Adsorption of Hydrogen Sulfide at low temperature

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From an ecological perspective is biogas an important source of energy. It is produced from fermentation of organic material, e.g. household waste and wastewater sludge. The composition of the gas depends on the raw material and varies between 65-85% methane, 15-35% carbon dioxide and small amounts of ammonia and hydrogen sulfide. To use the biogas it is important to purify it from hydrogen sulfide, because of the toxicity and corrosivity of hydrogen sulfide. This study aims to find an appropriate adsorbent for dry adsorption of hydrogen sulfide at the temperature of production, that is 30-60°C. The adsorbents tested are two iron oxides and one commercial adsorbent, SulfaTreat. The experiments were performed at 0, 40, 61, 81 and 100 % relative humidity. This to determine the influence of the relative humidity on the adsorption. The adsorption, for all three adsorbents, seemed to be only slightly depending on the relative humidity. The results indicates that the Fe$_3$O$_4$-adsorbent has the same and even somewhat better adsorption ability than the adsorbent SulfaTreat, which is on the market.

Introduction

From an ecological perspective is biogas an important source of energy. The positive environmental factors are e.g. low emission of sulfur and nitrogen oxides and the waste volume decreases. Biogas can be used as vehicle fuel, to heating and to production of electricity. Biogas is produced from fermentation of organic material, e.g. household waste and wastewater sludge. Except for the two main components methane and carbon dioxide are small amounts of ammonia and hydrogen sulfide also produced during the fermentation. The hydrogen sulfide is toxic, smells very badly when the concentration is low, it is extremely corrosive and it forms sulfur dioxide when it is combusted. Due to these bad properties the biogas has to be purified from the hydrogen sulfide before it can be used. The methods available today are either expensive to run or space demanding. If the hydrogen sulfide could be adsorbed in a fixed bed at the temperature and relative humidity the gas has when it leaves the reactor would the gas cleaning process be easier. This study aims to examine if this is possible and how effective the process would be.

According to A. Dahl¹ tries most of the biogas producers in Sweden to take care of the sulfur in the reactor. One method is to add iron chloride which will react with the sulfur to form FeS which will leave the reactor with the outgoing sludge. The problems here are that it will be relatively expensive to run and the iron chloride can not take care of all sulfur, some hydrogen sulfide will be produced and a complementary method has to be used. This can for example be a water scrubber in which the water absorbs the hydrogen sulfide, the washing water is then cleaned with micro organisms, another possibility is to adsorb the hydrogen sulfide in a fixed bed. One existing plant in Sweden uses the commercial adsorbent SulfaTreat, which is one of the adsorbents tested in this study. In Denmark and Germany is it common to use micro organisms to oxidize the hydrogen sulfide in a sludge bedding or in a bedding of activated carbon. Air oxygen is used to oxidize the hydrogen sulfide to elementary sulfur. The use of air as oxygen source leads to difficulties to reach vehicle fuel quality because of the high nitrogen content.

Previously studies about hydrogen adsorption at low temperatures has been searched. According to Rodriguez et al (1998)², who have studied some metal oxides, is the reactivity order inverse proportional towards the band gap. The studied oxides have a reactivity order as follow:

\[ \text{Al}_2\text{O}_3 < \text{Cr}_2\text{O}_3 < \text{ZnO} < \text{Cu}_2\text{O} < \text{Cr}_3\text{O}_4 \]

\(\alpha\)-Fe$_2$O$_3$, which has a high theoretical adsorption maximum 0.6g H$_2$S/g Fe$_2$O$_3$, has been studied by Davydov et al (1998)³. The study shows that the hydrogen sulfide interacts with all available sites on the surface and that adsorbed carbon monoxide or ammonia does not affect the H$_2$S adsorption because the H$_2$S has greater affinity towards the adsorption sites. The reaction that takes place was found to be: Fe$_2$O$_3$ + H$_2$S \rightarrow 2 \text{FeS} + \text{S} + 3 \text{H}_2\text{O}
This study has focused on the comparison of two iron oxides Fe$_3$O$_4$, Fe$_2$O$_3$ with the on the market available adsorbent SulfaTreat.

**Experimental sector**

The flow-sheet is shown in figure 1. To each gas tube is a mass flow meter connected, the gases mixes after the mass flow meters and is led through a moisturizer. The moisturizer has a temperature of 95°C and the water is added by a motor driven syringe. To secure a homogeneous gas mixture the moisturizer is filled with Rächig-rings. The gas mixture is then led through a cooler, thereafter it enters the reactor and passes the bed of adsorbent. The reactor is held at constant temperature by recirculating water, which also keeps the cooler at the temperature in question. The amount of hydrogen sulfide in the outgoing gas from the reactor is then determined by a hydrogen sulfide detector, General Monitors S4100T Hydrogen Sulphide Addressable Transmitter. The last step is a FTIR-analyzer in which the water content is measured to make sure that the gas had correct relative humidity. After the FTIR-analyzer is it possible to connect a gas flow meter to control that there is no leakage.

Methane assumes to be inert and is replaced with nitrogen. The concentration of hydrogen sulfide is 100ppm in all of the experiments, the carbon dioxide is 20%, the water content is varied between 0, 5, 7.5 or 10%, which equals to a relative humidity of 0, 40, 61, 81 and 100%, the rest is nitrogen. The adsorption is performed at 50°C except for 100% relative humidity which has an adsorption temperature of 45.5°C (temperature of saturation for 10% water content).

The adsorbents tested are Fe$_3$O$_4$, Fe$_2$O$_3$, and SulfaTreat. The two iron oxides are powders and are mixed with sand to avoid pressure drops and channel forming. The sand was tested in blank experiments to make sure that it did not adsorb any hydrogen sulfide. The SulfaTreat is delivered in wet granules most likely with the active component on the surface. When SulfaTreat was analyzed by powder diffraction could the two main components Fe$_3$O$_4$ and SiO$_2$ be identified. The amount of iron was determined in an element analyze. The element analyze also showed that the dry SulfaTreat consist 11% aluminum. In the evaluation of the results it is assumed that the only active component is Fe$_3$O$_4$.

The expected reactions are the previously mentioned reaction from Davydov et al

\[
\text{Fe}_3\text{O}_4 + \text{H}_2\text{S} \rightarrow 2 \text{FeS} + \text{S} + 3 \text{H}_2\text{O}
\]

and

\[
\text{Fe}_2\text{O}_3 + \text{H}_2\text{S} \rightarrow 3 \text{FeS} + \text{S} + 4 \text{H}_2\text{O}
\]

The characteristics of the adsorbents is shown in table 1. The BET-surface is more than six times larger for SulfaTreat than both iron oxides but some surface might be the inactive porous carrier.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET-surface $m^2/g$</th>
<th>% iron in dry adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>8.9</td>
<td>69.94</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.9</td>
<td>72.36</td>
</tr>
<tr>
<td>SulfaTreat</td>
<td>55.3</td>
<td>16.89</td>
</tr>
</tbody>
</table>

**Result**

The system can be equaled to a tube followed by a tank reactor, equation 1. To show this, it was tested by blank experiments. Figure 2a, following page, shows the results without sand in the reactor and does not match the model, however when the reactor was filled with the same amount of sand as it was in the adsorption experiments was a perfect match received, figure 2b, following page. This implies that it, for the accuracy, is important to have the same height of adsorbent in the reactor.

\[
y = 1 - e^{-\frac{m_1 \cdot t}{m_2}}
\]

$m_1$ is the retention time for the tube, where the adsorption takes place, and $m_2$ is the retention time for the tank reactor, here the hydrogen sulfide detector.

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*Element analyze performed by Analytica, Luleå, 2004-02-20*
The first step in the experiments was to get the right water content in the gas. This varied in amount of time depending on the wanted relative humidity, because the dry bed of adsorbent had to be saturated before the humidity could be stabilized. The variation in time before the adsorption experiments were started can be a source of error because the hydrogen sulfide detector seemed to be very sensitive towards longer periods without any hydrogen sulfide in the gas. The actual adsorption was started by adding the gas stream of hydrogen sulfide to the rest of the gas flow. The adsorption went on until the outgoing hydrogen sulfide content had reached a plateau. Before each adsorption experiment was a standardized curve for the hydrogen sulfide from the detector measured in bypass. The results from the adsorption was then presented relative the standardized curve. An example of a typical graph is shown in figure 3, the upper curve is the standardized curve. For each adsorbent and relative humidity were two experiments performed. The variation in results between them is shown in figure 4. In the calculation is an average between the two results used, these are presented in table 2.

To be able to compare the different adsorbents adsorption ability are the rate coefficients, \( k \), calculated, equation 2. \( C_A \) is the concentration of hydrogen sulfide. The unit for \( k \) is \( m^3 \cdot g^{-1} \cdot s^{-1} \).

\[
k = - \ln \left( \frac{C_A}{C_{A0}} \right) \cdot \frac{F_{tot} \cdot R \cdot T}{P \cdot W}
\] (2)

Figure 5 shows how \( k \) varies between the adsorbents and with the relative humidity, the calculations are per gram iron in the adsorbent. Since the value of \( C/C0 \) is taken relatively early in the coarse of adsorption can this model only describe the initial rate of adsorption and nothing can be said about the adsorbents total ability to adsorb hydrogen sulfide or what happens at high values of turnover.
Conclusion

When the rate constants were calculated could it be seen that the adsorption was only slightly depending on the relative humidity. The rate constants were calculated with the value for the plateau it reached and the differences in adsorption rate before the plateau was neglected. The plateau was almost instantly reached in all of the experiments besides the experiments with dry SulfaTreat and Fe$_3$O$_4$ with dry gas. In those were the adsorption of hydrogen sulfide much higher in the beginning. This indicates that the water constricts the hydrogen sulfide in the experiments with higher relative humidity. This theory is confirmed when wet SulfaTreat is used as adsorbent with dry gas. The rate of adsorption is lower in the beginning than the experiment with dry SulfaTreat. It can also be seen that the rate of adsorption increases as the wet SulfaTreat dries, figure 6.

In the calculation is neither exterior nor interior resistance of mass transportation taken under consideration. The two iron oxides are powders and can therefore be assumed be without exterior mass transportation. SulfaTreat seems to have the active component as powder on a carrier of silica compound. In that case should it also here be a correct assumption. The adsorption experiments with dry SulfaTreat and dry gas shows initial an adsorption of more than 99% of the hydrogen sulfide. If exterior resistance of mass transportation had existed would this kind of initial adsorption not been possible. The interior resistance can be neglected because the reaction assumes to be a surface reaction.

In a biogas plant can the gas velocity be estimated to 0.1 m/s. With the results from this study will the initial adsorption front, figure 7, move 1 cm/day when Fe$_3$O$_4$ and sand is used as adsorbent.

![Figure 7. The movement of the initial adsorbent front](image)

- **Figure 6.** Wet SulfaTreat and dry gas

**Literature cited**


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