating tank 3 with time of each experiments. It is indicated that the double columns mode can degrade the H_2S dissolving in the absorbent as the lower level of H_2S in the scrubbing water (100 mg/l) comparing to the single absorption operation (150 mg/l). Then the absorbent solution can use and absorb more H_2S from the biogas flow.

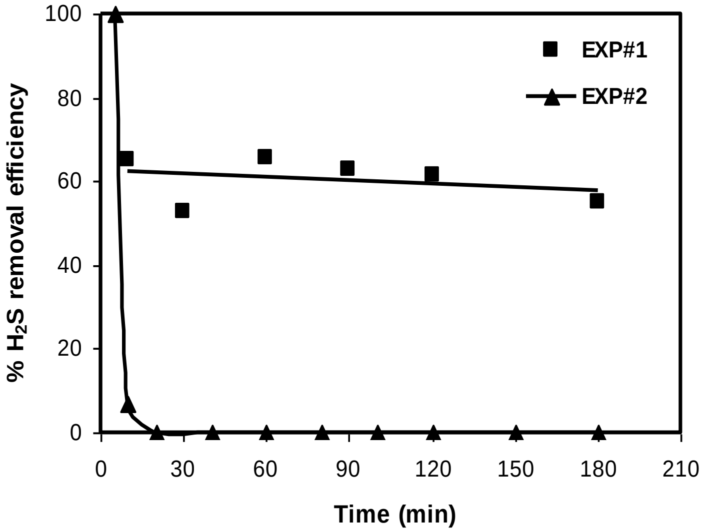

Figure 6
The efficiency of H_2S removal from biogas using double packed columns and single absorption column operation.

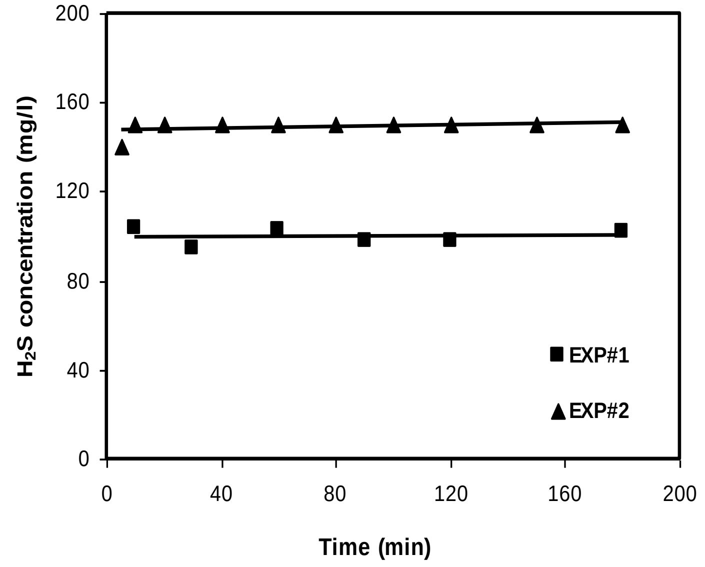

Figure 7
H_2S concentration in absorbent solution in double packed columns and single absorption column operation.

In double packed columns, H_2S in the scrubbing solution was degraded by oxidation reaction of S^{2-} with Fe^{3+} on the foam ceramic honeycomb in redox cycles (reduction/oxidation) as given in Eqs.(2)–(3). The Fe^{3+} is reduced to Fe^{2+} by S^{2-}, and regenerated back to Fe^{3+} via a re-oxidation reactions involving oxygen in the air stream on the heterogeneous catalyst. So the removal efficiency of H_2S in biogas using double packed columns system (EXP#1) with the catalyst was constantly high efficiency. In contrast, the scrubbing water in the single absorption column system (EXP#2) was saturated with H_2S in a prior short time and could not be used to absorb more H_2S from biogas then the efficient was immediately downed.

3.3 Performance of double packed columns in H_2S removal from biogas

The laboratory scale of double packed columns was used to test for the effect of operating parameters in H_2S removal from biogas. The experimental parameters of liquid to gas flow ratio and gas flow rate in absorption column and amount of catalyst (pieces) using in catalytic column were investigated. All experiments were operated at 40 l/min of air flow rate and the biogas samples were taken every 10 minutes along 1 hr of experiments.

3.3.1 Effects of liquid to gas flow ratio in absorption column operation

The liquid to gas flow ratio (L/G) is the most important parameter for design of an absorption column. In this experimental part, 2 l/min of biogas flow rate was fixed and 0.2–0.8 l/min of absorbing solution flow rate were varied to get the effect of L/G ratio on H_2S removal efficiency of the system. Constant amount of 10 pieces catalyst in the catalytic column was performed. The results of L/G ratio in H_2S removal from biogas are showed in Fig.8. The empirical equations described the effect of L/G ratio on percentage of H_2S removal efficiency is proposed as given in equation (6).

$$\%\ H_2S \text{ removal efficiency} = 44.09\ (L/G) + 44.26,\ R^2 = 0.9712 \tag{6}$$

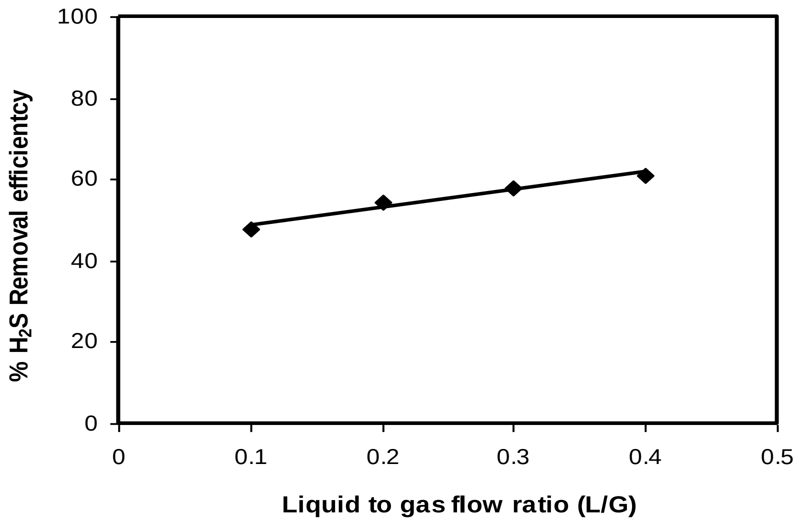

Figure 8
Effect of liquid to gas flow ratio (L/G) of absorption column in double packed columns system on H_2S removal efficiency from biogas.

3.3.2 Effects of biogas flow rate feeding to the absorption column

Fig. 9 shows the effect of biogas flow rate on the removal of H_2S from biogas using double packed columns system. In this experimental part, 0.6 l/min of absorbing solution flow rate and 10 pieces of catalyst were fixed. The empirical equations described the effect of biogas flow rate (G) on percentage of H_2S removal efficiency is proposed as given in equation (7).

$$\% \ H_2S \text{ removal efficiency} = -26.186(G) + 103.16 \quad , R^2 = 0.8654 \qquad (7)$$

The result showed that the H_2S removal efficiency was decreased when the biogas flow rate was increased. It is because the higher biogas flow rate had negative impacted to contacting efficiency and mass transfer of liquid and gas phase. Also the increasing in H_2S amount according to increase biogas flow rate has affected to the dissolving of H_2S in the absorbent liquid

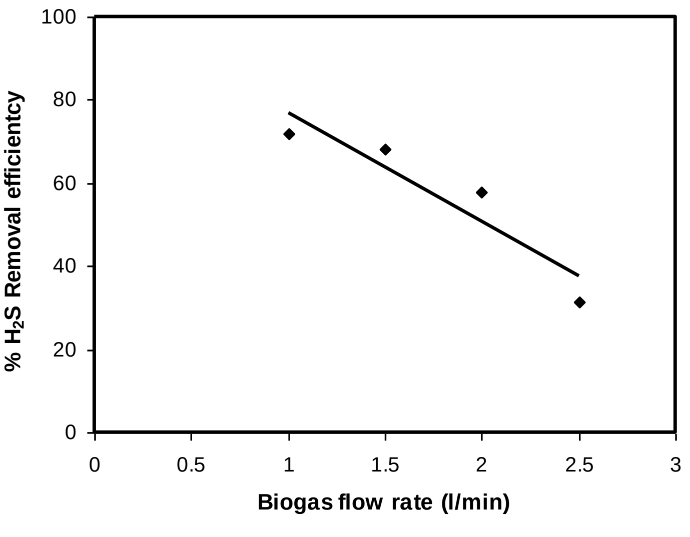

Figure 9
Effect of biogas flow rate in absorption column on H_2S removal efficiency of the double packed columns system.

3.3.3 Effect of amount of catalyst using in catalytic column

The amount of catalyst (1-8 pieces) using in catalytic column on H_2S removal from biogas was studied as shown in Fig. 10. The constant conditions of liquid to gas flow ratio (L/G = 0.3), gas flow rate (2 l/min) and absorbent liquid flow rate (0.6 l/min) in double packed columns operation were controlled. The result shows that the increasing in amount of catalyst increased the H_2S removal efficiency of the system. It is indicated that the amount of catalyst is an important parameter for H_2S removal from biogas as the catalyst has directly worked for oxidizing the H_2S in absorbent liquid to sulfur element.

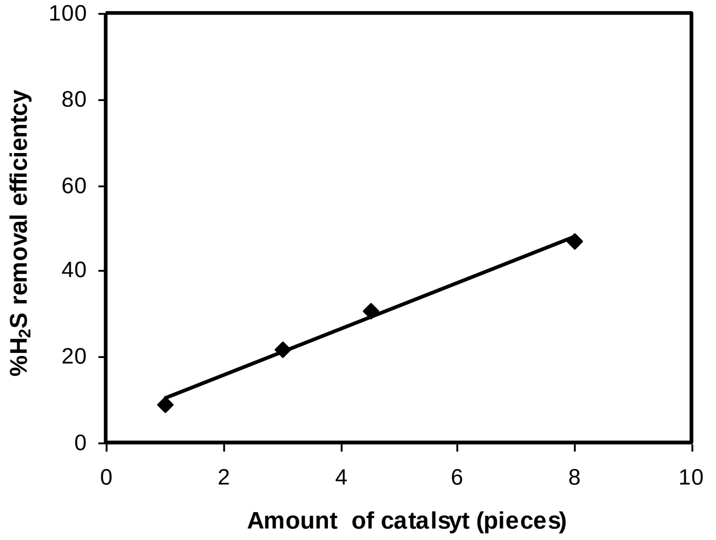

Figure 10
Effect of amount of catalyst on H_2S removal from biogas in double packed columns operation.

3.4 Composition of treated biogas

The inlet and outlet biogas compositions (CH_4 and CO_2) of double packed columns system were determined by gas chromatography, expressed in a mass percentage as shown in Table 1. It was probed that the main component of CH_4 and CO_2 was not absorbed and reacted by the catalyst. Thus Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst can effectively be used for the removal of H_2S from biogas without any effect to heating value of the biogas according to the percentage of CH_4.

Table 1
Mass percent composition of biogas from Inlet and outlet of double packed columns system.

Sample	% CH_4	% CO_2
Inlet	74.03	23.37
Outlet	74.17	23.81

IV. Conclusions

Fe^{3+}-doped MgO catalyst was effectively prepared by sol–gel dip coating on foam ceramic honeycomb supporting media for H_2S oxidation. XRD and SEM tests showed the well dispersion of Fe^{3+} in Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst. The double packed columns have effectively performed in H_2S removal from biogas with absorption column and catalytic column. The using of deionized water as working absorbent and Fe^{3+}-doped MgO on foam ceramic honeycomb catalyst can absorb the H_2S from biogas and degrade the absorbed H_2S in absorbing water. The system gave constantly 60% removal capacity along 3 hr operating time. The optimum operating condition of the double packed columns system are 0.6 of L/G ratio, 1 l/min of biogas and 10 pieces of catalyst in catalytic column to get 72% of H_2S removal efficiency without lose CH_4 in the biogas.

ACKNOWLEDGEMENT

The authors would like to thank Department of Chemical Engineering, Faculty of Engineering and the Graduate school, Prince of Songkla University for equipment facility and the Thailand Research Fund for financial support.

REFERENCES

[1] L. V. A. Truong and N. Abatzoglou, "A H_2S reactive adsorption process for the purification of biogas prior to its use as a bioenergy vector," *Biomass and Bioenergy*, vol. 29, no. 2, pp. 142-151, 2005.

[2] E. K. Lee, K. D. Jung, O. S. Joo, and Y. G. Shul, "Support effects in catalytic wet oxidation of H_2S to sulfur on supported iron oxide catalysts," *Applied Catalysis A: General*, vol. 284, no. 1-2, pp. 1-4, 2005.

[3] E. K. Lee, K. D. Jung, O. S. Joo, and Y. G. Shul, "Selective oxidation of hydrogen sulfide to elemental sulfur with Fe/MgO catalysts in a slurry reactor," *Bulletin of The Korean Chemical Society*, vol. 26, no. 2, pp. 281-284, 2005.

[4] K. D. Jung, O. S. Joo, S. H. Cho, and S. H. Han, "Catalytic wet oxidation of H_2S to sulfur on Fe/MgO catalyst," *Applied Catalysis A: General*, vol. 240, no. 1-2, pp. 235-241, 2003.

[5] E. K. Lee, K. D. Jung, O. S. Joo, and Y. G. Shul, "Influence of iron precursors on catalytic wet oxidation of H_2S to sulfur over Fe/MgO catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 239, no. 1-2, pp. 64-67, 2005.

[6] G. Plesch , M. Gorbar, U. F. Vogt, K. Jesenak, and M. Vargova, "Reticulated macroporous ceramic foam supported TiO_2 for photocatalytic applications," *Materials Letters*, vol. 63, no. 3-4, pp. 461–463, 2009.

[7] V. Meille, S. Pallier, G. Gabriela, S. C. Bustamante, M. Roumanie, and J. P. Reymond, "Deposition of γ-Al_2O_3 layers on structured supports for the design of new catalytic reactors," *Applied Catalysis A: General*, vol. 286, no. 2, pp. 232–238, 2005

[8] W. Ji, Y. Chen, S. Shen, S. Li, and H. Wang, "Structure and reactivity of the iron oxide specimen supported magnesia via different preparation methods," *Materials Chemistry and Physics*, vol. 47, no. 1, pp. 68-74, 1997.

[9] Environmental Protection Agency (EPA) Method 11, Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries, Code of Federal Regulations (CFR) 40, Part 60-Standards of Performance for new Stationary Sources, Appendix A- Test Methods, pp. 788-815.