A Study on H_2S efficiency through membrane technique and Activated Carbon (CKC) Performance Improvement with Oxygen

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Abstract- **In this paper we are discuss H2S efficiency through membrane technique and Activated Carbon (CKC) Performance Improvement with Oxygen. Once the gas is compressed to high methane concentration and high pressure, it can be used as a vehicle fuel or other use. Since the gas mainly contains methane, the calorific value also increases. Before the purification process, the amount of carbon dioxide in the raw biogas was 48.8% which was quite high. The presence of CO2 in biogas reduces the energy value. As the CO2 present in biogas, the CH4 ratio will decrease. This situation leads to poor use of biogas for energy production such as for transport fuel or domestic cooking.**

Index terms- **Fuel, Energy, Ratio, Production etc**

I.INTRODUCTION

Fig. 1.1 shows the biogas components after purification. Before the purification process, the amount of carbon dioxide in the raw biogas was 48.8% which was quite high. The presence of CO2 in biogas reduces the energy value. As the CO2 present in biogas, the CH4 ratio will decrease. This situation leads to poor use of biogas for energy production such as for transport fuel or domestic cooking. For those purposes, biogas should have a methane concentration of up to 98 and 1% and is called CH4-enriched biogas [8]. Once the gas is compressed to high methane concentration and high pressure, it can be used as a vehicle fuel or other use. Since the gas mainly contains methane, the calorific value also increases. Biogas produced from AD released some H2S at a significant amount (263 ppm) as shown in Figure 1.1. The presence of H2S in the atmosphere should satisfy a low toxic limit (at least 10 ppm) [9]. It is an extremely dangerous gas due to H2S, very

toxic, corrosive that is harmful to both health and the environment. Exposure to very high H2S concentration can also result in death. Therefore, in addition to CO2, H2S must also be reduced or removed from biogas. The research yielded very promising results where, after purification, all H2S gas was removed from the crude biogas
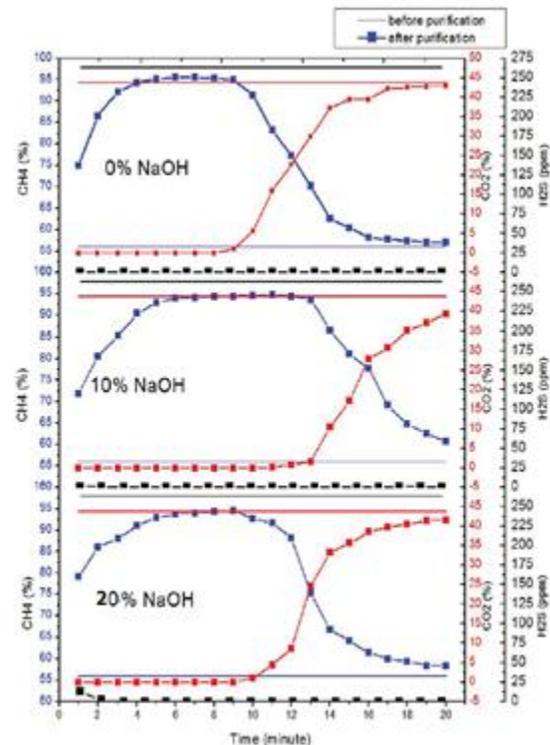
Figure 1.1: Unpurified and purified biogas concentrations with 0%, 10% , and 20% NaOH

It was found that CO2 and H2S concentrations were significantly reduced through biogas uptake by the use of active zeolite with and without NaOH at different concentrations. Up to 100% reduction of

CO2 and H2S was achieved in the biogas scrubbing method. The purification performance was further improved with the use of NaOH. This showed that with 5% NaOH, 0% CO2 was kept in pure biogas for eleven minutes, which was better than 15% NaOH and without NaOH. However, as seen from the graph, the concentration of CO2 increased. After the eleventh minute, the CO2 concentration increases continuously, reaching slightly below the CO2 concentrations of the raw biogas. Similar trends were obtained on other experimental variables. However, in experimental studies for all NaOH concentrations on the other hand, the concentration of H2S remained zero. The ability of adsorbed CO2 in zeolite micropores was supported by the tendency of CH4 to avoid CH [3] as a result of low molecular transport rates inside zeolite crystals. This is due to the low polarity characteristics of CH4 [9]. This phenomenon provides evidence that hydrophilic zeolite, such as natural zeolite, has a high affinity for polar molecules such as CO2. The presence of CO2 inside the zeolite micropores serves to eject CH4 molecules from the structure. The schematic shape of the CO2 molecular structure allows the molecules to be arranged regularly inside the pores. However, after most of the zeolite holes are filled by CO2 molecules, the adsorption capacity drops significantly [10, 11]. This testifies that the adsorption process has a time limit.
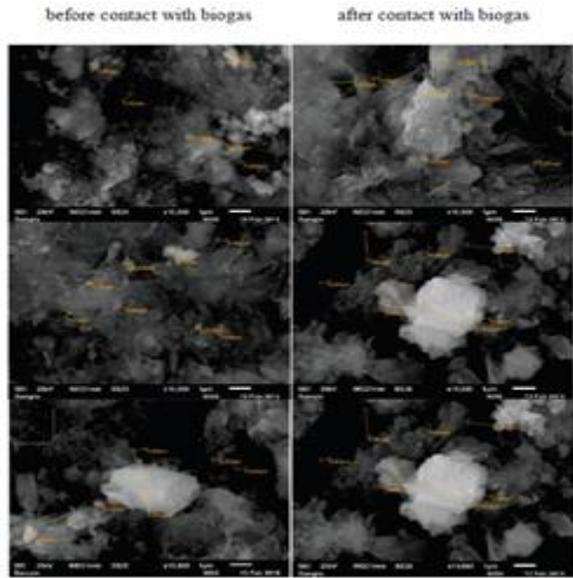
Figure 1.2: Surface morphology of activated natural zeolite before and after contact with biogas a and b). 0% NaOH, c and d). 10% NaOH, e and f). 20% NaOH

II. H2S EFFICIENCY THROUGH MEMBRANE TECHNIQUE

Based on the review and discussion of the above information, various adsorption, absorption, and membrane technologies have advantages and disadvantages that lead to optimal efficiency and minimal cost for operating processes. However, hollow fibers show the best way to remove H2S through membrane gas adsorber (HFMGA) membrane technologies.

Therefore, Table 1.1 shows a summary of the techniques and techniques used in biogas purification, including their advantages and disadvantages.

Table 1.1: H2S efficiency through membrane technique

Technique	Efficiency	References
High pressure RO (600 kpa)	58 vol.%	Dolejs et al. (2014)
Low pressure RO (500 kpa)	45 vol.%	Wellinger et al. (2005)
Micro-porous hydrophobic gas-liquid absorption membrane -High pressure -Low temperature (30 °C)	99%	Mahdavian et al. (2012)
Hollow fibers membrane gas adsorber (HFMGA) -Pressure: 10 atm	100%	Mahdavian et al. (2012)

Table 1.2: Advantages and disadvantages of technologies used for H2S removal

Method	Advantages	References	Disadvantages	References
1)Absorption Amine	High removal efficiency -Regenerable	Mckinsey (2003)	- Portion of amine gas is either lost or degraded - Expensive process - Intensive energy to regenerate or replace the solution -Complicated flow scheme - Foaming problems - Other steps required for disposal of foul regeneration	- Wang et al. (2008) - Mckinsey (2003)
- Fe2(S	Complete H2S	- Kim et al.	- Additional chemical input	- Zhao et al.

O4)	removal - High efficiency and reaction rate compared with the water scrubbing - Use in industrial application and natural gas purification - Low energy consumption	(2004) - Palmeri et al. (2008) - Ebrahimi et al. (2003)	needed - Pre-treatment of waste	(2010)
2) Adsorption - Chemicals	Dehumidify gas - Remove odor or pollutant from stream - Recover valuable solvent vapors from the stream - Parameter of temperature and pressure affected the high efficiency - Low cost - Low energy consumption - Catalytic carbon is easy to operate - Have lower space and maintenance requirements	- Wark et al. (1998) - Mohammadtaghi et al. (2012)	- Additional chemical inputs needed - High cost of activated carbon	- De Hullu et al. (2008)
3) Me	Compact process in	De Hullu	- Low methane yield	- De Hullu

mbrane - Conventional method - RO membrane using TFC	light in weight - Low energy consumption - Low-maintenance requirement - Easy processing - High efficiency of H2S at permeate - High selectivity - Low CH4 at permeate	et al. (2008) - Dolejs et al. (2014)	- High membrane cost - Less expensive	et al. (2008) - Dolejs et al. (2014)

3) Membrane
- Conventional method
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III. ACTIVATED CARBON (CKC) PERFORMANCE IMPROVEMENT WITH OXYGEN

According to the literature [8,5], trace concentrations of oxygen in biogas play an important role in H2S adsorption. Depending on the type of carbon, the unit of correction is subject to change. This behavior was not studied for supposed carbon. Given the same "boundary" conditions always used in the SMAT clean-up section (L / D = 1.7; biogas velocity = 0.038 m / s), the removal results are shown in Table 1.3.

Table 1.3: Results for removal of H2S with oxygen

% (vol.) Oxygen	Weight (g)	Breakthrough Time (h)	Adsorption Capacity (mgs/g$_{AC}$)
0	12.5	8.93 ± 0.2	1.16 ± 2%
0.1	12.6	29.2 ± 0.3	3.72 ± 3%
0.3	12.5	31.35 ± 0.3	4.08 ± 4%
0.5	12.7	36.41 ± 0.2	4.74 ± 3%

The sample weight ranges from 12.5 to 12.7 g, since we have fixed L/D to 1.7. The breakthrough time was calculated considering Equation (1), where the breakthrough time is obtained from the Lab view program
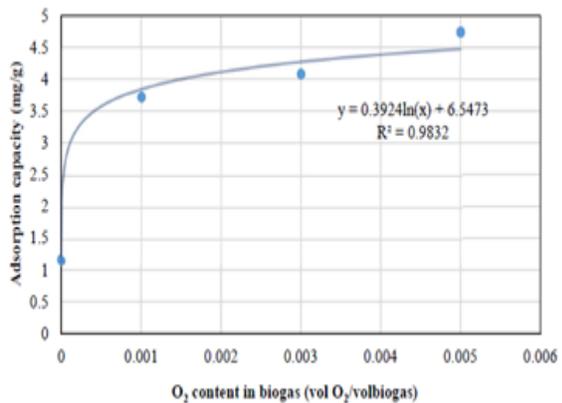
Figure 1.3: Experimental correlation for adsorption with CKC at different % (vol.) of oxygen.

Starting from these experimental data, an experimental correlation was detailed, as shown in Figure 1.3. An approximate logarithmic correlation between oxygen percentage and adsorption capacity was found with $R2 = 0.9832$.

Activated carbon provides a catalytic surface for oxidation of elemental sulfur and sulfate, greatly enhancing the removal efficiency of H2S. In the presence of oxygen, the following reaction occurs [18]:

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O \qquad (2)$$

$$2H_2S + O_2 \rightarrow \frac{1}{4}S_8 + 2H_2O \qquad (3)$$

IV. REGENERATION

For the evaluation of regeneration efficiency, the most suited method is the calculation of "regeneration ratio" [19].

$$Rr = \frac{\left(\frac{X}{M}\right)_{reg} \left(\frac{mg}{g}\right)}{\left(\frac{X}{M}\right)_{virg} \left(\frac{mg}{g}\right)} \qquad (4)$$

where X is the mass of sorbate (H2S) and M is the mass of sorbent.

V. REGENERATION WITH NITROGEN

The results of tests with N2 are shown below.

As reported in Table 1.4, the regeneration ratio values (i.e., Rr) are very close to each other. Considering also the thermal and electric expenditure to reach the experimental desired conditions, the best regeneration with N2 is the thermal treatment at 200 ◦C.

Table 1.4: Regeneration test under inert atmosphere and 180 min.

Regeneration Temperature (°C)	Virgin CKC Breakthrough Time (h)	Virgin CKC Ads. Capacity (mg/g)	Regenerated CKC Breakthrough Time (h)	Regenerated CKC Ads. Capacity (mg/g)	Rr (-)
100	8.47	1.09	0.94	0.13	0.121
200	7.36	0.93	1.03	0.14	0.148
300	8.55	1.09	1.14	0.16	0.149

In Table 1.5, comparison of the sample weights is shown: the weight loss increases with the temperature. It is reasonable to think that this is due to a better sulfur and volatile organic compounds (VOCs) removal with increasing temperature during the regeneration.

Table 1.5: Weight loss under inert atmosphere and 180 min.

Regeneration Temperature (◦C)	Weight Loss (%)
100	8.7
200	10.2
300	10.2

The same phenomenon, but less clearly, was observed at 300 ◦C and 15 min of regeneration exposure. Indeed, in this case, a higher value of regeneration ratio was recorded. Finally, the test at 200 ◦C and 75 min was carried out to study the dependence on the temperature: the regeneration ratio increases with the temperature. In this case, no ash content was recorded after regeneration.

Table 1.6: Weight loss during air regeneration

Regeneration Temperature (◦C)	Weight Loss (%)
200 *	13.3
300 *	14.1
300 **	11.7

* 75 min treatment; ** 15 min treatment.

Considering the results obtained, sulfur removal efficiency with the regeneration in air registered lower performance than in the literature [14].

VI. REGENERATION WITH CARBON DIOXIDE

The main drawback of this regeneration process is related to the limitation for real applications at the industrial scale due to combustion problems. The test campaign results are shown in Table 1.7.

Table 1.7: Regeneration tests results with air.

Regeneration Temperature (°C)	Virgin CKC Breakthrough Time (h)	Virgin CKC Ads. Capacity (mg/g)	Regenerated CKC Breakthrough Time (h)	Regenerated CKC Ads. Capacity (mg/g)	Rr (-)
200 *	5.41	0.69	0.59	0.09	0.124
300 *	5.88	0.75	0.69	0.1	0.138
300 **	5.18	0.66	0.7	0.1	0.153

* 75 min treatment; ** 15 min treatment.

The same phenomenon, but less clearly, was observed at 300 °C and 15 min of regeneration exposure. Indeed, in this case, a higher value of regeneration ratio was recorded. Finally, the test at 200 °C and 75 min was carried out to study the dependence on the temperature: the regeneration ratio increases with the temperature. In this case, no ash content was recorded after regeneration.

Table 1.8: Weight loss during air regeneration

Regeneration Temperature (°C)	Weight Loss (%)
200 *	13.3
300 *	14.1
300 **	11.7

* 75 min treatment; ** 15 min treatment

Considering the results obtained, sulfur removal efficiency with the regeneration in air registered lower performance than in the literature [17].

As previously done for inert atmosphere, further analysis was carried out in this case also, reducing the regeneration time to 75 min. Unlike the inert atmosphere, a clear improvement is observed at 300 °C. This regeneration ratio value is the best result found and it is in line with the objective, considering the reference values found in literature [16]. In addition, the weight loss of 13.3%—from 12.8 (virgin carbon) to 11.1 (regenerated carbon)—is the highest recorded value. This is a sign of efficient removal of adsorbed species during the regeneration [15].

Table 1.9: Weight loss under CO2 atmosphere

Regeneration Temperature (°C)	Virgin CKC Weight (g)	Regenerated CKC Weight (g)	Weight Loss (%)
100 *	12.8	11.3	11.7
200 *	12.6	11.3	10.3
300 *	12.6	11.1	11.9
400 *	12.8	11.4	10.9
300 **	12.8	11.1	13.3

* 180 min treatment; ** 75 min treatment.

VII. ECONOMIC EVALUATIONS

The SMAT real plant configuration was used in the calculation, where there are two vessels for H2S adsorption, each vessel containing 250 kg of CKC.

The investment cost, i.e., the installation cost of the reactors, is the same in both scenarios, as shown in Table 1.10 (data provided by Bio-komp Company, Villaverla, Italy).

Table 1.10: Installation cost for each reactor

Item	Cost (€)
Carbon	2375
Bagging	240
Transport	160
Labor	240
Lifting means	135
Total	3150

The final calculations for a plant lifetime of 4 years were performed and are shown in Table 1.11 where an interesting comparison between the two scenarios is made. The adsorption capacity of virgin CKC is the value found in the analysis of CKC performance with different oxygen percentages in the biogas, and it refers to 0.1% (vol.) of oxygen, chosen as the average value during the plant lifetime. The adsorption capacity of regenerated CKC is the value found in the best situation for regeneration, i.e., CO2 at 300 °C and 75 min treatment. The cost evaluation proves the applicability of regeneration to the real case, since it would be efficient both in environmental and economic terms; according to these estimates, this could lead to savings of about 35,000 €, carbon needed for the reactors and, consequently, amount of carbon to be disposed.

Table 1.11: Cost evaluation for CKC reactor management

Item	No Regeneration	Regeneration
Carbon	Virgin CKC	Virgin + Regenerated CKC
Ads. capacity at breakthrough (mg/g)	3.72	4.84
One reactor (250 Kg) breakthrough time (days)	27.54	34.75
Substitutions/35,040 h (4 years)	53	42
Substitutions (kg/4 years)	13,250	10,500
CAPEX (€)	6300	6300
OPEX (€/4 years)	219,950	184,464
Total cost (€)	226,250	190,764

VIII. CONCLUSION

Work has been completed to investigate the ability of activated zeolite to improve the quality of raw biogas. The results confirm that activated zeolite provides superior adsorption performance without activation. By activating zeolite, more microprocesses with smaller crystal stacks were generated. This phenomenon increases the loading capacity of zeolite. Higher base solutions such as NaOH as chemical activates deteriorate the microstructure of the active zeolite. The reaction within the zeolite particles produces larger agglomerations for fewer micropore sites, reducing the rate of adsorption of impurities gases in the raw biogas. Generally, for chemical zeolite activation, the base solution volume must be within a certain amount for better adsorption performance.

The H2S removal technique incorporates several techniques that require absorption, adsorption, and membranes. Adsorption through activated carbon and membrane technology has been studied by many researchers, and the method was found to be economically advantageous and has a higher H2S removal efficiency than other techniques. However, the adsorption technique was also studied economically more favorably through modification of cellulose crystals and was prompt for active substitution. The appropriate method should be chosen to maximize the efficiency of removing H2S and unwanted impurities in biogas fuel. The method increases the quality of raw biogas, which may possibly be a new source of renewable energy, such as fuel cell applications.

In this work, experiments were focused on the removal of H2S with commercial sorbents, considering various regeneration agents such as nitrogen, carbon dioxide, and air. The adsorption process was experimentally investigated in fixed-bed reactors with comparable real plant conditions. An experimental test was detailed to remove H2S adsorption, starting with adsorption capacity calculations with three different oxygen concentrations in simulated biogas. The oxygen concentrations used for the investigation were: 0.1%, 0.3% and 0.5% considering the biogas composition from the actual wastewater plant. Commercial sorbents showed an adsorption capacity to be linearly dependent on increasing oxygen concentrations. These results were encouraging, especially for the real case, where the average oxygen concentration was 0.1%. In the second part of the tests, the regeneration process on selected commercial activated carbon was intensively studied. Early literature research was necessary to identify regenerative agents: passive atmosphere, carbon dioxide and air regeneration caused partial combustion of carbon samples at 300 0C with both 75 min and 15 min. At 200 0C, there was no combustion - here, the efficiency of regeneration resulted in better performance than in a passive environment. Unfortunately, the dangerousness and difficulty of controlling the partial oxidation reaction is the main drawback for the actual case. Sublimation with CO2 showed the best solvation ratio values. In particular, the best condition obtained was that of a thermal treatment time of 300 0C and 75 min with an uplift ratio of 30%. Then, cycle adsorption / regeneration with CO2 / adsorption was applied to CKC, adding a trace concentration of oxygen to the biogas mixture (0.1%) and guaranteeing its applicability to SOFC, for low cost for the cleaning system Thanks, for the carbon needed to dispose of the reactors and the amount of carbon. Results obtained without oxygen content in biogas mixtures show low performance. Future investigations need to consider the scale of uptake with carbon dioxide.

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