

# CHEMICAL ABSORPTION OF H<sub>2</sub>S FOR BIOGAS PURIFICATION

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**Abstract** - This work presents an experimental study of purification of a biogas by removal of its hydrogen sulphide (H<sub>2</sub>S) content. The H<sub>2</sub>S was removed by means of chemical absorption in an iron-chelated solution catalyzed by Fe/EDTA, which converts H<sub>2</sub>S into elemental sulphur (S). Preparation of the catalyst solution and the results of biogas component absorption in the catalyst solution (0.2 mol/L) are presented. These results are compared with those for physical absorption into pure water under similar conditions. Experimental results demonstrate that, under the same experimental conditions, a higher percentage of H<sub>2</sub>S can be removed in the catalytic solution than in water. In a continuous counter current using adequate flow-rate phases contact at room temperature and low gas pressure, the results demonstrate that is possible to totally remove the H<sub>2</sub>S from the biogas with the prepared catalytic solution.

**Keywords:** biogas purification, H<sub>2</sub>S removal, Fe/EDTA catalyst.

## INTRODUCTION

The anaerobic process has frequently been used to treat wastewaters and solid residues. As it causes the degradation of organic compounds in the absence of molecular oxygen, this biological process produces the co-product biogas, a mixture composed mainly of methane, carbon dioxide and hydrogen sulphide (H<sub>2</sub>S) (Corbitt, 1990).

Biogas emissions can cause damage to the environment due to the presence of the pollutant hydrogen sulphide, which is harmful to human beings and animals. At lower concentrations, this gas has an unpleasant odour; at higher concentrations, it can be life-threatening. The recommended industrial exposure limits are from 8 to 10 ppm for 8 hours a day per week (Horikawa, 2001).

On the other hand, biogas is an attractive source of energy due to its high methane content. However, direct utilisation of biogas as fuel without removal of H<sub>2</sub>S leads to the formation of sulphur dioxide (SO<sub>2</sub>), which is another toxic pollutant and a major contributor to acid rain in the atmosphere.

There are several processes presented in literature (Bland and Davidson, 1967; Kohl and Riesenfeld, 1985; Horikawa, 2001) that deal with means of removing H<sub>2</sub>S. Many of them only remove this pollutant from the gaseous stream, but do not convert the H<sub>2</sub>S into a more stable or valuable product, as do processes that transform H<sub>2</sub>S into S. The advantage of these processes is the conversion of a pollutant into a chemical product or at least a solid residue that can be disposed of easily and safely.

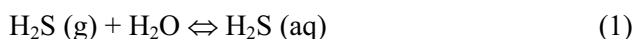
The process of chemical absorption of H<sub>2</sub>S into

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iron-chelated solutions does fit in this approach and offers extra advantages, such as the high efficiency of H<sub>2</sub>S removal, the selective removal of H<sub>2</sub>S and the low consumption of the chemicals because iron-chelated solutions functions as a pseudo-catalyst that can be regenerated.

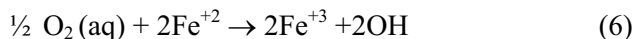
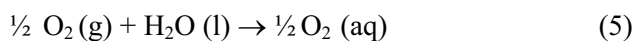
In processes based on iron chelating, H<sub>2</sub>S is initially physically absorbed into water undergoing the dissociation according to reactions 1, 2 and 3 (O'Brien, 1991).



The formation of S occurs by means of sulphide oxidation by the chelated iron according to the reaction described by Equation (4).



Regeneration of the aqueous iron-chelated solution occurs by means of its oxygenation, according to Equation (5), followed by conversion of the pseudo-catalyst into its active form Fe<sup>+3</sup> [Equation (6)].



The overall reaction is expressed in Equation (7) (O'Brien, 1991).



Several chelate agents that can be used for the specific proposal of reaction (7) have been studied in the literature (Wubs and Beenackers, 1993), with the EDTA (ethylenediaminetetraacetate) being the most common chelate used.

In the iron chelated based process, the sulphur produced is easily recoverable from the slurry by sedimentation or filtration operations and the whole process can be carried out at ambient temperature. These advantages are quite important for biogas purification because of the low content of H<sub>2</sub>S in the biogas and the ambient temperature in the bioreactor.

Although EDTA is the most common agent reported in the literature, there is very little information about preparation of the Fe-EDTA

catalyst complex. In addition, no process data is available in the published literature that allows designing a process for biogas purification (Horikawa, 2001).

In addition to obtaining the Fe-EDTA catalyst complex, this work aims at studying the potential offered by the more environmentally appropriate process for transforming gas sulphide from biogas into S.

## MATERIALS AND METHODS

### Preparation of Fe-EDTA Catalyst Solution

FeCl<sub>2</sub> was reported in the literature (Wubs and Beenackers., 1994) as the salt used to prepare the iron chelate Fe-EDTA. Preparation of this salt is difficult due to its extreme instability. In this work, FeBr<sub>2</sub> salt was used instead for synthesis of the homogeneous Fe-EDTA catalyst. The FeBr<sub>2</sub> salt was prepared at a controlled temperature in argon in a closed system. In this system iron powder was added to HBr (98%) solution under controlled stirring for 5 to 6 hours until iron powder had been completely transformed into FeBr<sub>2</sub>. After filtering, the solution was dried in vacuum to obtain the salt.

The Fe-EDTA catalyst solution was synthesised from a 0.2 M solution of EDTA, which had been previously prepared and standardized with a 0.1 M zinc solution and had its pH adjusted to a value of 9.5. In argon, the prepared FeBr<sub>2</sub> salt was added into the EDTA solution to form the final Fe-EDTA catalyst solution. The ratio of iron to chelate agent used in the preparation of the catalyst was 1.06 (Horikawa, 2001).

### Experimental Rig for H<sub>2</sub>S Removal

Figure 1 shows a sketch of the experimental rig used to test removal of the H<sub>2</sub>S from the biogas stream.

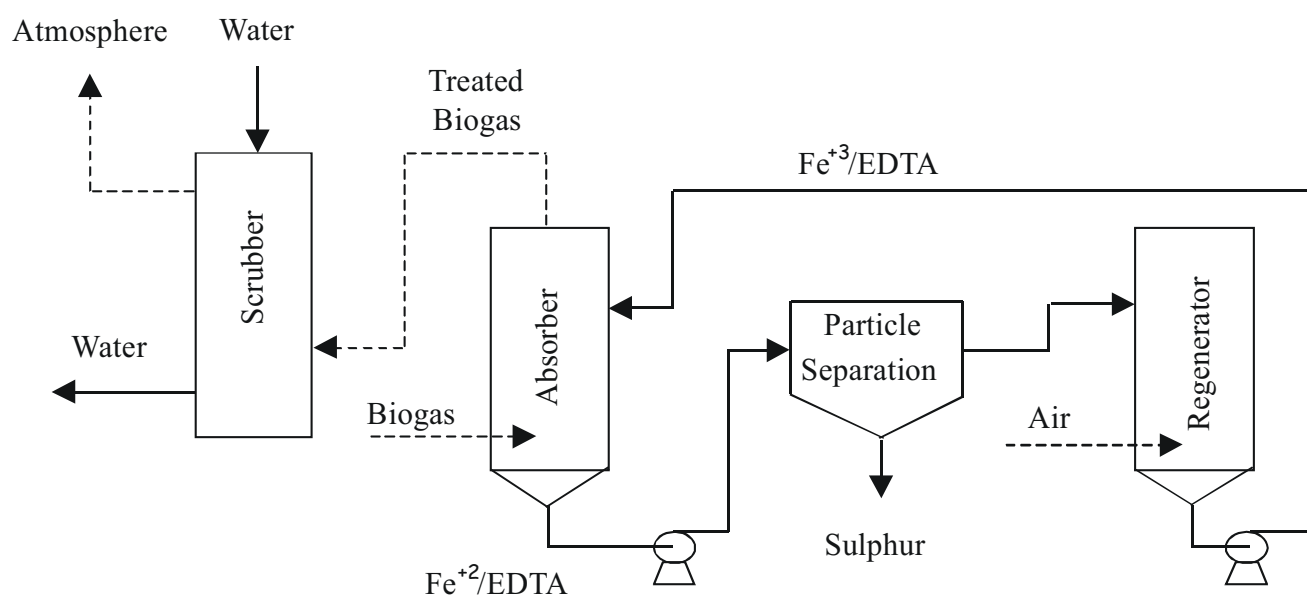
The complete system comprises an absorber column (ID 5.4 cm, height 36 cm), a particle separator (filter) and a regenerating column (ID 5.4 cm, height 36 cm). Under continuous operational conditions, the biogas is introduced at the bottom of the absorber column as small bubbles, passing through the Fe/EDTA solution flowing downwards to the particle separator. In this column the H<sub>2</sub>S is absorbed and transformed into S, according Equations (1) to (4). In the particle separator a filtering operation is used to separate small particles of the S formed. The out-flowing filtered Fe<sup>+2</sup>/EDTA

solution is regenerated into Fe<sup>+3</sup>/EDTA in a bubbling air column.

Samples of the inlet and outlet (or treated) biogas were taken during experimental tests. The compositions of these samples were determined by gas chromatography using a Porapak Q column in a 2000 Thermo Quest Varian model chromatograph. H<sub>2</sub>S removal, expressed as a percentage, was calculated by dividing the difference between the inlet and the outlet volume compositions by the inlet composition.

A synthetic biogas was used in all experiments. The composition of this biogas was very similar to that of a biogas from a UASB (Up-flow Anaerobic Sludge Biodigester) used to treat gelatine industry wastewater (Horikawa, 2001). Compositions of both biogases are presented in Table 1.

For safety and environmental reasons, in all experiments the treated biogas leaving the absorption column was washed with water in a packed column to remove residual traces of H<sub>2</sub>S.



**Figure 1:** Experimental rig for biogas purification

**Table 1: Biogas compositions in % of volume**

Gases	UASB* Biodigester	Synthetic Mixture
CH <sub>4</sub>	81.1	79.68
CO <sub>2</sub>	14.0	14.13
H <sub>2</sub> S	2.2	2.36
N <sub>2</sub> + O <sub>2</sub>	2.7	3.66

\*(Horikawa, 2001).

## RESULTS AND DISCUSSION

The first test was carried out in the experimental rig under batch operation conditions, using only the absorption column. The aim of this test was to verify the efficacy of the prepared catalyst solution for removing H<sub>2</sub>S and the behaviour of gases other than H<sub>2</sub>S and also to determine the catalyst deactivation

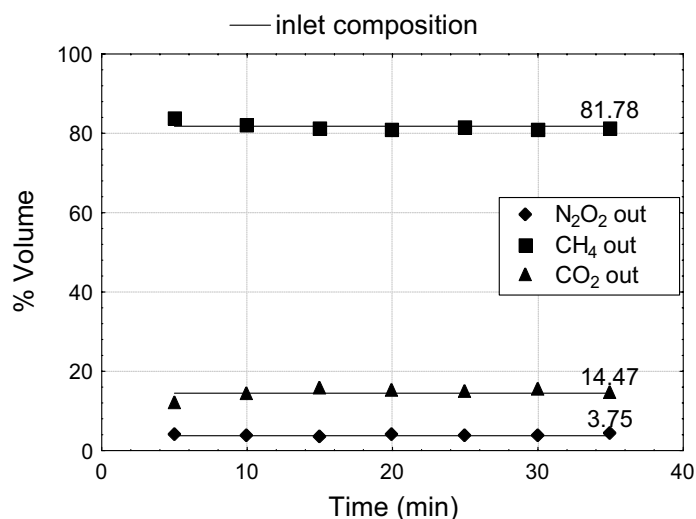
time. Results of this test, conducted using a volume of 500 ml of catalyst solution, are presented in Figures 2 and 3.

In Figure 2 the volumetric compositions are presented on an H<sub>2</sub>S-free basis. The straight lines represent the measured inlet composition of the biogas (81.78% CH<sub>4</sub>; 14.47% CO<sub>2</sub>; 3.75% NO<sub>2</sub> + O<sub>2</sub>), while the marked points are the compositions of

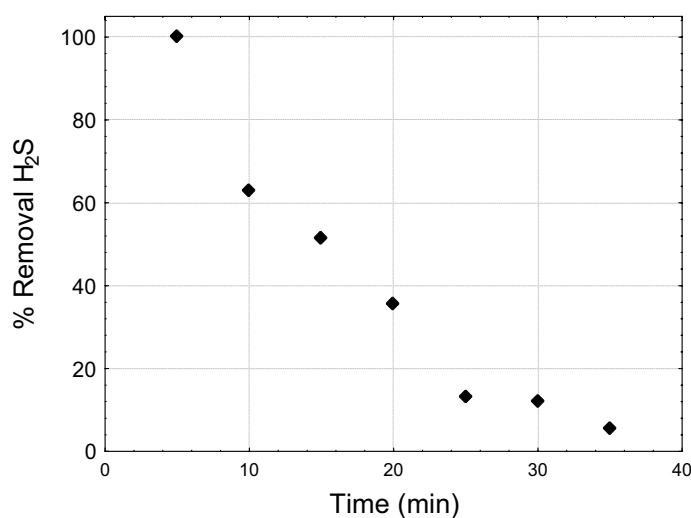
the absorber outlet biogas, measured according to elapsed time. Results in this figure demonstrate that volumetric compositions (without  $H_2S$ ) of gases other than  $H_2S$  are maintained constant, except for the component  $CO_2$ , which is slightly absorbed at the beginning of bubbling, thus increasing the outlet composition of the  $CH_4$ . After the saturation of the catalyst solution with the absorbed  $CO_2$  the outlet composition is restored to the inlet value.

The batch test demonstrated that the volume of solution used, containing 0.2 mol/L of Fe-EDTA catalyst, is effective in initially removing all  $H_2S$  present in the biogas. The catalytic solution begins to loose removal efficiency after 4 min and its complete deactivation occurs after 35 min., as illustrated in Figure 3.

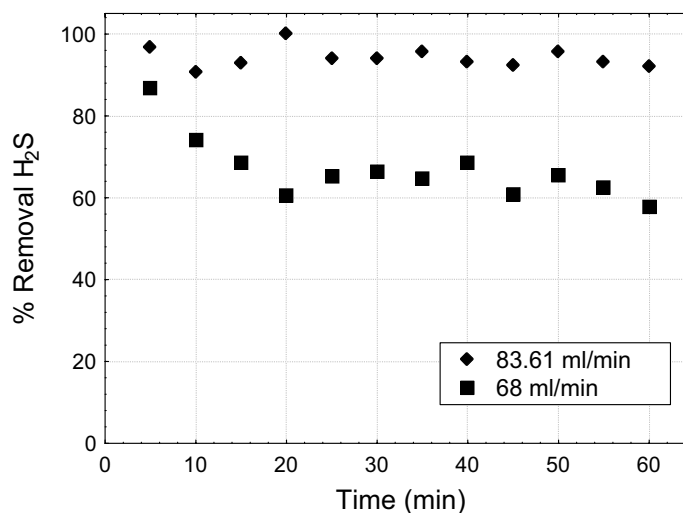
Choosing the deactivation time as the space-time (Levenspiel, 1994), flow-rates of the catalytic solution were estimated in order to obtain the required percentage of  $H_2S$  removal for a known biogas flow-rate, in continuous counter-current contact. The estimated flow-rates of 83 and 68 ml/min of catalytic solution were used in continuous mode operation experiments, for which results are presented in Figure 4. It can be seen in this figure that, for a biogas flow-rate of 1000 ml/min and 2.2 kgf/cm<sup>2</sup> pressure, approximately 90% and 70% of the  $H_2S$  can be removed with the catalytic solution flowing at 83 and 68 ml/min, respectively. This means that above a flow-rate of 83 ml/min or with an appropriate ratio of gas contacting phases, it is possible to achieve total removal of  $H_2S$ .



**Figure 2:** Inlet and outlet biogas composition of the absorption column (free base of  $H_2S$ ,  $G = 1000$  ml/min,  $P=2.2$  kgf/cm<sup>2</sup> – Batch experiment)



**Figure 3:**  $H_2S$  removal using Fe-EDTA solution ( $G= 1000$  ml/min,  $P=2.2$  kgf/cm<sup>2</sup> – Batch experiment)



**Figure 4:** H<sub>2</sub>S removal using Fe-EDTA solution  
(G = 1000 ml/min, P = 2.2 kgf/cm<sup>2</sup>)

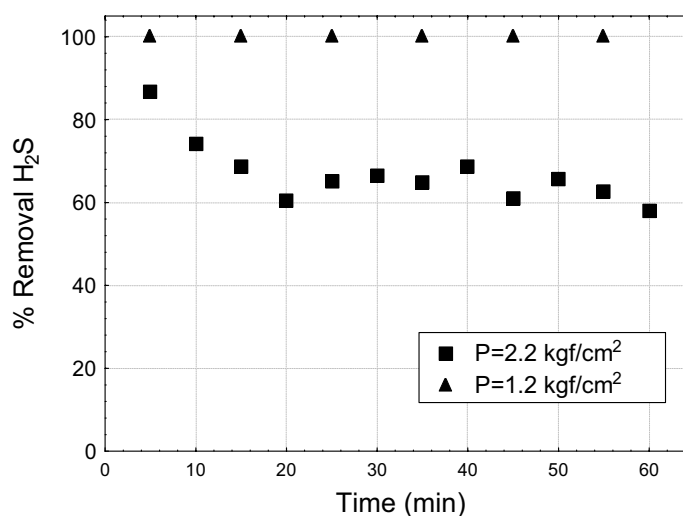
Figure 5 shows the effect of inlet biogas pressure on the removal of H<sub>2</sub>S through counter-current continuous absorption. As expected for a lower inlet pressure, which corresponds to a lower H<sub>2</sub>S concentration, a higher percentage of H<sub>2</sub>S removal is achieved more easily.

Similarly to the batch test, for continuous counter current contacting the outlet volumetric composition (H<sub>2</sub>S free base) of all gases was compared to the respective inlet value. The results of this comparison allowed the observation that CO<sub>2</sub> was continuously absorbed into the catalytic solution, while no absorption was observed for other gases than H<sub>2</sub>S.

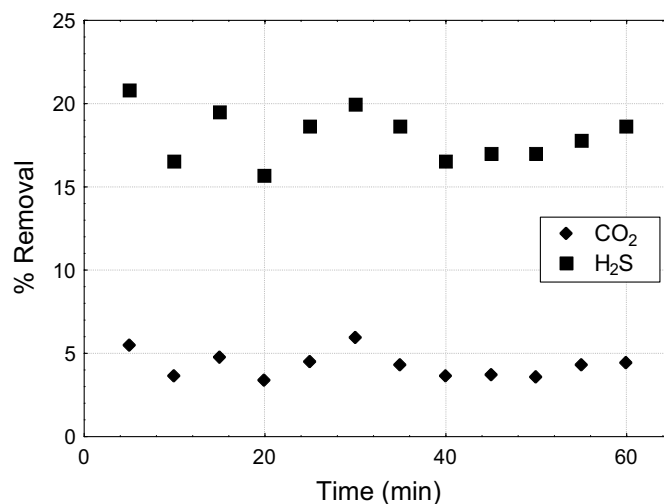
Physical absorption of biogas components was carried out in the experimental rig using distilled water under the same experimental conditions as

those for absorption into Fe-EDTA catalyst solution. These results, as presented in Figure 6, show a higher removal of H<sub>2</sub>S than of CO<sub>2</sub>. No physical absorption into water was verified for other biogas components.

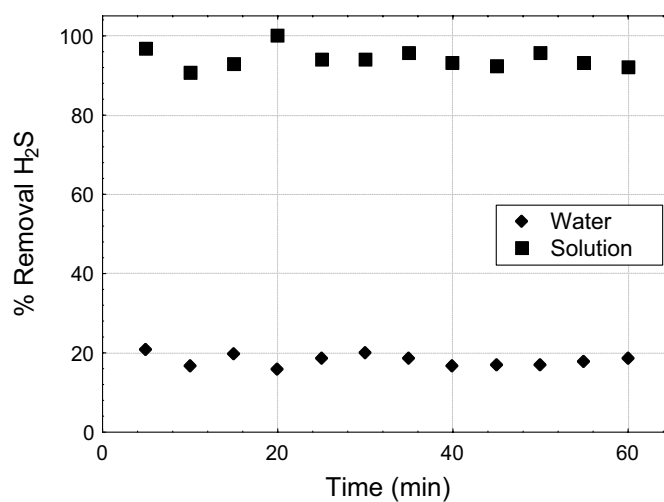
Figures 7 and 8 contain comparisons of the absorption into distilled water and into the Fe-EDTA catalytic solution for H<sub>2</sub>S and CO<sub>2</sub>, respectively. In Figure 7 the increase in the rate of absorption of H<sub>2</sub>S caused by the chemical reaction is evident, thus demonstrating the effectiveness of the prepared catalyst. In Figure 8, no chemical reaction seems to take place in the absorption of CO<sub>2</sub> into the Fe-EDTA solution; even so, increased removal is observed, which may be due to an increase in CO<sub>2</sub> solubility in the Fe-EDTA solution.



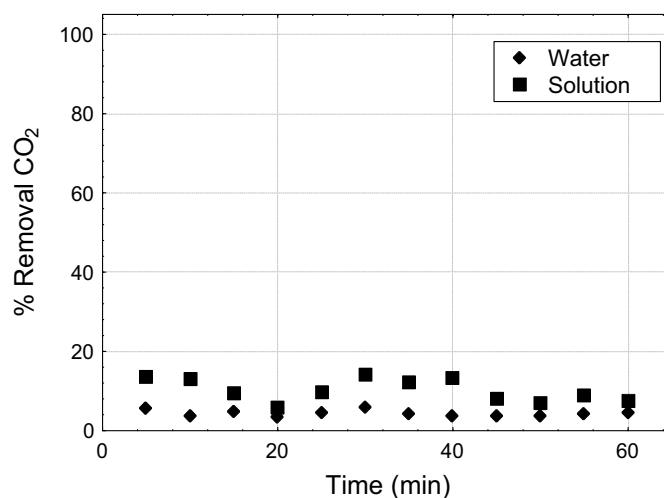
**Figure 5:** H<sub>2</sub>S removal using Fe-EDTA solution  
(G = 1000 ml/min, L = 68 ml/min)



**Figure 6:** Absorption of CO<sub>2</sub> and H<sub>2</sub>S into pure water (G = 1000 ml/min, P=2.2 kgf/cm<sup>2</sup>, L = 88 ml/min)



**Figure 7:** Removal of H<sub>2</sub>S in distilled water and in Fe-EDTA solution (G = 1000 ml/min, P=2.2 kgf/cm<sup>2</sup>, L<sub>water</sub> = 88 ml/min, L<sub>solution</sub> = 83 ml/min)



**Figure 8:** Absorption of CO<sub>2</sub> into pure water and in Fe-EDTA solution (G = 1000 ml/min, P=2.2 kgf/cm<sup>2</sup>, L<sub>water</sub> = 88 ml/min, L<sub>solution</sub> = 83 ml/min)

Froning et al. (in Kohl and Riesenfeld, 1985) obtained the following equations to estimate the distribution coefficient K from experimental data on liquid-vapor equilibrium for the H<sub>2</sub>S – CO<sub>2</sub> – CH<sub>4</sub> – water system:

$$K_{\text{CH}_4} = \frac{306000}{P} + \frac{2.19}{T} + 3910 \frac{T}{P} - 14.5 X_{\text{AG}} - 121.6 \phi$$

$$K_{\text{CO}_2} = \frac{-3500}{P} + 0.12 T + 360 \frac{T}{P} + 8.3 X_{\text{AG}} - 5825 \frac{\phi}{P} \quad (8)$$

$$K_{\text{H}_2\text{S}} = 4.53 - \frac{1087}{T} + 110 \frac{T}{P} + 4.65 X_{\text{AG}}$$

In Equation (8) P is system pressure (psia), T the temperature (°F), X<sub>AG</sub> the molar fraction of CO<sub>2</sub> plus H<sub>2</sub>S in the gas phase, and φ the ratio between the molar fraction of H<sub>2</sub>S in the gas phase and the value of X<sub>AG</sub>.

In Table 2 the values of K for CO<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub>, estimated by means of the set of Equations (8) for conditions used in the absorption of the biogas into pure water, are presented. In making these estimates the small amounts of N<sub>2</sub> and O<sub>2</sub> gases were incorporated into that of CH<sub>4</sub>.

According to Coulson and Richardson (1991), by

using Equation (9) it is possible to estimate the composition of gases leaving the absorber from K values, if it is assumed that equilibrium has been reached.

$$G_m(Y_1 - Y) = L_m(X_1 - X) \quad (9)$$

where G<sub>m</sub> and L<sub>m</sub> are the molar flow-rates for the gas and liquid phases and the pairs (X<sub>1</sub>, Y<sub>1</sub>) and (X, Y) are the liquid and gas compositions at the bottom and top of the absorber column, respectively.

From experimental values of G<sub>m</sub> = 9.51.10<sup>-2</sup> mol/min and L<sub>m</sub> = 4.89 mol/min the values of the exit compositions (Y<sub>out-equil</sub>) were estimated by assuming equilibrium was reached in the absorption of biogas into water. In Table 3 these values together with those obtained experimentally are presented.

Data in Table 3 show that values of Y<sub>out</sub> obtained under the assumption of equilibrium are smaller than the experimental values. This demonstrates that equilibrium was not reached in the experiments. However, it can be observed that, as the difference between the values is quite small, the experimental conditions used for contacting liquid and gas phases by means of bubbling have provided quite a good mass transfer.

**Table 2: Values of the distribution coefficient K in pure water**

Compound	(y)	K (y/x)
CH <sub>4</sub>	0.8351	19380.8
CO <sub>2</sub>	0.1413	757.9
H <sub>2</sub> S	0.0236	261.8

**Table 3: Physical absorption of biogas compound into pure water**

Compound	Y <sub>out-equil.</sub>	Y <sub>out-exp</sub>
CH <sub>4</sub>	0.8478	0.8457
CO <sub>2</sub>	0.1317	0.1351
H <sub>2</sub> S	0.0189	0.0192

## CONCLUSIONS

Results obtained in this work demonstrate that it is possible to achieve the complete removal of H<sub>2</sub>S from biogas using an iron-chelated process that operates at ambient temperature. In this process the total removal of H<sub>2</sub>S depends on the use of the adequate ratio of gas to liquid flow-rates.

Results presented show that the almost selective increased rate of H<sub>2</sub>S removal is not the only advantage of this process of chemical absorption. The main advantage is the transformation of H<sub>2</sub>S into S thereby eliminating the pollution potential of H<sub>2</sub>S.

The catalytic solution Fe-EDTA used in the experiment was prepared using FeBr<sub>2</sub>, a salt different from that reported in the literature. The catalytic

solution prepared based on this salt was quite effective in removal of the H<sub>2</sub>S gas. Results demonstrate that this catalytic solution is able to absorb more CO<sub>2</sub> than pure water.

### NOMENCLATURE

X <sub>AG</sub>	Molar fraction of CO <sub>2</sub> plus H <sub>2</sub> S in the gas phase
G <sub>m</sub>	Molar flow-rate for the gas phase (mol/min)
K	Distribution coefficient (Y/X)
L <sub>m</sub>	Molar flow-rate for the liquid phase (mol/min)
P	System pressure (psia)
φ	Ratio of molar fraction of H <sub>2</sub> S to molar fraction of CO <sub>2</sub> plus H <sub>2</sub> S in the gas phase
T	Temperature (°F);
X	Composition in the liquid phase
Y	Composition in the gas phase

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