OPTIMISING BIOLOGICAL DESULPHURISATION OF BIOGAS BY ADDITION OF HUMIC SUBSTANCES

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Abstract

This paper presents a possible optimisation of biological desulphurisation of biogas with the addition of humic substances. The idea of the optimisation is the addition of solubilisers (humic substances in this instance) into the washing liquid in order to achieve an upgrade of the absorption of hydrogen sulphide (H$_2$S).

The whole process consists of a bioscrubber and a downstream bioreactor. In the bioscrubber the absorption is improved by the addition of humic substances. The downstream bioreactor acts as a regenerator of the washing liquid. An additional aim in this investigation is to obtain elemental sulphur which can be used e. g. as fertiliser in agriculture.

In laboratory experiments the efficiency of humates as solubilisers for the absorption of H$_2$S, as well as their suitability for the application in the bioscrubber, were investigated. In steady state experiments the optimising of absorption was carried out. These experiments showed that the humic substances “Humin-P” (potassium humate) and “Humin-S” (sodium humate) achieved significant improvements in comparison to pure water as washing liquid. In two laboratory bioreactors the regeneration of humic substances as well as their effect on the sulphur bacteria, Thiobazilli, was investigated. Humic substances have characteristics like hardly biological degradable and non-toxic which recommend their application in this system. The laboratory experiments show that the use of humates in the biogas treatment is effective. The desulphurisation is simplified by the increased solubility of H$_2$S in humate solutions. In a pilot plant at a biogas power station site the efficiency of this treatment will be tested.
1- INTRODUCTION

This paper deals with optimising the biogas treatment. Before using biogas the sulphur content shall be removed in order to avoid an impact on the incineration process. When upgrading biogas to biomethane an effective and economical desulphurisation is also needed. Biogas has typical hydrogen sulphide (H$_2$S) concentrations from 2000 to 5000 ppm. One option is the separation of H$_2$S and organic sulphur compounds by biological means. Thereby microorganisms oxidise H$_2$S to elemental sulphur and sulphate [1]. Processes for this purpose have not been optimised yet.

An improvement of gas scrubbers can be achieved by using adapted washing liquids. The idea of the optimisation of biogas treatment concerns the addition of solubilisers into the washing liquid of a bioscrubber in order to improve the absorption of H$_2$S. Bioscrubbers can also be built smaller, thereby reducing the costs. Up to now, humic substances have not been tested as solubilisers in the biogas treatment. As they are a natural product their use in this process has clear advantages in comparison to the use of artificial solubilisers in optimising this treatment. Besides, the biological regeneration aims to produce elemental sulphur, which can be used further as fertiliser. Due to the declining atmospheric sulphur input, farmers have to fertilise regularly in order to ensure a sufficient sulphur supply and crop productivity [2].

The humic substances were tested in laboratory experiments for their application in the bioscrubber-system. In a pilot plant the efficiency of this treatment will be tested.

2- MATERIALS AND METHODS

An improvement of the efficiency of gas scrubbers can be achieved by using adapted washing liquids. Humic substances were investigated as solubility agents to upgrade the absorptive separation in bioscrubbers for the desulphurisation of biogas.

With the addition of solubilisers into the washing liquid the solubility of H$_2$S is improved. For the application in biological desulphurisation, the solubilisers should offer amongst others the following characteristics:

- water soluble
- non-toxic
- non- or hardly biological degradable
- non-volatile

Humic substances fulfil these criteria. The principally tested humic substances are a potassium humate (Humin-P) and a sodium humate (Humin-S) from the company Humintech. Humates are the salts of humic acids; they consist of 70-80% of humic acids and are completely soluble in water. Humic substances have been identified as good solubilisers for odorous substances [3].

The effectiveness of humates as solubilisers for the absorption of H$_2$S was investigated in steady state experiments. In these experiments according to the head space method the reduction of H$_2$S in the gas-phase was analysed. For equilibrium purposes a sample bag, filled with biogas and washing liquid, was stored for several hours in the laboratory at a constant temperature.
The measurements in the gas-phase were carried out by three different methods:

1. Mass spectrometry
2. H$_2$S Data Logger OdaLog (electro-chemical detector)
3. Dräger-test-tubes

The samples of the biogas were taken at source, directly at the biogas plant. The degree of reduction indicates the effect of the washing liquid. Table 1 demonstrates the different varied parameters in the series of experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of humic substances</td>
<td>0.5% - 4%</td>
</tr>
<tr>
<td>Amount of washing liquid</td>
<td>0.1 - 1000 ml/l</td>
</tr>
<tr>
<td>pH-value</td>
<td>3-12</td>
</tr>
<tr>
<td>Temperature</td>
<td>2 – 40</td>
</tr>
<tr>
<td>Kind of humic substances</td>
<td>Nature and company</td>
</tr>
<tr>
<td>H$_2$S concentration of biogas</td>
<td>150 – 4000 ppm</td>
</tr>
<tr>
<td>Source of biogas</td>
<td>Renewable, waste, landfill</td>
</tr>
<tr>
<td>Storage of samples</td>
<td>Shaken and unshaken</td>
</tr>
<tr>
<td>Repeated usage of washing liquid</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1: Varied parameters in steady state experiments*

The high requirements of separation efficiency of gas treatment plants lead to the need for a high performance regeneration. Therefore the ability to be regenerated and the effort for this regeneration is one of the main selection criteria for the washing liquid.

Regeneration by microorganisms is a low cost possibility. The H$_2$S which is dissolved in the washing liquid will be transformed microbiologically to elemental sulphur that can easily be eliminated from the system. Humic substances are difficult to degrade biologically thus their use in a biological regeneration is attainable.

The objective in the biological regeneration of the bioscrubber-system is on one hand the regeneration of the washing liquid and on the other hand the production of elemental sulphur.

This process is based on aerobic oxidation by the group of colourless sulphur bacteria. The advantages of such a process are lower oxygen requirement (less energy consumption), the possibility of recovering elemental sulphur (S$^0$) and reducing discharge of sulphate (SO$_4^{2-}$). Elemental sulphur is hardly water-soluble and therefore easy to separate from the system.

In this process the oxidation of sulphide must be controlled in such a way that mainly sulphur is produced instead of sulphate. The following pathways exist for inorganic oxidation of sulphur compounds by Thiobazilli:

\[
\text{HS}^- \rightarrow \text{membrane bound } [S^0] \leftrightarrow S^0 \\
\text{membrane bound } [S^0] \rightarrow \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}
\]

At low sulphide concentrations, the oxygen concentration has a distinct influence on the amount of sulphate formed. [4]
The production of elemental sulphur by the species Thiobazilli was analysed in two laboratory bioreactors (2 litre volume). Thereby the influences of the parameters pH and oxygen concentration, as well as the kinetics of the Thiobazilli activity were determined. The two bioreactors were inoculated with a mixture of H$_2$S oxidising bacteria from a bioscrubber which operates under acidic conditions. They were fed with H$_2$S and thiosulphate (S$_2$O$_3^{2-}$) as substrate and aerated continuously.

The compatibility of the humic substances with the Thiobazilli is an important factor in the bioscrubber-system. Only with compatibility this system can operate efficiently and to that effect the influence of the humic substances on the microorganisms was analysed in the laboratory. Comparison tests of two laboratory bioreactors were arranged. The only difference between the two parallel operated bioreactors was, that in one bioreactor humates were added. In both bioreactors the following parameters (amongst others) were analysed and compared: pH, O$_2$, SO$_4^{2-}$, S$^0$, conductivity, turbidity, oxygen removal rate, dry residue and dry matter.

The results of the laboratory experiments will be verified practically in a bioscrubber-system at a biogas power station site. In this system the humates are added into the stream of washing liquid in a counter-current bioscrubber. The bioscrubber-system contains a bioscrubber and a downstream biological regenerator. Due to the aeration of a separately connected bioreactor, a dilution of the biogas is avoided and consequently a reduction of its calorific value as well. This system will be optimised on the one hand by adding solubilisers (humic substances) and on the other hand by the variation of pH, oxygen concentration and air to water flow ratio. The pilot plant is shown in figure 1.

![Figure 1: Pilot plant in Albersdorf, Germany](image-url)
3- RESULTS AND DISCUSSION

In the steady state experiments it turns out that only minimal amounts of humate solutions were necessary for a degree of reduction of more than 90%. Due to different initial concentrations of biogas and different concentrations of the used humate solution, the necessary amount varied between 0.1 and 60 ml of humate solution per litre of biogas. The pH value of the humate solutions was between 9 and 10. In comparison tests with pure alkaline water it needed more than 100 ml solution per litre biogas for this reduction. This shows the improvement of the absorption of H$_2$S by the addition of humic substances.

The total series of steady state experiments, see table 1, underlined that the absorption of H$_2$S from biogas is improved by adding humates. The results were not dependent on the used analysing method.

Figure 2 presents the degree of reduction according to the wash volume of a 3.5% humate solution. This example shows that for a reduction of H$_2$S in the gas-phase less than 10 ml of the washing liquid per litre of biogas (content of H$_2$S: 1000 ppm) are necessary to reduce this to almost zero ppm.

![Figure 2: Reduction of H$_2$S with varying volumes of washing liquid](image)

The process of H$_2$S removal runs as follows:
1. Absorption occurs in accordance with Henry’s Law
2. Dissolved H$_2$S dissociates into HS$^-$ and S$^{2-}$
3. Reaction between the H$_2$S and the humic substances

A further series of steady state experiments (variation of pH value and concentration of the humate solution) are carried out to analyse the reason behind the very good reduction rates. This experiment underlines that the reduction of H$_2$S does more depend on the concentration...
of humates than on the pH value. The improvement of the absorptive capacity is minor linked to a high pH value of the humate solution. Even with only a 0.5 % Humin-P solution the required amount of washing liquid is less than with a pure alkaline solution. This was shown when alkaline solutions at pH values between 8.5 and 12 were analysed. The specific interaction of the humic substances with the H2S will be analysed in detail in further experiments.

In the experiments with the laboratory bioreactor it was firstly successfully verified that the sulphur bacteria, living in acidic conditions, could adapt to a neutral pH environment. A pH value from 6 to 8 is the optimum for the sulphur producing Thiobazilli [5].

According to the reaction equations, the production of elemental sulphur should proceed at low oxygen concentrations. The accumulation of elemental sulphur at low oxygen supply was verified through analysis. In addition, elemental sulphur accumulates at saturation concentrations of oxygen with sufficient substrate supply. This means that the production of elemental sulphur does not depend on the oxygen supply at high feed rates of H2S or S2O32-. This is in accordance with Buisman [4].

Analyses proved there to be no markable difference regarding addition of humates. The first entire laboratory tests showed that the humate Humin-P does not inhibit the bacteria and the microbiological production of elemental sulphur. The humate Humin-P seems to be inert in the bioreactor.

4- CONCLUSIONS

In summary the results of the laboratory experiments show that the use of humates in the biogas treatment is effective. A bioscrubber-system can be improved substantially by the addition of humic substances. The desulphurisation is simplified by the increased solubility of H2S in a humate solution. Humic substances do not inhibit the microbiological oxidation of H2S by Thiobazilli. In addition, humic substances ameliorate the soil activity and can be used in combination with the obtained elemental sulphur as agricultural fertiliser. Altogether biogas can be desulphurized efficient and environmental-friendly by adding humic substances.

The experiences of the laboratory experiments will be verified by tests carried out at the pilot plant. In addition, further experiments in the laboratory are necessary to determine the reactions between the H2S and the humic substances, as well as the characteristics of their regeneration and the kinetics of the sulphur bacteria.

REFERENCES