CHEMICAL ENGINEERING TRANSACTIONS
VOL. 37, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus

ISBN 978-88-95608-28-0; **ISSN** 2283-9216
DOI: 10.3303/CET1437108

Purification of Biogas for Energy Use

Djeine C. Schiavon Maia*[a], Fernando H. Cardoso[a], Laercio M. Frare[b], Marcelino L. Gimenes[a], Nehemias C. Pereira[a]

[a]State University of Maringá (UEM), Av. Colombo, 5790, 87020-900. Maringá - PR. Brazil
[b]Federal University of Technology - Paraná (UTFPR), Brazil
djeine.cr@ig.com.br

This work determined the absorption efficiency of H_2S in the solution of Fe-EDTA in synthetic biogas flows, as well as the efficiency of physical absorption of CO_2 in Fe-EDTA. Biogas was bubbled through a pseudo-catalytic solution of Fe-DTA resulting in the formation of sulfur particles. H_2S absorbed in the Fe-EDTA suffered a redox reaction. The Fe-EDTA solution used was regenerated with air. It was used two types of catalysts, in order to compare the efficiency of a catalyst of Fe-EDTA synthesized in the laboratory in an inert atmosphere, in relation to a commercial catalyst containing Fe-EDTA. In the batch study, removing H_2S from biogas indicated that the concentration of Fe-EDTA applies great influence on the catalytic activity. For a system operating in a continuous regimen, it was possible to completely eliminate the H_2S from biogas with Fe-EDTA synthesized in laboratory. The removal of CO_2 present in the biogas was also evaluated. It was possible to achieve maximum efficiency of the CO_2 absorption in 90 % in steady state, it was obtained an increase of 16 % in the calorific value of biogas, from 8.03 to 9.28 kWh/m^3.

1. Introduction

According to Authayanun et al. (2013), among the various types of the renewable sources, biogas is a potential fuel, which can be produced through an anaerobic digestion of organic material, such as biomass, municipal waste and sewage. Biogas mainly consists of methane and carbon dioxide together with smaller amounts of other gases and vapours, such as hydrogen, nitrogen and hydrogen sulfide (H_2S) (Makaruk et al., 2010). The main component of biogas is methane, other combustible hydrocarbons of biogas do not contribute much to the calorific value of the gas (Makaruk et al., 2010). Thus, the high concentration of methane makes biogas an attractive fuel and its use solves an emission problem since methane (as a greenhouse gas) is several times more harmful than CO_2 (Niesner et al., 2013).
On the other hand, removing CO_2 increases the heating value and leads to a consistent gas quality, similar to natural gas (Appels et al., 2008). Although the hydrogen sulfide is present in small quantities in the biogas, the presence of H_2S usually prohibits the direct use of these gases because of its toxic properties, the formation of SO_2 upon combustion (acid rain), and the problems it (usually) gives in downstream processing (Maat et al., 2005). Beside, H_2S is frequently encountered in the field of odour monitoring because of its high odorous power (Zaouak et al., 2012). The type and the amount of pollutants depend upon the biogas source and determine which cleaning and upgrading techniques are the most suitable for gas purification (Gamba and Pellegrini, 2013).
Systems chelates of Fe-EDTA are used as catalysts for the removal of H_2S by chemical absorption of various gas streams (Martell et al., 1996). According Wubs and Beenackers (1993), absorption of hydrogen sulfide with Fe-EDTA is represented by Equations 1 and 2.

$$H_2S(g) \leftrightarrow H_2S(aq) \quad (1)$$

$$H_2S(aq) + 2Fe^{3+}chelate^{n-} \rightarrow S\downarrow + 2H^+ + 2Fe^{2+}chelate^{n-} \quad (2)$$

In this (1) n denotes the charge of the chelant anion. The product, ferrous chelate, can be regenerated into the active ferric form by oxidation of the solution with air or oxygen.

Please cite this article as: Schiavon Maia D.C., Cardozo F., Frare L., Gimenes M., Pereira N., 2014, Purification of biogas for energy use, Chemical Engineering Transactions, 37, 643-648 DOI: 10.3303/CET1437108

$$O_2(g) \leftrightarrow O_2(aq) \quad (3)$$

$$O_2(aq) + 4Fe^{2+}chelate^{n-} + 2H_2O \rightarrow 4Fe^{3+}chelate^{n-} + 4OH^- \quad (4)$$

The sulphur produced is easily recoverable from the slurry. Another advantage of Fe-EDTA processes is that they essentially operate at ambient conditions and are selective to H_2S relative to CO_2 (Demmink et al., 1994).
In this sense, this work was devoted to investigate the absorption efficiency of H_2S into catalyst solutions of Fe-EDTA, in a synthetic biogas streams, as well as to investigate the physical absorption efficiency of CO_2 into Fe-EDTA.

2. Material and methods

2.1 Solution Catalytic Synthesis of Fe-EDTA
The Fe-EDTA 0.03 and 0.06 mol/L was synthesized second Horikawa et al. (2004) in an inert atmosphere.

2.2 Preparation of Commercial Solution containing Fe-EDTA
A reagent powder whose composition is 13% Fe-EDTA complex was used, from which the commercial solutions were prepared at concentrations of 0.06, 0.07 and 0.10 mol/L in deionized water at pH 5.5.

2.3 Characterization by Atomic Absorption Spectrometry
The technique atomic absorption spectrometry was used to experimentally determine the concentration of iron in solution of Fe-EDTA synthesized in the laboratory.

2.4 Experimental system
Figure 1 illustrates the experimental system, bench scale, used for the tests of removal of H_2S and CO_2 from biogas.

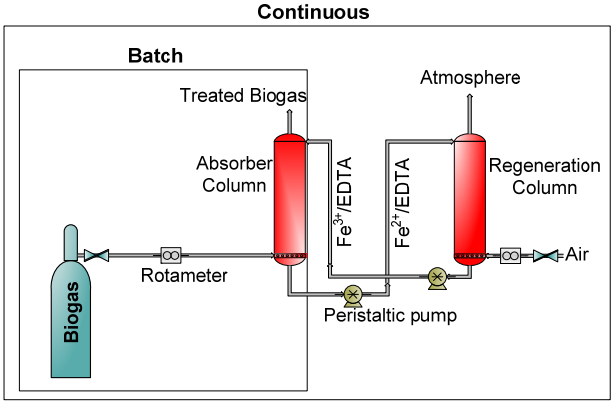

Figure 1: Absorption experiments

The composition mol/mol of the synthetic biogas was 2.2 % H_2S, 0.3 % O_2, 14 % CO_2, 2.4 % N_2 and 81.1 % CH_4. Biogas composition was measured by gas chromatography. In batch tests, bubbled 250 mL/min synthetic biogas in the 250 mL Fe-EDTA in the chemical absorption column. The H_2S present in the form of biogas insoluble sulfur is converted to sulfur in the chemical absorption column. Samples were collected periodically biogas at the top of this column. The end of the race was determined by detection of H_2S in the sample, indicating the deactivation of the same. Then, Fe-EDTA solution was vacuum filtered in order to remove the sulfur present in it. Filtered the solution, it was left in ambient conditions, and presence of regenerated with atmospheric air.
In trials where there was a steady constant regeneration of the catalyst Fe-EDTA by injecting excess air into the regeneration column. The volume of liquid chemical in the absorption column and the regeneration column was kept constant with 250 mL for all experiments. After regeneration solution is to feed the chemical absorption column with a peristaltic pump (Figure 1). The ratio of liquid flow rate to gas flow rate, L/G, for efficient removal of hydrogen sulfide from biogas in continuous operation was 0.46.
The solution Fe-EDTA is synthesized in inert atmosphere and the total time for synthesis of this catalyst can take up to 10 h. In view of the great difficulty of synthesis of Fe-EDTA, was also studied using a

commercial solution containing Fe-EDTA on chemical absorption of H_2S. For tests in batch and continuous operation with commercial solution was also used 250 mL/min synthetic biogas. The L/G ratio in continuous operation was 1.00.
Although the Fe-EDTA is the selective H_2S, also occurred physical absorption of carbon dioxide in the aqueous solution as this is. The calorific value of biogas was estimated according to Magalhães et al. (2004), assuming it depends on the existing percentage of methane in biogas.

3. Results and Discussion

3.1. Atomic Absorption Spectrometry

The concentration of iron in the catalyst Fe-EDTA 0.03 mol/L synthesized in the laboratory, obtained by atomic absorption, is shown in Table 1.

Table 1: Concentration of Iron

Samples Fe-EDTA	Average concentration of iron in solution (mg/L)	Relative error (%) in relation to the theoretical value
1	1,471.53	6.79 ± 0.01
2	1,580.21	0.55 ± 0.01

Sample1 was synthesized from a solution of EDTA 0.2 mol/L (Horikawa et al., 2004) and sample 2 was synthesized from EDTA 0.1 mol/L. Therefore, both solutions were obtained with the same concentration of iron.

3.2. Removal of H_2S and CO_2 with Fe-EDTA 0.03 mol/L synthesized in laboratory

Figure 2 shows the results obtained for the removal of H_2S and CO_2 in batch with the Fe-EDTA 0.03 mol/L. The Solution A were complexed from a solution of EDTA 0.2 mol/L in excess, the same concentration used by Horikawa et al. (2004). The solution B is the regenerated Solution A. The Solution C was complexed with an EDTA solution 0.1 mol/L also in excess.

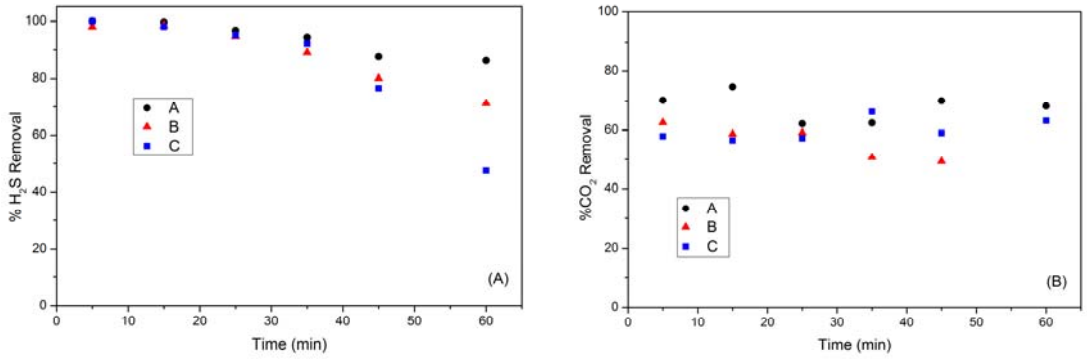

Figure 2: Efficiency of removal of (A) H_2S and (B) with the CO_2 concentration of Fe-EDTA 0.03 mol/L, as follows: (●) Solution A, (Δ) and Solution B (□) Solution C

Figure 2 (A) shows that after 25 min of reaction the solution of Fe-EDTA 0.03 mol/L began to lose the H_2S removal efficiency for the three tests. The CO_2 removal showed the highest value of the removal was introduced of Solution A. At the end of this test was being withdrawn 68 % of CO_2.

3.3. Removal of H_2S and CO_2 with Fe-EDTA 0.06 mol/L synthesized in laboratory

Figure 3 shows the results obtained for the removal of H_2S and CO_2 with the Fe-EDTA 0.06 mol/L batch. It was used for testing three samples called Solution D (not regenerated), and (D regenerated solution once) and F (solution D regenerated twice).

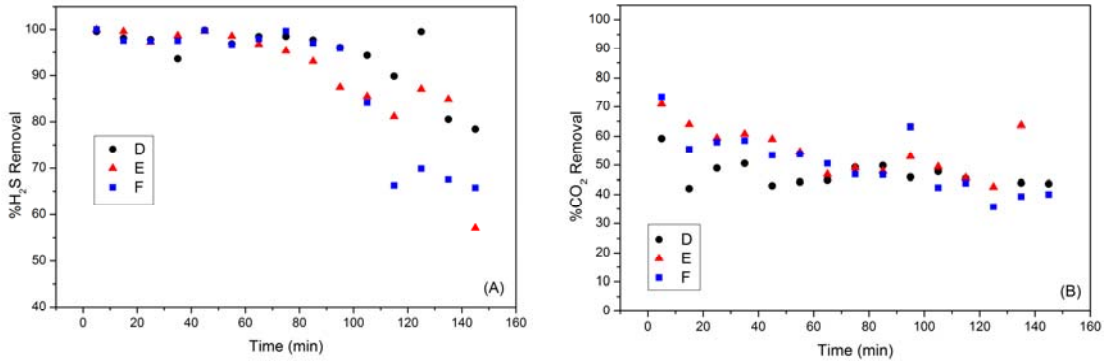

Figure 3: Removal efficiency of (A) H_2S, and (B) CO_2 Fe-EDTA 0.06 mol / L, as follows: (●) Solution D, (Δ) and Solution E (□) Solution F

The solution of Fe-EDTA 0.06 mol/L began to lose its effect in about 76 min for the three tests with the presence of H_2S in the treated biogas, Figure 3 (A). The saturation time for both solutions was 145 min. For removal of CO_2, the more concentrated solution, Figure 3 (B), presents generally less efficient than Fe-EDTA 0.03 mol/L, Figure 2 (B). Tippayawong and Thanompongchart (2010) verified the removal of CO_2 and H_2S from biogas by aqueous solutions in a packed column, saturation was reached in about 50 min for $Ca(OH)_2$, and 100 min for both NaOH and MEA.

3.4. Removal of H_2S and CO_2 with Commercial Solution containing Fe-EDTA

The results of the efficiency of removal of H_2S and CO_2 in batch are shown in Figure 4.

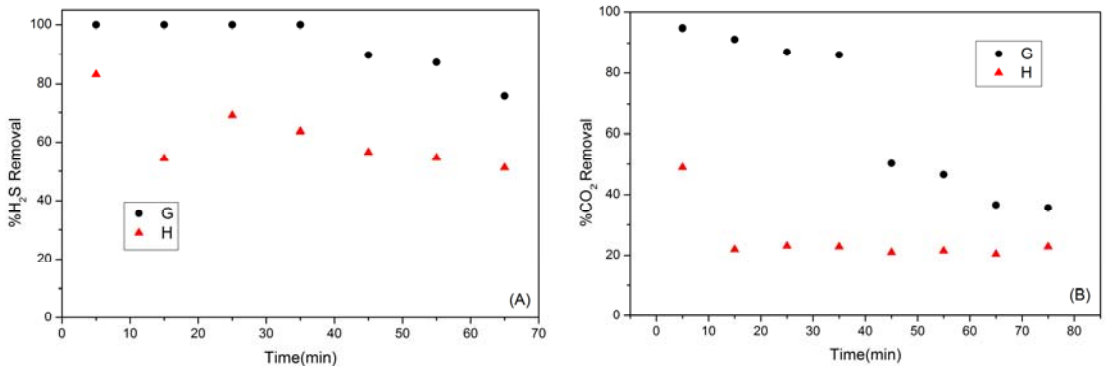

Figure 4: Removal efficiency of (A) H_2S, and (B) CO_2, as follows: (●) Solution G, Fe-EDTA 0.10 mol/L and (Δ) Solution H, Fe-EDTA 0.07 mol/L

For the second trial there was complete removal of H_2S up to 35 minutes after which time the commercial solution began to be disabled, Figure 4 (A). At the end of test G it was possible to obtain a CO_2 removal efficiency of 36 %, Figure 4 (B). This represents a 6 % increase in calorific value of biogas.

3.6. H_2S removal Steady State with Commercial Solution containing Fe-EDTA

Figure 5 shows the removal efficiency of H_2S and CO_2 in steady state with a commercial solution.

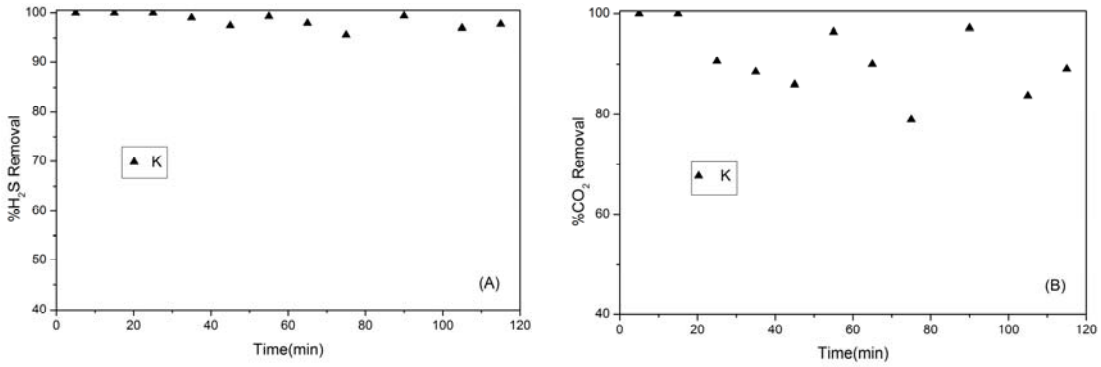

Figure 5: Removal efficiency of H_2S (A) and CO_2 (B) in continuous operation with Fe-EDTA 0.06 mol/L and L/G ratio 1.00, as follows: (Δ) Solution K

The test with commercial solution showed absorption efficiency of H_2S around 98 %. It was possible to eliminate the biogas, on average, a total of 90 % carbon dioxide. In the study by Horikawa et al. (2004) 90 % of the H_2S was removed with the catalytic solution (Fe-EDTA 0.2 mol/L) flowing at 83 ml/min under continuous regeneration, in counter-current contact with biogas flow-rate of 1000 mL/min.

3.5. H_2S and CO_2 removal Steady State with Fe-EDTA synthesized in the laboratory

Figure 6 shows the H_2S and CO_2 removal efficiency in steady state with Fe-EDTA 0.06 mol/L.

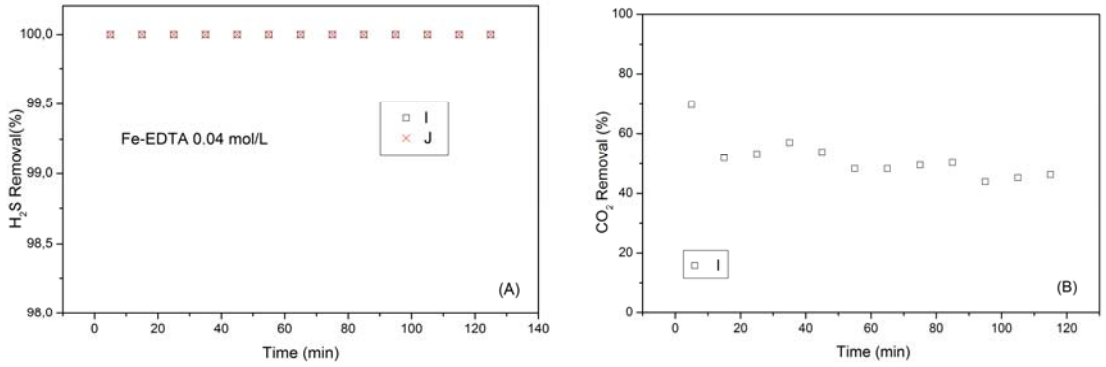

Figure 6: Removal efficiency of H_2S (A) and CO_2 (B) in continuous operation with Fe-EDTA 0.06 mol/L and L/G ratio 0.46, as follows: (□) Solution I and (x) Solution J

There was complete removal of H_2S from biogas. Madaeni et al. (2010) examined the H_2S removal of gas stream from oil refinery using metal membranes. A constant removal of 95 % of the H_2S from the gas was achieved up to 30 min of contact.

The removal of CO_2 averaged 51 %, this equates to an increase of 9 % in the calorific value of biogas. Magalhães et al. (2004) studied the removal of CO_2 from biogas through a packed column using water as solvent. From an initial concentration of CO_2 equal to 33 %, it was possible to remove 45 % of CO_2.

4. Conclusions

Experimental results were similar for the solutions of Fe-EDTA 0.03 mol/L synthesized from various concentrations of EDTA. Therefore, the synthesis of Fe-EDTA solution from EDTA 0.1 mol/L represents a great reduction in the use of reagents with a view to its application on an industrial scale.

The concentration of Fe-EDTA solution has a strong influence on the catalytic activity as evidenced in the results of the removal of H_2S. In a steady state with Fe-EDTA 0.06 mol/L synthesized in the laboratory, it was possible to completely remove hydrogen sulfide from biogas during the two hours that the system was monitored. In steady state, the test with commercial solution containing Fe-EDTA 0.06 mol/L showed absorption efficiency of H_2S around 98 %. The maximum efficiency of the CO_2 absorption in 90 % in steady state with commercial solution. As a result, it was obtained an increase of 16 % in the calorific value of biogas, from 8.03 to 9.28 kWh/m^3.

References

Appels L., Baeyens J., Degreve J., Dewil R., 2008, Principles and potential of the anaerobic digestion of waste-activated sludge, Progress in Energy and Combustion Sci., 772 – 777.

Authayanun S., Aunsup P., Im-orb K., Arpornwichanop A., 2013, Systematic analysis of proton electrolyte membrane fuel cell systems integrated with biogas reforming process, Chemical Engineering Transactions, 35, 607-612 DOI:10.3303/CET1335101.

Demmink J.F., Wubs H.J., Beenackers A.A.C.M., 1994, Oxidative Absorption of Hydrogen Sulfide by a Solution of Ferric Nitrilotriacetic Acid Complex in a Cocurrent Down Flow Column Packed with SMV-4 Static Mixers. Ind. Eng. Chem. Res., 33(12), 2989-2995.

Gamba S., Pellegrini L., 2013, Biogas Upgrading: Analysis and Comparison between Water and Chemical Scrubbings, chemical Engineering Transactions, 32, 1273-1278, DOI: 10.3303/CET1332213.

Horikawa M.S., Rossi F., Gimenes M.L., Costa C.M.M., Silva M.G.C., 2004, Chemical Absorption of H_2S for Biogas Purification. Brazilian Journal of Chemical Engineering, 21(03), 415-422.

Maat H., Hogendoornb J.A., Versteeg G.F., 2005, The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent. Part I. The absorption of hydrogen sulfide in metal sulfate solutions, Separation and Purification Technology, 43, 183–197.

Madaeni, S.S.; Aalami-Aleagha, M.E.; Taei, B.; Amirinejad, M.; Daraei, P., 2010, Removal of Hydrogen Sulfide from Gas Stream Using a Novel Metal Membrane Prepared by Wire Arc Spraying. International Journal of Chemical Reactor Engineering, 8, A70.

Magalhães E.A., Souza S.N.M., Afonso A.D.L., Ricieri R.P., 2004, Preparation and evaluation of a system for removal of CO_2 contained in the biogas, Acta Scientiarum Technology, 26, 11-19.

Makaruk A., Miltner M., Harasek M., 2010, Membrane biogas upgrading processes for the production of natural gas substitute, Separation and Purification Technology, 74(1), 83-92.

Martell A.E., Motekaitis R.J., Chen D., Hancock R.D., McManus D., 1996, Selection of new Fe(lll)/Fe(ll) chelating agents as catalysts for the oxidation of hydrogen sulfide to sulfur by air. Canadian Journal of Chemistry, 74, 1872 - 1879.

Niesner J., Jecha D., Stehlik P., 2013, Biogas upgrading techniques: state of art review in European region, Chemical Engineering Transactions, 35, 517-522, DOI:10.3303/CET1335086.

Tippayawong, N., Thanompongchart, P., 2010, Biogas quality upgrade by simultaneous removal of CO_2 and H_2S in a packed column reactor. Energy, 35, 4531 - 4535.

Zaouak O., Ben Daoud A., Fages M., Fanlo J.L., Aubert B., 2012, High Performance Cost Effective Miniature Sensor for Continuous Network Monitoring of H_2S, Chemical Engineering Transactions, 30, 325-330, DOI: 10.3303/CET1230055.

Wubs H.J., Beenackers A.A.C.M., 1993, Kinetics of the Oxidation of Ferrous Chelates of EDTA and HEDTA in Aqueous Solution. Ind. Eng. Chem. Res., 32, 2580 – 2594.