Biogas Clean-up and Upgrading by Adsorption on Commercial Molecular Sieves

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The effect of the competitive adsorption of H_2S, Water and CO_2 on molecular sieves 13X is here reported. The uptake of trace amounts (100 ppmv) of H_2S was experimentally calculated by means of short term breakthrough tests either in the presence of small percentages of water (0.2 % vol.) or biogas type concentrations (35 % vol.) of carbon dioxide. Results show that in the absence of water, the adsorption process is substantially enhanced, thus the molecular sieves can be successfully employed both for sulphur clean up and carbon dioxide capture.

1. Introduction

Biogas is a mixture comprising principally methane and carbon dioxide resulting from the decomposition of organic matter operated by micro-organisms either in the presence or absence of oxygen. Biogas production can therefore take place in a landfill site (LFG), or in an anaerobic digester (ADG). Indeed, the energy content of the biogas is directly dependent on the methane content; on the other hand, as the proportion of carbon dioxide increases and methane decreases, the fuel becomes more difficult to ignite. At ratio 3:1 of CO_2, ignition can no longer be maintained and different options, such as fuel cells, must be considered for power production from biogas.

With an average methane content ranging between 50 - 65 % vol. and CO_2 up to 30 - 35 % vol., both LFG and ADG are normally collected and processed to yield energy. LFG may further contain nitrogen and oxygen, which are indicative of air incursion into the gas collection system; moreover, water can be present either at trace or saturation level. Biogas collected from a landfill site may also contain a variety of trace compounds, as reported for example by Steinfeld et al. (1998), and more than 140 substances have been identified so far, which may account for about 0.15 % vol. (2,000 mg/m^3) of the total amount. Among these, sulphur compounds, and particularly H_2S, can reach concentrations as high as 1000 ppmv, which are far from those limit values (i.e. 0.1 ppmv H_2S for solid oxide fuel cells) required to avoid catalyst poisoning or equipment failure.

Because of the substantial differences on both type and relative amount of biogas contaminants, establishing a standard clean-up process is a challenging task from either a technical and economic point of view. In this regard, removal of contaminants by adsorption on single/multiple porous beds of selected sorbents (e.g. activated carbons, zeolites) proved to be a cost effective solution in a wide range of industrial applications, which require the removal or separation of a few substances from a gas mixture.

Lately, synthetic and natural zeolites received particular attention because of their higher removal efficiency when used to depurate gas mixtures from water, sulphur compounds and carbon dioxide. In fact, competitive adsorption studies from Siriwardane et al. (2001) indicate that an excellent separation of CO_2 from a binary gas mixture of N_2 and CO_2 (14.8 % vol.) can be achieved by adsorption on 13X

molecular sieves (MS 13X), the measured uptake of carbon dioxide being very close to the equilibrium values. Furthermore, results, reported by Alonso-Vicario et al. (2010) from medium pressure adsorption tests carried out on a biogas model mixture, show comparable H_2S adsorption capacity between MS 13X and Clinoptilolite (natural zeolite), but also a higher CO_2 uptake of the former. Therefore, MS 13X are potential candidate not only as selected sorbents for biogas clean up, but they can be employed to increase the methane to carbon dioxide ratio, thus upgrading the energy content of biogas. In this work, the effect of competitive adsorption on the sulphur (H_2S) uptake by MS 13X is investigated for N_2-H_2S-Water and N_2-H_2S-CO_2 gas mixtures.

2. Experimental

2.1 Materials

Molecular sieves 13X with average particle diameter of 2.0 mm were obtained from Sigma-Aldrich. A gas cylinder containing a mixture of Nitrogen and H2S (1000 ppmv, prepared by SIAD S.p.A) was used as main carrier gas in each experiment, whilst three different gas mixtures, namely Nitrogen (99.999 purity), Nitrogen-Carbon Dioxide-Oxygen (60 %, 35 % and 5 % respectively), and Air from the lab tap (water content about 0.2 %) were mixed with the carrier gas according to each test..

Adsorption experiments were carried out by means of an air tight stainless steel column, 10 cm long and 2.5 cm i.d.; the inlet H_2S concentration and flow rate were manually set by means of two mass flow controllers (Brooks Instrument): one of them was steadily connected to the Nitrogen-H_2S cylinder, while the other was pre-calibrated and, depending on type of experiment, connected with one of the available gas sources.

The outlet H_2S concentration was measured by an in-line electro-chemical device (Gasman, Crowcon, max H_2S detection limit about 150 ppmv, resolution 0.1 ppmv). After leaving the gas detection stage, the gas mixture is first bubbled through a solution of zinc acetate and then let flow to the vent.

2.2 Method

Competitive adsorption among H_2S, Water and CO_2 was studied by carrying out breakthrough tests over a diluted bed of MS 13X beads according to the following procedure: prior to each run, a known amount, m_{ads}, of molecular sieves was regenerated under Nitrogen atmosphere at 280 - 300 °C for 5 h. After regeneration, the sample was weighted and mixed with a known amount of equally sized glass beads in order to obtain a volumetric dilution up to 50 %; the mixed sample was then sandwiched between two layers of glass beads that are used as filling material for the top and bottom part of the column. Dilution of the porous bed is a widely accepted technique that is required in order to achieve a bed length sufficiently long to avoid straight breakthrough during testing. The amount of weight gained by the mixed sample before the actual experimental run was evaluated between 1.5 and 2 % and the average value was taken into account in all calculations that are presented in this work.

The experimental conditions for a typical breakthrough test are listed in Table 1. Each test was run for 120 min at constant room temperature and atmospheric pressure; during this time the H_2S concentration C in the gas released by the column was recorded at least every 180 seconds and the relative H_2S uptake was calculated by using Equation 1 and Equation 2:

$$q_{ads} = \frac{34 Q_f C_0 t_t p}{RT m_{ads}} \tag{1}$$

where

$$t_t = \int_0^{120} \left(1 - \frac{C}{C_0}\right) dt \tag{2}$$

At the end of each run, the content of the column (i.e. glass+13X) was weighted and the relative gain of weight was calculated for the 13X sample.

Table 1: Experimental conditions for breakthrough tests. C_0 is the H_2S concentration in the feed. Q_f is the feed flowrate and m_{ads} is the mass of 13X.

Q_f [mL/min]	C_0 [ppmv]	m_{ads} [g]
1800	100	1.500

A similar set of experiments was also run in order to determine the relative uptake of the 13X sample at the same experimental conditions indicated in Table 1, but without feeding H_2S to the column. Each of these experiments lasted 60 and 120 min and the relative uptake was calculated by difference between the initial and final weight of the sample.

3. Results and discussion

Competitive adsorption between H_2S and CO_2 and H_2S and Water was investigated by keeping some process variables, such as the gas flowrate, contact time and initial H_2S concentration, constant for all tests performed.

Results from the 60 min (Test 1 and 2) and 120 min (Test 3) tests without H_2S in the feed mixture are shown in the comparative chart of Figure 1, where the experimental uptake of Water, CO_2 and Nitrogen have been compared with equilibrium values calculated from the relevant adsorption isotherms reported by Rege et al. (2000).
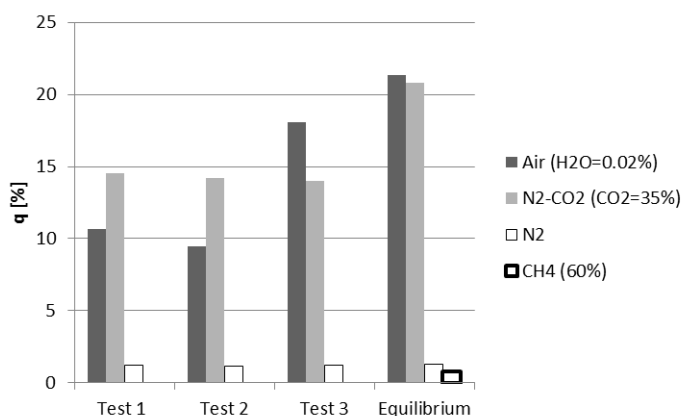

Figure 1: Relative gain of weight of a 13X sample when exposed to different gas mixtures. Test 1 and 2 present results for a 60 min run; Test 3 is the result of 120 min run either under Wet Air (H_2o=0.2 %), N_2-CO_2 or N_2.

Results in Figure 1 show that when feeding the system with either Wet Air or N_2-CO_2 , the 13X sample would be enriched with water or carbon dioxide accordingly, the overall uptake being very close to saturation values yet after 120 min test; particularly, CO_2 uptake was found close to the predicted equilibrium values yet after 60 min. As expected from thermodynamic considerations, Nitrogen and methane uptake represent only a small part compared to water and carbon dioxide capacity.

In Figure 2, reproducibility results are reported for two breakthrough tests, Tb1 and Tb2, carried out by feeding the column with a mixture of Wet Air and N_2 – H_2S ; the experimental conditions are indicated in Table 1.
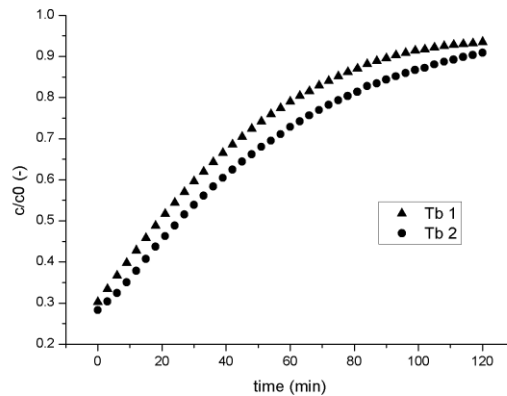
Figure 2: Reproducibility of breakthrough curves. System Wet Air and $N_2 - H_2S$; feed composition and flowrate as indicated in Table 1

In Figure 3, the breakthrough of H_2S is reported (Test Tb 3); here the feed composition is a mixture composed by the carrier gas (N_2-H_2S) with N_2-CO_2; experimental conditions are indicated in Table 1.
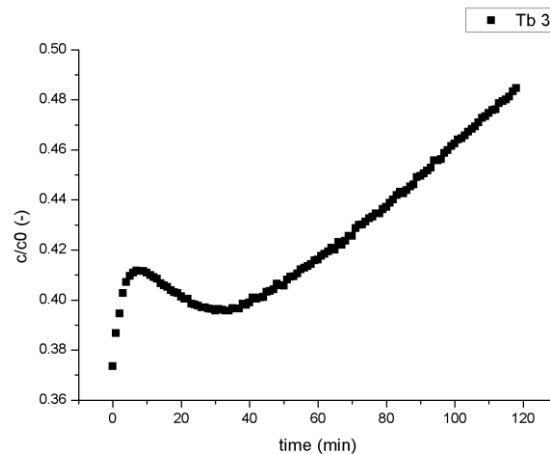

Figure 3: H_2S breakthrough when the feed is a mixture of carrier gas (N_2-H_2S) and N_2-CO_2 .Feed composition and flowrate as indicated in Table 1.

Indeed, by comparing the results from Figure 2 and 3, a small amount of water in the feed would substantially decrease the H_2S uptake: in fact, within the duration of the tests, breakthrough of H_2S is almost completed in the former case, the latter being only half way to its completion.

The chart illustrated in Figure 4 summarizes the results for the three systems investigated by reporting the average H_2S uptake and both the experimental relative weight gained by the 13X sample at the end of the tests and the relevant H_2O, CO_2 and N_2 equilibrium values, which have been previously reported in Figure 1.
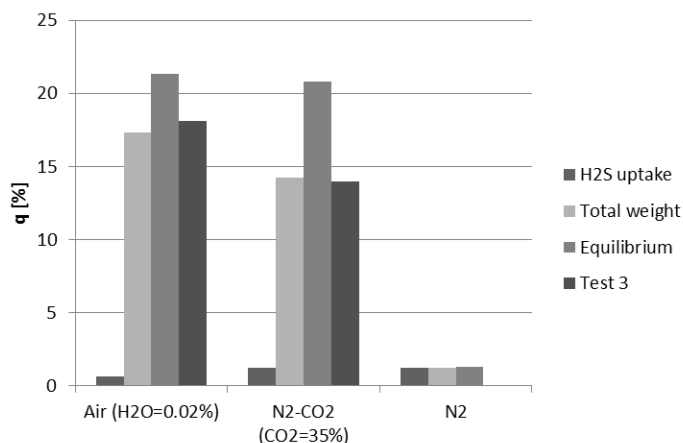
Figure 4: Summary of results obtained from breakthrough of H_2S for the three systems investigated.

Discussion of the results shown in Figure 4 will start by analyzing the N_2-H_2S system: the H_2S uptake, which is about 1.2 %, could be considered as a maximum reference value since, theoretically, there is no competition between the two species on the adsorption sites. In fact, Nitrogen is replaced by H_2S in the early stages of adsorption and the uptake of the latter depends on its concentration. Therefore, as expected, the reported result shows equal amounts of H_2S adsorbed (calculated through equations 1 and 2) and total weight gained by the 13X sample at the end of the test.

Because of the highly hydrophilic behavior of the 13X molecular sieves, the experimental tests carried out with wet air represent the worst case in terms of H_2S uptake, which is about 0.65 %, since the sulphur capacity is halved in respect to the former case. Water is preferentially adsorbed and the total weight gained by the 13X sample, that is 17.3 %, is consistent with the result, 18.1 %, of Test 3 shown in Figure 1; however, although only a small amount of H_2S was captured, we didn't detect its complete replacement by water during breakthrough, as it was in some cases observed by other authors, see for example Meeyoo et al. (1998).

In the hierarchy of species that have strong affinity with MS 13X, H_2S can be found right after water, leaving to carbon dioxide the last place among the three species here investigated. In fact, the H_2S uptake in the N_2-CO_2-H_2S system was similar to the maximum reference value calculated for the N_2-H_2S test, that is 1.23 %. However, unlike what was observed for the wet air system, the total weight gained by the 13X sample at the end of the test is comparable to the results of 60 and 120 min tests shown in Figure 1 (Test 1, 2 and 3 N_2-CO_2); that is, on a longer run the uptake of CO_2 couldn't be improved. A possible explanation is that the saturation limit of CO_2, which is quickly reached in the first 60 min, in presence of H_2S is lowered, whereas the uptake of H_2S is enhanced, as its breakthrough didn't reach half of the completion within the whole duration of the test.

4. Conclusions

The adsorption process for the removal of H_2S from three different gas mixtures has been tested at lab scale. Particularly, the experimental work presented in this paper addresses the change in the removal efficiency of sulphur by Molecular sieves 13X in the presence of either small percentages of water or biogas type concentrations of carbon dioxide. The effect of competitive adsorption of the three species was investigated by producing short term breakthrough curves and by keeping constant both the contact time and inlet sulphur concentration. Because of the experimental conditions, the breakthrough curves resemble the mass transfer controlled adsorption processes and a part of the H_2S is not retained by the bed and exits the column from the very beginning of the experiments. Results show that the presence of water will shorten the breakthrough of H_2S, thus decreasing the sulphur (and CO_2 as a consequence) adsorption capacity. However, in the early stages of the process and in the

presence of a dry gas mixture, the uptake of H_2S and CO_2 is enhanced and resemble values close to equilibrium.

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