Purification of Biogas for Energy Use


This work determined the absorption efficiency of H2S in the solution of Fe-EDTA in synthetic biogas flows, as well as the efficiency of physical absorption of CO2 in Fe-EDTA. Biogas was bubbled through a pseudo-catalytic solution of Fe-DTA resulting in the formation of sulfur particles. H2S 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 H2S 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 H2S from biogas with Fe-EDTA synthesized in laboratory. The removal of CO2 present in the biogas was also evaluated. It was possible to achieve maximum efficiency of the CO2 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/m3.

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 (H2S) (Makanuk 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 (Makanuk 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 CO2 (Niesner et al., 2013). On the other hand, removing CO2 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 H2S usually prohibits the direct use of these gases because of its toxic properties, the formation of SO2 upon combustion (acid rain), and the problems it (usually) gives in downstream processing (Maat et al., 2005). Beside, H2S 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 H2S 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.

\[ H_2S(g) \leftrightarrow H_2S(aq) \]  

\[ H_2S(aq) + 2Fe^{3+}\text{chelate}^{n-} \rightarrow S \downarrow +2H^+ + 2Fe^{2+}\text{chelate}^{n-} \]  

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.
\( O_2(g) \leftrightarrow O_2(aq) \) 

\( O_2(aq) + 4Fe^{2+}_{\text{chelate}} + 2H_2O \rightarrow 4Fe^{3+}_{\text{chelate}} + 4OH^- \) 

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](image)

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 H₂S. 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 H₂S, 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

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

Sample 1 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 H₂S and CO₂ with Fe-EDTA 0.03 mol/L synthesized in laboratory
Figure 2 shows the results obtained for the removal of H₂S and CO₂ 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) H₂S and (B) CO₂ concentration of Fe-EDTA 0.03 mol/L, as follows: (●) Solution A, (△) 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 H₂S removal efficiency for the three tests. The CO₂ removal showed the highest value of the removal was introduced of Solution A. At the end of this test was being withdrawn 68 % of CO₂.

3.3. Removal of H₂S and CO₂ with Fe-EDTA 0.06 mol/L synthesized in laboratory
Figure 3 shows the results obtained for the removal of H₂S and CO₂ 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).
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$_2$S 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$_2$S 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$_2$S and CO$_2$ with Commercial Solution containing Fe-EDTA

The results of the efficiency of removal of H$_2$S and CO$_2$ in batch are shown in Figure 4.

For the second trial there was complete removal of H$_2$S 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$_2$S removal Steady State with Commercial Solution containing Fe-EDTA

Figure 5 shows the removal efficiency of H$_2$S and CO$_2$ in steady state with a commercial solution.
Figure 5: Removal efficiency of H\textsubscript{2}S (A) and CO\textsubscript{2} (B) in continuous operation with Fe-EDTA 0.06 mol/L and L/G ratio 1.00, as follows: (A) Solution K

The test with commercial solution showed absorption efficiency of H\textsubscript{2}S 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\textsubscript{2}S 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. \textit{H\textsubscript{2}S and CO\textsubscript{2} removal Steady State with Fe-EDTA synthesized in the laboratory}

Figure 6 shows the H\textsubscript{2}S and CO\textsubscript{2} removal efficiency in steady state with Fe-EDTA 0.06 mol/L.

There was complete removal of H\textsubscript{2}S from biogas. Madaeni et al. (2010) examined the H\textsubscript{2}S removal of gas stream from oil refinery using metal membranes. A constant removal of 95 % of the H\textsubscript{2}S from the gas was achieved up to 30 min of contact.

The removal of CO\textsubscript{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\textsubscript{2} from biogas through a packed column using water as solvent. From an initial concentration of CO\textsubscript{2} equal to 33 %, it was possible to remove 45 % of CO\textsubscript{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\textsubscript{2}S. 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\textsubscript{2}S around 98 %. The maximum efficiency of the CO\textsubscript{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\textsuperscript{3}.
References


