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H_2S and Siloxane D5 Removal from Anaerobic Digestion Gas by Adsorption

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Abstract:

Global warming and depletion of fossil fuel enhances people to obtain alternative clean sources of energy. The key objective of this study was to develop adsorbent systems for sulphur (from H_2S) and siloxanes removal from the anaerobic digestion gas (ADG) by commercially available adsorbents for a solid oxide fuel cell (SOFC) application. The target limits for removal of sulphur and siloxane compounds were less than 1 ppmv and 100ppbv respectively for the SOFC application. Based on the results of this work (this work is a part of a European Union project named SOFcom) and some other projects of SOFcom, a pilot plant of SOFC (capacity 100 kW fuel energy) will attempt to operate using the ADG produced from the Torino Sewage Plant, Italy. Different types of siloxanes were available in the ADG, among them D5 was chosen as representative for their higher concentrations (1200ppbv) in Torino, Italy. However, all types of siloxanes are also possible to remove from ADG by the same adsorbent. Commercially available adsorbents such as Activated Carbon (sigma), Zeolite 5A, FCDS GS-1(ZnO) and FCDS GS6, Active carbon (Norit RST3) and Soxsia were explored in the fixed bed reactor in laboratory. Artificially simulated ADG was tested in the laboratory (for simplicity) to determine the adsorption capacities of adsorbents. FCDS GS-1 (48 mg/g) and Norit RST3 (55.7 mg/g) were performed as best adsorbents for sulphur and siloxane D5 removal respectively.

1. Introduction

Global warming as well as the exhausting of fossil fuel, it is essential to obtain alternative fuels for the survival of the modern civilization. Biogas from the landfills or the anaerobic digestion can be a source of fuels. Moreover, using biogas suppresses the emissions of one of the greenhouse gases, methane. Otherwise, methane gas will be released to the atmosphere and increase the greenhouse gas concentration. SOFC is one of the green technologies for generating power from hydrogen, natural gas and other renewable fuels. Biogas is one of the beneficial sources of fuels for SOFC for two main reasons: increasing amount of available bio-waste and commercially available biogas production technology. However, impurities in raw biogas, such as sulphur compounds (hydrogen sulphide (H_2S) and mercaptans (R-SH)), halogenated hydrocarbons (primarily chlorinated hydrocarbons), organic compounds (alkene compounds, acetylene and ethane), siloxanes and condensed water vapour are the biggest challenges for SOFC to compete with the gas engines and turbines [1]. The main impurities of ADG gas of Torino, Italy are hydrogen sulphide (100 ppmv) and siloxanes (3.5 ppmv) and halogenated (chlorinated) hydorcarbon (200 ppbv). For SOFC sulphur level should be below 0.1 ppmv [2] , siloxanes level should be less than 100 ppbv [3] and halogenated hydrocarbon should be below 1 ppmv [1]. As halogenated hydrocarbon is below the poisonous limit, so the target impurities are hydorgen sulphide and siloxanes.

The amount of impurities may vary even when they are from the same source. Consequently, cleaning technology should cover a wide possible range. There are different methods available to remove sulphur and siloxanes from biogas. Adsorption method was chosen as the target method in this study. In the literature part of this study, the target was to find the most optimal adsorbents for SOFC using commercially available adsorbents at low temperature and in the atmospheric pressure.

The best available adsorbents were reviewed and special attention was paid to commercially available solid adsorbents. On the basis of the literature, zinc oxide, impregnated activated carbon (IAC) and zeolite 4A were the best adsorbents for sulphur removal. Though there are different types of siloxanes present in the biogas, same adsorbent can be used to remove all type of siloxanes. Silica gel, molecular sieves and activated carbon (AC) were the best adsorbents to remove siloxanes based on the literature survey.

In the experimental part, different adsorbents, chosen on the basis of literature review, were tested and evaluated. Among them Sigma charcoal, FCDS GS6, FCDS GS1,silica gel, Soxsia, zeolite 5A and Norit RST 3 were used in this study . FCDS GS1 was found as the best adsorbent for sulphur removal with 48 $mg_S/g_{FCDSGS1}$ adsorption capacity at 40ºC and Norit RST3 as the best adsorbent for siloxane removal with 55 mg_{D5}/g_{AC2} adsorption capacity at 200ºC.

2. Materials and Research Method

Artificially simulated gas was tested to obtain the adsorption capacities of commercially available adsorbents. Gases were fed from the cylinders supplied by AGA and the purities were N_2 99.999 %, CO_2 99.990 %, CH_4 99.995 %, H_2S 0.500 % in N_2 and O_2 99.999 %. Liquid siloxane D5 was supplied from Sigma- Aldrich and it had 97% purity. Seven different types of commercially available adsorbents were tested

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in the experiments and their supplier name and chemical compositions are listed in the Table 1.

Table 1 Supplier name and chemical composition of adsorbents

Commercial name	Supplier	Chemical composition
Soxsia	GTS	Iron oxide max 50 %, Silicon oxide max 50 %, aluminium oxide max 20 %,magnesium oxide max 2 %.
Norit RST3 (AC 1)	GTS	Activated Carbon
FCDS GS1(ZnO)	Sud-Chemie	Zinc Oxide
FCDS GS6	Sud-Chemie	$(MnO_2+CuO)>25$ %, rest is unknown
Silica gel	BDH laboratory	Silicon dioxide
Zeolite 5A	Merk	$^*Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$
Charcoal (AC 2)	Sigma-Aldrich	Activated Carbon

*Some Na^+ are replaced with calcium ions

The adsorbents except FCDS GS-6 were crushed and sieved to the particle size of 0.2 to 0.3 mm for experiments. The sieves (used to separate the particles) were supplied by the German company Retsch. Adsorbent parameters such as BET surface area, pore diameter and pore volume were measured for AC1, AC2, ZnO and soxsia and the values are listed in Table 2. The parameters were measured in the lab by Barrett-Joyner-Halenda (BJH) adsorption principles.

Table 2 Adsorbents parameters obtained from BJH adsorption isotherm

Adsorbents	BET surface area, m^2/g	Pore diameter, nm	Pore volume, cm^3/g
AC1	648.42	2.96	0.48
AC2	735.24	2.24	0.41
ZnO	44.37	20.85	0.23
Soxsia	299.27	4.82	0.36

Dräger tubes (Dräger Safety AG & Co.KGaA. Revalstrasse 1.D-23560 Luebeck.Germany) indicate the concentration of hydrogen sulphide by changing colour white to pale brown in the outlet gas and it could be detect from 1 ppmv to 100 ppmv. The accuracy of the Dräges tube is ±5% to 10%. The following reaction following happens when Drägers detects sulphur in the gas:

$$\mathbf{H_2S + Pb^{2+} \rightarrow PbS + 2H^+} \qquad \textbf{(1)}$$

Liquid siloxanes were fed through the High Performance Liquid Chromatography (HPLC) pumps. The breaks through time of siloxanes for different adsorbents were obtained from the FTIR analysis.

3. Experimental Setup

The gases were fed through mass flow controllers and mixed together after the controllers and worked as simulating and simplified anaerobic digester gas (ADG). Water and siloxane D5 were fed through the HPLC pumps with the other gases. Water was also evaporated by the vaporizer before mixing with the simulated gas. For making the laboratory work simpler, H_2S and siloxane were tested separately and obtain the adsorption capacities of H_2S and siloxane. The concentrations of the simulated ADG were CH_4 58 %, CO_2 38%. The concentrations of the impurities of the feed gas were different for different experiments.

The adsorbents were packed in the quartz tube which was placed in the oven. The oven heated the adsorption bed to the desired temperature (for sulphur removal at 40ºC and for siloxane removal at 200ºC) at a rate of 20ºC/min. A thermocouple was situated in the analysed middle of the adsorption bed to provide the exact temperature of the adsorption process. The gas pipelines were also kept at the same temperature (40ºC or 200ºC) as the oven. Pressure tests were done by nitrogen gas flow through the adsorption tube to be sure that there were no leaks in the adsorption tube. The outlet of the gas was connected to an online Gas analyser and to an online Fourier Transform Infrared (FTIR) analyser.The concentration of H_2S in the out let gas was analysed by Dräger tubes. The gas flow meter measured the outlet gas flow rate. The process flow diagram (PFD) of the experimental set up is shown in the Figure 1.

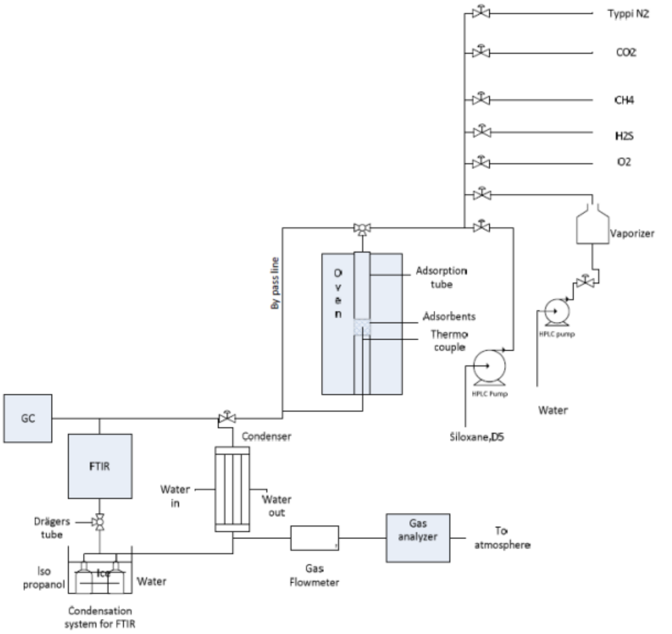

Figure 1 PFD of the experimental setup

4. Results and Discussion

4.1 H_2S adsorption

Adsorption capacity for sulphur was determined by using six different adsorbents such as Charcoal (AC1), Zeolite 5A, FCDS GS1 (ZnO), FCDS GS6 (GS6), Norit RST3(AC2) & Soxsia. The main target was to remove the H_2S to concentration below 1 ppmv at 40ºC and 1 atm. from the wet gas (3 % water content). Among these FCDS GS 1 performed best. Several experiments were performed using FCDS GS 1 with different experimental conditions and the obtained results listed in Table 3.

Table 3 Results obtained for FCDS GS1

Exp No.	Flow velocity, L/min	H2S feed, ppmv	Minimum adsorption capacity, mg of S/ g adsorbent	Maximum adsorption capacity, mg of S/ g adsorbent
1	2	20	0.3	2.143
2	2	20	60	60.0
3	1	100	47.24	82.63
4	2	100	20.4	61.0
5	**2**	**100**	**48**	**49.9**
6	2,5	100	33.75	43.05

Polychronopoulou *et al*. [4] studied sulphur removal with the feed containing 1% water and they found water acting as positive component to increase the adsorption capacities of ZnO below 100ºC. They found the adsorption capacity at 25ºC with 1% water which is 4 times compared to capacity without water. The experimental results (experiment no.1 without water) also agreed with the literature. The adsorption capacity is lower without water at 40ºC. The deviation between the minimum and maximum adsorption capacities can be explained by the Dräger tube sampling interval between the last two samples, which was e.g. in the experiment no.3 four hours. Experiment no. 5 was performed in the same way and the Dräger tube measurements were taken with half an hour interval and the minimum and maximum adsorption capacities were found 48 and 49.9 mg/g. Haimour *et al.* [5] also found adsorption capacity to be 45 mg/g at 35ºC. Experiment no. 2 and 5 were performed to check the effect of Gas hourly space velocity (GHSV) in adsorption capacity. Experiment no.3 was performed with different volumetric flow rate (1l/min) and the GHSV was 45496 h^{-1}. The minimum adsorption capacity was 47.24 mg/g and the maximum adsorption capacity was 82.63 mg/g. In experiment no. 6 the bed height was also changed with the gas flow rate (2.5 l/min) to maintain the same contact time and the GHSV. In Experiment no. 6 the minimum adsorption capacity was 33.75mg/ g and the maximum adsorption capacity was 43.05 mg/g. Based on these results, it may be concluded that changing the contact time has no significant effect. Kiesok K. and Nokuk P. [6] different GHSV (6000 h^{-1} to 12000 h^{-1}) and obtained the change in adsorption capacity from 125 mg / g of ZnO to 109gm/g of ZnO at 363ºC.

H_2S removal results for other adsorbents were listed in Table 4. FCDS GS 6 was other promising adsorbents for sulphur removal. However, for the cylindrical particle size of FCDS GS6 created problem to test in smaller reactor. Activated carbon could not remove sulpur up to the target limit. Zeolite 4A may remove sulphur, however pore size of zeolite 5A was not suitable to capture H_2S (molecular size is 3.6 Å) in the pore.

Table 4 Other adsorbents adsorption capacities

Adsorbent material	H_2S feed, ppmv	Water content, %	Maximum adsorption capacity, mg S/ g adsorbent
Zeolite 5A	20	0	0.00
Zeolite 5A	20	3	0.8
GS-6	20	3	10.6
GS-6	20	3	3.1
GS-6	20	3	6.1
GS-6	100	3	23.3
Soxsia	100	0	2.7
Soxsia	100	3	2.0
Activated carbon 1 (Sigma)	20	3	0.7
Activated carbon 2 (Norit)	100	0	3.7

Sena Y. [7], studied on mixed oxides and at high temperature (600ºC) and obtained too short breakthrough for iron manganese oxide. However, soxsia is also mixed iron manganese oxide.

Table 5 Siloxane adsorption capacities

Adsor bents	Adsor bent weight, g	Break through time, min	Adsorption capcity,mg D5/g adsorbents
Soxsia	1.0185	17.72	17.39
Silica gel	1.0125	19.62	19.37
AC 2	0.4221	21.22	55.7

4.2 Siloxane adsorption

Among siloxanes, highest amount of siloxane D5 was found in Torino, Italy. So, D5 was taken as the representative of all siloxanes and was mixed with the synthetic gas to determine the adsorption capacities for siloxane. Siloxane adsorption capacities were obtained for silica gel, soxsia and AC2.Siloxane D5 adsorption capcities are listed in Table 5.

The highest adsorption capacity 55.7mg /g were found for the AC2 which is consistent with the result found in the study of Matsui T. and Imamura, S. [8]. The concentration of siloxane D4 is the second highest found in the ADG of Torino, Italy, According to Matsui, T. and Imamura, S., [8] the break through time for D4 siloxane is lower compared to D5 siloxane. So, more tests should be performed to determine the breakthrough time of siloxane D4.

Shweigkofler M., and Niessner, R., [9] tested the adsorption capacity of siloxane by flowing nitrogen gas stream through the tempered siloxane and then diluting the concentration of siloxane with a second flow of nitrogen gas. Similar type of experimental setup can be used to determine the siloxane adsorption capacity using vapor pressure curve of siloxane D5. For example, the gas may be vaporized in 25ºC in the water bath by nitrogen flow and the then feed through the gas pipeline whose temperature is 40ºC to avoid the condensation problem (Figure 2).

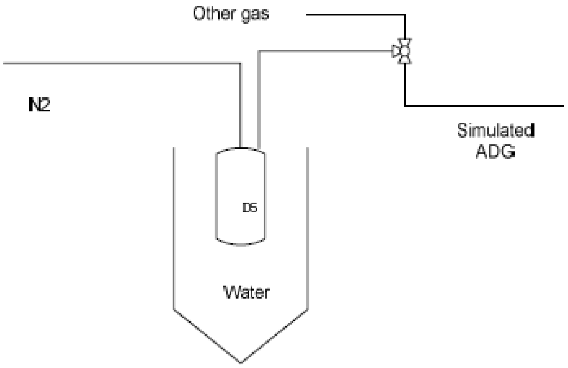

Figure 2 Siloxane feeding with other gas for testing in the lab scale.

5. Conclusion

The objective of this study was to investigate the removal of impurities of ADG by commercially available solid adsorbents in order to allow the gas in SOFC. Sulphur removal experiments were performed at 40ºC and ZnO was found as the best adsorbent. The adsorption capacity of ZnO was 48mg /g. Siloxane removal test were performed at 200ºC and AC2 was found as the best adsorbent. The capacity of AC 2 was 55.7 mg/g. The obtained adsorption capacity of siloxane with AC2 is consistent with the literature value. More tests should be performed at 40ºC and 1 atmosphere pressure to obtain the exact adsorption capacity for siloxane D5. Because, the target temperature for siloxane removal is also 40ºC and normally the adsorption temperature should be below/equal to 50ºC, two attempts were made to perform the experiments at 40º and 60º C. Condensation problems disturbed the determination of the adsorption capacity of siloxane at 40ºC and even at 60ºC.

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