

H₂S AND CO₂ FILTRATION OF BIOGAS USED IN INTERNAL COMBUSTION ENGINES FOR POWER GENERATION

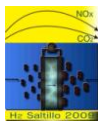
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ABSTRACT

Currently, there is an increasing interest in connecting thousands of small electrical plants powered by renewable energy sources to national electrical grids. The use of biogas as fuel for internal combustion engines connected to an electric generator is emerging as one of the most attractive alternatives because of its very low cost benefit ratio and very high positive impact on the environment. However, the use of biogas to generate electricity has been limited by its high content of H₂S (~3500 ppm) and CO₂ (~40%). CO₂ presence reduces the energetic density of the fuel and therefore the power output of the system. The high content of H₂S corrodes important components of the engine like the combustion chamber, bronze gears and the exhaust system. This work aims to design and manufacture a low-cost industrial filter for this application. Among the different available methodologies, CaO, NaOH and amines were selected as the most appropriate for a typical farm application of 100 kW electric generations. Since there is not reported data for the H₂S absorbing capacity of these substances, it was proposed to measure it by means of a bubbler. It is an experimental set up where the gas stream passes through a fixed amount of the absorbing substance until it becomes saturated. The absorbing capacity is determined as the amount of substance being trapped divided by the mass of the absorbing substance being used. Results showed an absorbing capacity of 2.8, 41.4 and 124.8 g of H₂S per Kg of NaOH, CaO and monoethanolamine respectively. A gas absorbing system of amines was designed and manufactured for H₂S and CO₂ biogas filtration. Three different types of amines were evaluated: Monoethanolamine, Diethanolamine, and methyldiethanolamine. Results show that all the amines require a ratio of amines to biogas flow of 0.7 to obtain a 95% of H₂S filtering efficiency. This data represent only a 30% of H₂S mass transfer efficiency of the filter when it is compared against the mass transfer expected under quasi equilibrium conditions. Work is under way to design a high efficiency amine column for biogas treatment.



1. - Introduction

Biogas is a fuel derived from organic waste under anaerobic conditions¹. Anaerobic processes generate a fuel with medium-energy content (~ 22 MJ / kg). They also reduce pollution problems, control odors, reduce greenhouse emissions and generate high quality natural fertilizer. Currently thousands of farms have implemented biodigesters to reduce pollution generated by their organic waste. However, in most of the cases, the biogas produced is being released to the atmosphere or burned to control the emission of the methane present in the biogas. Methane has a greenhouse effect 25 times greater than CO_2 ².

Currently there is a growing interest in using this biogas to generate electrical power in thousands of small stations connected to a national electrical grid. It is also considered to interconnect the hundreds of the existing small aero generators and solar power plants³. Even though, there are still several technical issues to be resolved⁴, this alternative is being considered as the best alternative to bring electricity to the rural communities located far away from the large urban centers. Biogas electrical power systems include a container to mix and homogenize the organic waste produced in farms and some industrial processes. Organic matter is then fed in to a biodigester where the microbiological processes produce biogas. Then the fuel is fed into an internal combustion engine. Finally, the engine is mechanically connected to an electric generator. Sometimes these systems include an attachment that allows selling the excess energy produced to the electrical grid.

Biogas is made up mainly of methane (CH_4), carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Its composition varies depending of the type of biomass used. Table 1 shows typical compositions. The biogas calorific power is proportional to the CH_4 concentration. To be used as fuel for internal combustion engines, it has been recommended a CH_4 concentration greater than 70%. However CO_2 has a typical concentration of $\sim 40\%$ ⁵. This high concentration of CO_2 reduces the power output of the engine by the same percentage as its concentration, limiting the use of biogas in electrical power plants driven by internal combustion engines. The high content of H_2S (~ 3500 ppm) is responsible for the corrosive problems that undergo the metallic parts inside the engine. The H_2S is an inorganic acid that attacks the surface of the metal when they are placed in direct contact. The SSC is the most common corrosive mechanism that appears when the metal makes contact with H_2S . Sulfides of iron and atomic hydrogen are formed in this process. It is considered that this mechanism starts to take place when the H_2S concentration is higher than 50 ppm⁶. The admission valves and the exhaust system are also attacked by the presence of H_2S . The degree of deterioration of the engines varies considerably. Results obtained experimentally on this regard are contradictory⁷. It has been found that H_2S in biogas diminishes the life time of the engine by 10 to 15%⁸. Finally, time between oil changes is reduced since lubricant oils contain H_2S and corrosion inhibitors to protect the engine. It increases the

maintenance cost of the engine. Farmers consider the high maintenance cost as the main withdraw of these types of systems.

Table I. Biogas composition ⁹

| Component | Composition (%) | | | |
|-----------------------|--------------------|---------------|------------------|---------------------|
| | Agricultural waste | Sewage sludge | Industrial waste | Desired composition |
| CH₄ | 50-80% | 50-80% | 50-70% | >70% |
| CO₂ | 30-50% | 20-50% | 30-50% | <30% |
| H₂O | Saturation | Saturation | Saturation | N/S |
| H₂ | 0-2% | 0-5% | 0-2% | N/S |
| H₂S | 0.001-0.70 | 0-1 | 0-8 | <0.02 |
| NH₃ | Traces | Traces | Traces | N/S |
| CO | 0-1% | 0-1% | 0-1% | N/S |
| N₂ | 0-1% | 0-3% | 0-1% | N/S |
| O₂ | 0-1% | 0-1% | 0-1% | N/S |

Therefore there is a need for a CO₂ and H₂S biogas filter that allows using this biofuel in internal combustion engines. Considering a typical application of 100 kW of electrical power generation, the design specifications for such filter are: H₂S concentration at lower than 100 ppm ^{5,6}, CO₂ concentration lower than 10% ¹⁰, biogas volumetric flow of 66 m³/hr and minimum pressure drop across the filter. Literature reports several alternatives to filter H₂S and CO₂ from gas streams.

Methodologies for H₂S elimination are classified in regenerative processes, non-regenerative and biological ones. Figure 1 illustrates this classification. To select one of these methodologies it should be taken into account: a) the amount of biogas to treat, b) percentage of removal required, c) disposition of the saturated reagent or viability to regenerate it and d) the need of sulphur recovery ¹¹. Table 2 compares these alternatives. CO₂ filtration has become of great interest to sequestrate greenhouse gas emissions in thermal power plants ¹². Table 3 compares the different existing technologies

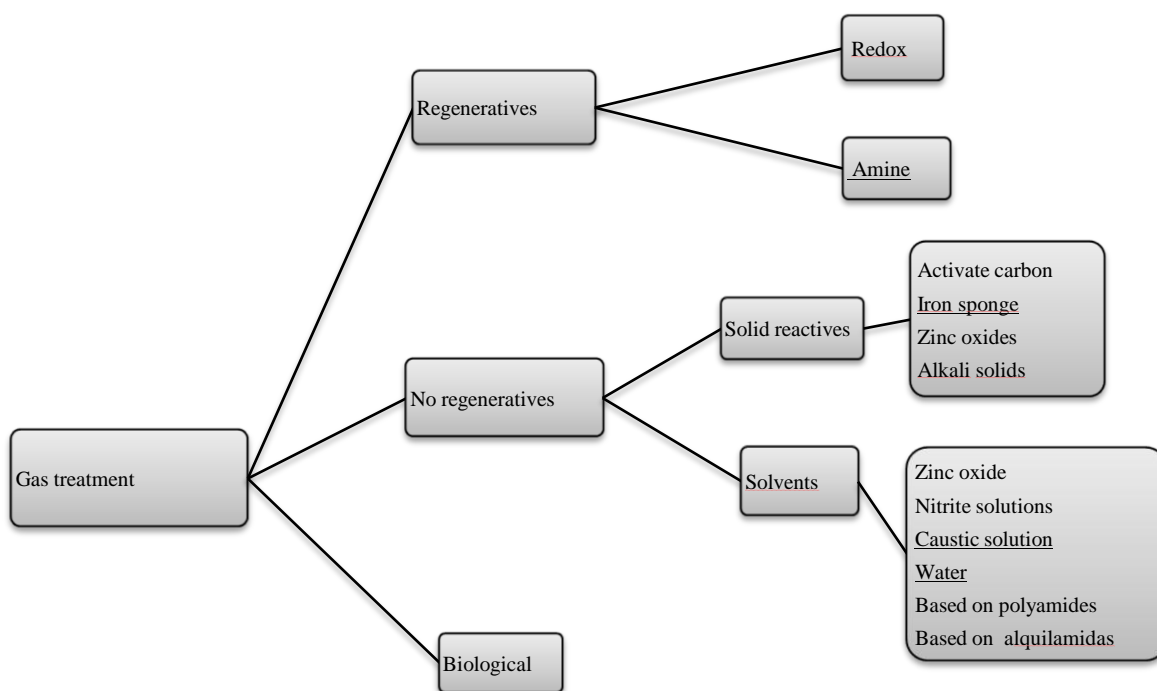


Figure 1. Alternatives to filter H_2S from gas streams¹¹

Table 2. Alternatives to filter H_2S from gas streams¹³

| Alternative | Range of application | Advantages | Disadvantages |
|--------------------------------|---|--|--|
| Solid reactive: Iron sponge | It's useful for flows between 0.3-500 kg/day of H_2S . | Low cost, high selectivity, operational flexibility and simple disposal. | It must be replaced continuously. |
| Liquid reactive | Low H_2S concentration 0-300 ppm. | Reduce H_2S composition to sulfur bars. Low costs. | Difficult dispersion and disposal. |
| Claus | More than 14 ton/day of H_2S . | H_2S becomes in high quality sulfur. | Requires supervision, high operational costs and high complexity. |
| Redox | Between 0.5-15 ton/day of H_2S . | H_2S becomes in elementary sulfur | Requires specialized supervision, Low quality product, high pressure problems. |
| Amines | H_2S concentrations higher than 30 ppm and gas flows higher than 10000 m ³ /day. | High efficiencies on H_2S and CO_2 removal. | Amine stream with high content of H_2S , operation problems, corrosion, amine degradation. |
| Biological | It's useful for streams between 50-20000 kg/day of H_2S . | H_2S becomes in elementary sulfur | Incomplete H_2S absorption, low quality product, strict control of bacterial conditions |

Table 3. Alternatives to filter CO₂ from gas streams ¹⁴

| Alternative | Range of application | Advantages | Disadvantages |
|--------------------------------|---|---|---|
| High pressure, low temperature | Gas flow between 0-10.000 m ³ /day | Low cost | High pressure requirements. |
| Membrane separation | Gas flow higher than 50.000 m ³ /day | High selectivity, | It requires specialized supervision, high cost. |
| Caustic solutions | Gas flow between 0-200.000 m ³ /day | High selectivity and operational flexibility. | High reactive consumption, difficult disposal |
| Activate Carbon | Gas flow lower than 1000 m ³ /day | Low cost | Reactive saturation, high pressure regeneration |

Present work aims to explore the use of these technologies for biogas treatment prior to be used in internal combustion engines for electrical power generation. Comparing table 2 and 3 it can be concluded that for the present application the alternatives of caustic solutions (CaO and NaOH) and amines are the most suitable to filter both H₂S and CO₂ from the biogas.

2. - Experimental work

To evaluate the capacity of the solvents mentioned above in sequestrating H₂S and CO₂ from gas streams, Henry's law was used. It states than under equilibrium conditions ^{15,16}:

$$P_A = y_A \cdot P = H_A \cdot x_A \quad (1)$$

Where:

P_A Partial pressure of component A in gas phase

P Total pressure

H_A Henry constant of component A

y_A Molar concentration of component A in gas phase

x_A Mass concentration of component A in liquid phase

Therefore Henry's constant defines the capacity of a solvent to filter gas phase components. Unfortunately literature does not report this constant for the case of caustic solutions nor amines. As an alternative it was proposed to evaluate the performance of these substances using the gas bubbler setup illustrated in figure 2.

This set up looks for a full interaction of the gas stream with the absorbing substance such that it can be assumed thermodynamic equilibrium at the liquid-gas inter phase. Experiments are conducted under standard conditions of pressure and temperature (101 kPa, 25°C). To ensure constant temperature for exothermic or endothermic reactions the set up is placed inside a controlled temperature water bath.

Temperature, pressure, gas flow and degree of water dilution of the absorbing substance were measured. The amount of solution in the bubbler is kept constant in 1.0 L. The H_2S concentration at the inlet and outlet of the bubbler is measured by means of gas detector tubes with a H_2S resolution of 10 ppm.

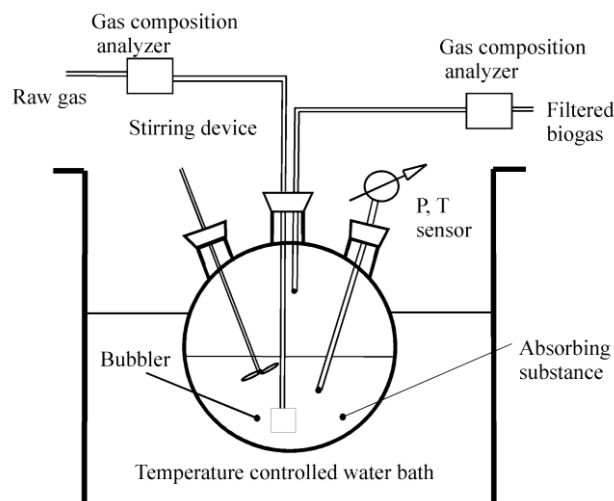


Figure 2. Setup used to evaluate the H_2S removal capacity of different absorbing solutions.

CaO solution: It is considered as the conventional method for gas treatment of sulphur components. It is a low cost, non regenerative method, for the absorption of H_2S and CO_2 . During the process the following reactions take place ¹:



NaOH solution: It is also a non regenerative method. The absorption of H₂S takes place through the following reaction ¹:



Amine treatment: It is a regenerative method. Monoethanolamine was used for these types of tests. The absorption process of H₂S and CO₂ is carried out through the following reactions ¹⁷:

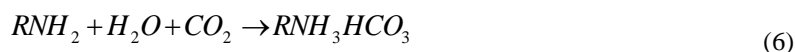


Figure 3 shows the results obtained in terms of filtering efficiency vs. time. H₂S filtering efficiency η_f is defined as:

$$\eta_f = \frac{y_i - y_o}{y_i} \quad (8)$$

Where

y_i H₂S molar concentration at the inlet

y_o H₂S molar concentration at the outlet

Figure 3 shows that any of the solutions can reach H₂S filtering efficiencies as close to 100% as desired. The difference is in the ratio of the gas flow and the mass of absorbing substance required. Figure 3 also shows this absorbing capacity in terms of the saturation time of a fix amount of absorbing substance filtering a constant volumetric flow of biogas with a fixed initial concentration of H₂S. Saturation time of the absorbing substance (t_s) is measured as the time where the filtering efficiency in the bubbler becomes lower than 95%.

In this regard, figure 3 shows that the amine presents the best performance among the absorbing substance being tested. It was obtained that the saturation time is less than a minute, 15 and 45 minutes for NaOH, CaO and amine respectively.

However the time for saturation depends on the ratio of biogas flow and the amount of absorbing substance within the bubbler. To take into account this variable here it is proposed to define absorbing capacity under quasi-equilibrium conditions ¹⁸($A_{c,e}$) as:

$$A_{c,e} = \frac{M}{R^o T m} \int_0^{t_s} (y_o - y_i) Q dt \quad (9)$$

Where:

- M H_2S molecular weight
- R^o Universal gas constant
- T Absolute temperature
- m Mass of the absorbing substance within the bubbler
- Q Gas volumetric flow measured at standard conditions

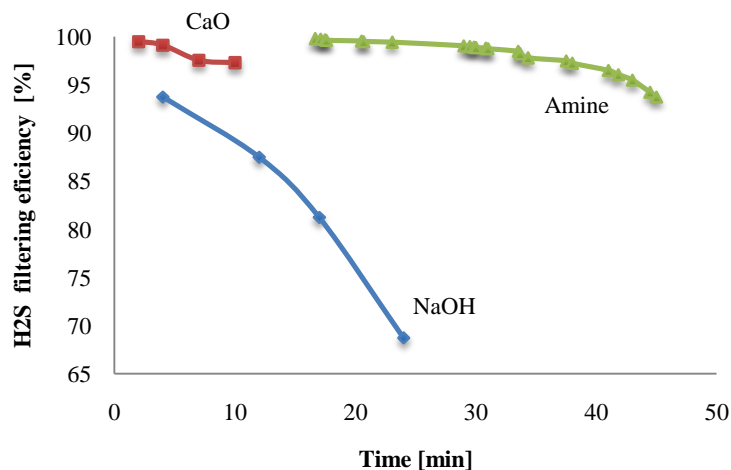


Figure 3. H_2S absorption of 1 SLPM biogas stream in 1.0 L of absorbing substance inside a bubbler at standard conditions.

This definition represents an absorbing capacity of 2.8, 41.4 and 124.8 g of H_2S per Kg of NaOH, CaO and monoethanolamine respectively.

3. - Design and construction of an H₂S and CO₂ absorbing column

Previous results were taken into account to design a H₂S and CO₂ filter of amines. Usually gas absorbing systems are designed as a counter flow column where the liquid phase substance flow by gravity the top to the bottom of the column and the gas phase flow from the bottom towards the top of the column. The column is fully packed with inert rashing rings or small inert spheres to increase the contact area between the gas and liquid phases¹⁸. In addition several disks are incorporated for flow orientation to ensure the uniform distribution of both flows across the column. The materials of the column are selected taking into account the corrosive working conditions and temperature variations along the column. A small turbine is installed at the exit of the amine column to ensure the biogas flow along the column.

It was included a second column for water washing the biogas after leaving the amine column. It was also considered a regeneration stage for the amines as it is illustrated in figure 4. It consists of a third column operating with water vapor at 120 °C. The gas absorbing systems was instrumented with temperature and pressure sensors at the inlet and outlet of the column. Flow meters were used for both the biogas and the liquid phase absorbing substance. Biogas H₂S concentration was measured at the inlet and outlet of the column by gas detector tubes with a resolution of 10 ppm. Three different types of amines were evaluated: Mono ethanolamine (MEA), Diethanolamine (DEA), and Methyl di ethanolamine (MDEA). All amines were diluted at 30% in water as recommended by manufacturer¹⁴.

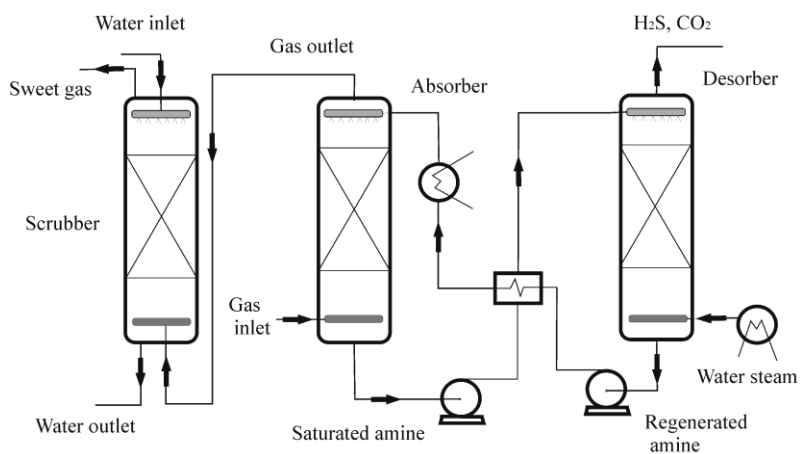


Figure 4. Gas absorbing systems of amines built for the H₂S and CO₂ filtration of biogas

Figure 5 shows the results obtained in terms of H₂S filtering efficiency vs. the flow ratio of amine and biogas measured at standard conditions. It shows that the different types of amines exhibit a similar behavior. It also shows that all amines require a flow ratio of 0.7 to reach efficiencies of 95%. This result means that the first version of the amine column designed under standard procedures of mass transfer has a low efficiency of mass transfer for this application.

Here, it is proposed to define the mass transfer efficiency of the column as:

$$\eta_c = \frac{A_{c,e}}{A_{c,r}} \quad (10)$$

Where:

$A_{c,r}$ Real absorbing capacity of the column

Using this definition, the manufactured amine column shows a H₂S mass transfer efficiency of 30%. Work is under way to design a high efficiency amine column for biogas treatment.

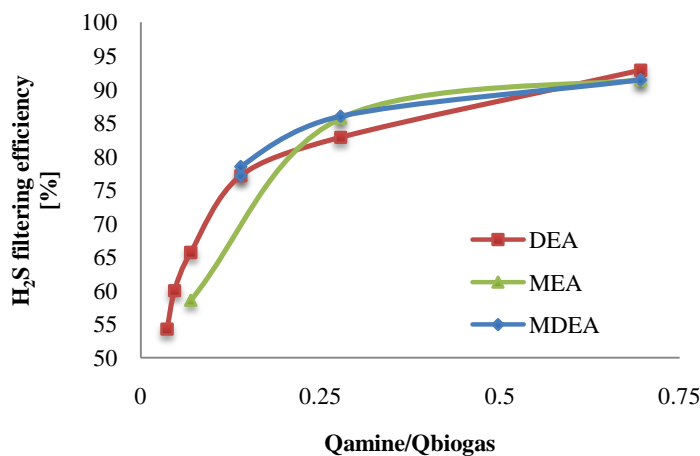
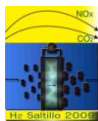


Figure 5. H₂S filtering efficiency of the amine column for different ratios of amine to biogas flow

4. - Conclusions

The use of biogas to generate electricity by power plants moved by internal combustion engines has been limited by the high content of H₂S (~3500 ppm) and CO₂ (~40%).

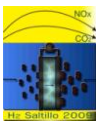


Several methodologies have been developed to filter these two components from gas streams. None of them have been used for the treatment of both H_2S and CO_2 in high volumes of biogas. Evaluating these methodologies in terms of their advantages, disadvantages and range of applications, CaO , NaOH and amines were selected as the most appropriate for a typical farm application of 100 kW of electrical power generation. Since there is not reported data of the H_2S absorbing capacity of these substances, it was proposed to measure it by means of a bubbler. It is an experimental set up where the gas stream passes through a fixed amount of the absorbing substance under thermodynamic quasi equilibrium conditions, until it becomes saturated. The absorbing capacity is determined as the amount of substance being trapped divided by the mass of the absorbing substance being used. Results showed an absorbing capacity of 2.8, 41.4 and 124.8 g of H_2S per Kg of NaOH , CaO and monoethanolamine respectively.

A gas absorbing systems of amines was also designed and manufactured for the H_2S and CO_2 biogas filtration. It consists of a counter flow amine column where biogas enters at the bottom and flows towards the top of the column interacting with liquid phase amine. Biogas is then water scrubbed in a second column to eliminate impurities due to the amine treatment. It was also included a third column operating with water vapor at 120 °C where amines are recovered. Three different types of amines were evaluated: Monoethanolamine, Diethanolamine, and Methyldiethanol amine. Results show that all the amines require a ratio of amines to biogas flow of 0.7 to obtain a 95% of H_2S filtering efficiency. This data represents only a 30% of H_2S mass transfer efficiency of the filter when it is compared against the mass transfer expected under quasi equilibrium conditions. Work is under way to design a high efficiency amine column for biogas treatment.

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