



Design and scale-up of an oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas

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ABSTRACT

Reliable and selective removal of hydrogen sulfide (H_2S) is an essential part of the biogas upgrading procedure in order to obtain a marketable and competitive natural gas substitute for flexible utilization. A promising biogas desulfurization technology has to ensure high separation efficiency regardless of process conditions or H_2S load without the use or production of toxic or ecologically harmful substances. Alkaline oxidative scrubbing is an interesting alternative to existing desulfurization technologies and is investigated in this work. In experiments on a stirred tank reactor and a continuous scrubbing column in laboratory-scale, H_2S was absorbed from a gas stream containing large amounts of carbon dioxide (CO_2) into an aqueous solution prepared from sodium hydroxide ($NaOH$), sodium bicarbonate ($NaHCO_3$) and hydrogen peroxide (H_2O_2). The influence of pH, redox potential and solution aging on the absorption efficiency and the consumption of chemicals was investigated. Because of the irreversible oxidation reactions of dissolved H_2S with H_2O_2 , high H_2S removal efficiencies were achieved while the CO_2 absorption was kept low. At an existing biogas upgrading plant an industrial-scale pilot scrubber was constructed, which efficiently desulfurizes $180\text{ m}^3/\text{h}$ of raw biogas with an average removal efficiency of 97%, even at relatively high and strongly fluctuating H_2S contents in the crude gas.

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1. Introduction

Biogas is a renewable and sustainable energy source which is produced by the anaerobic fermentation of organic matter. The common technology to use this energy source is the production of combined heat and power in internal combustion engines. An alternative approach developed in recent years is biogas upgrading and its utilization as a natural gas substitute in households and industry or as a vehicle fuel [1,2]. Although in recent years several biogas-upgrading procedures have been developed, much optimization effort still has to be done in order to turn upgraded biogas into a marketable and competitive energy carrier.

This work deals with the removal of hydrogen sulfide (H_2S), an important step in the biogas upgrading procedure. H_2S is a toxic, malodorous and sour gas, which is typically limited to a few ppm in the natural gas grids (e.g. in Austria this limit is $5\text{ mg}/\text{m}^3_{STP}$). Well developed processes for H_2S removal that are applied in the processing of coke gas, gasification gas, natural gas or in the petrochemical industry often require high temperature and pressure as

well as bulky constructions that are hard to scale down. A promising technology for biogas desulfurization should, on the other hand, provide a reliable and selective removal of varying H_2S loads at moderate process conditions using cheap and ecologically harmless reagents. Also, no toxic or ecologically harmful components should be produced and the construction should be designed in a compact and simple way.

A well-known method in the biogas upgrading technology is the biological conversion of H_2S to elemental sulfur and sulfate using the species *Thiobacilli* in biological scrubbers [3,4]. This technology meets the above-mentioned criteria owing to its low operational costs and harmless reagents and products, as biological scrubbers can be operated with air as the only reactant. However, a drawback is the high sensitivity of the bacteria to changing process conditions like the change of temperature or fluctuations in the H_2S content of the crude gas. As a result, this method is not able to guarantee constant and high removal efficiencies.

Another popular biogas desulfurization method is the adsorption on metal oxides or activated carbon [5,6]. With these methods, very low H_2S contents in the sweetened gas ($<1\text{ ppm}$) can be achieved. However, at higher H_2S contents in the crude gas the adsorption material has to be changed frequently due to sulfurous precipitations on its surface, which results in high operational costs.

Alternatively, H_2S can be removed by absorption into a liquid scrubbing solution (Eq. (1)). H_2S is a sour gas which dissociates in water in two steps as shown in Eqs. (2) and (3), each time releasing

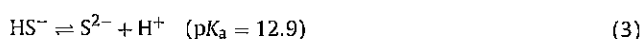
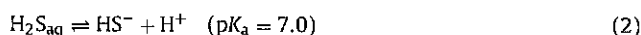
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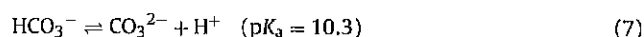
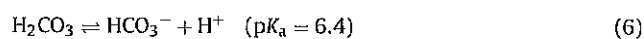
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one equivalent of protons. By adding a certain amount of base to the liquid, the produced protons can be removed. As a consequence, the equilibria are shifted to the right, resulting in an increased H₂S absorption rate.



Depending on the kind of base used, one can distinguish between two technologies. The first one is the amine scrubbing process using ethanolamines (diethanolamine, methyl diethanolamine, diisopropanolamine) for alkalinity [7–9]. This method is well established and mostly applied for combined H₂S and carbon dioxide (CO₂) absorption in natural gas processing or in the treatment of refinery off-gases. The scrubbing solution loaded with sulfide ions needs to be regenerated in a desorption unit at elevated temperature. The desorbed gas is treated in a Claus plant where H₂S is converted to elemental sulfur [10]. This configuration is rather complex and does not scale down well. As a result, it is not suitable for low-size biogas upgrading tasks because of the high specific costs. Moreover, in typical biogas plants all the energy needed to provide elevated temperatures has to be supplied externally, as there is not enough industrial waste heat to be used.

Another approach is the alkaline absorption into a solution of an inorganic base [11–17]. An issue to be considered in alkaline absorption processes used for biogas desulfurization is the concurrent absorption of CO₂, which exists in biogas in much higher concentrations than H₂S and shows similar acidic behavior. Absorption, hydrolysis and dissociation of CO₂ in water are shown in Eqs. (4)–(7). The pK_a values in Eq. (6) (first dissociation step of H₂CO₃) and Eq. (2) (first dissociation step of H₂S) are similar, thus H₂S and CO₂ absorption proceed at similar pH values. The CO₂ absorption leads to a consumption of large amounts of base and, therefore, high operational costs.

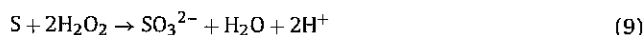
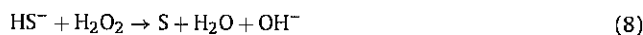


It is known that H₂S absorption occurs faster than CO₂ absorption, as CO₂ undergoes a slow hydrolyzing step [10,13] that is given in Eq. (5). This fact can be used to increase the selectivity towards H₂S by minimizing the contact time between gas and liquid [11,13,15]. The drawback of this method is that increasing selectivity is typically accompanied by lowered removal efficiencies of H₂S.

If an oxidizing agent is added to the scrubbing solution, both H₂S selectivity and removal efficiency can be improved. Since H₂S is a reducing gas, its dissociation products are oxidized and selectively removed from the dissociation equilibrium by irreversible reactions. A number of oxidizing agents can be used for this application: ferric ions [18–20], sodium hypochlorite (NaOCl) [17] or hydrogen peroxide (H₂O₂) [16]. In this work H₂O₂ was used, as it is a cheap and widely available chemical that is easy to handle and does not require elaborate safety measures. A stabilizer is necessary in order to inhibit H₂O₂ decomposition [16,21–23].

During the oxidation process, the sulfur atom passes through several oxidation states. In the first step the HS⁻ ions are oxidized to elemental sulfur consuming one equivalent of H₂O₂, as shown in Eq. (8). The produced elemental sulfur can react with two equivalents of H₂O₂ to form sulfite (SO₃²⁻), which can subsequently be oxidized to sulfate (SO₄²⁻), consuming another equivalent of H₂O₂

(Eqs. (9) and (10)). Additionally, elemental sulfur can react with sulfite to form thiosulfate (S₂O₃²⁻), as shown in Eq. (11). According to Couvert et al. [17], elemental sulfur, sulfate and thiosulfate are stable oxidation products and can be found in the liquid phase. Sulfite cannot be found in the liquid phase, it is an unstable intermediate for the formation of sulfate and thiosulfate.



In this study an aqueous solution of sodium hydroxide (NaOH), sodium bicarbonate (NaHCO₃) and H₂O₂ was used as a scrubbing solution for the H₂S absorption. In the first step, the general behavior of the absorption process was investigated in a discontinuous stirred tank reactor in laboratory-scale. After the method had proven to be efficient in terms of H₂S removal, a continuous absorption column was built in laboratory-scale for further experiments and optimization. An industrial-scale pilot scrubber was constructed at an existing biogas upgrading plant, which now efficiently desulfurizes 180 m³/h of raw biogas. As only stable oxidation products (sulfur, sulfate, thiosulfate) are present in the liquid phase, it can be fed back to the fermenter and discharged together with the digestate.

2. Materials and methods

2.1. Stirred tank reactor

A gas stream containing 50% (v/v) CO₂ and 1040 ppmv H₂S with methane (CH₄) being the balance was brought in contact with the liquid (an aqueous solution of NaOH and H₂O₂) and circulated through the system until all H₂S was absorbed. Then the system was emptied from the remnant gas and filled with a new dose of gas mixture containing H₂S. Each experiment was terminated when the capacity of the scrubbing solution was reached, i.e. when there was no further absorption of H₂S.

Dosage and mixing of the gases was done by mass flow controllers (type 5850S from Brooks Instruments, controlled by RS 485 digital). A mass spectrometer (type GSD 300 T2 Thermostar from Balzers Instruments) was used for gas analysis. Redox potential and pH of the liquid were measured by dual-chamber electrodes (JUMO tecLine equipped with KCl/KCl-bridge and temperature compensation by a Pt100-sensor). Signal conversion and data acquisition was done by PLC and computer software provided by GE-FANUC. Fig. 1 shows the flowsheet of the process. The operating parameters are shown in Table 1.

The aim of the experiments on the stirred tank reactor was to observe the influence of pH and redox potential on the absorption of H₂S and CO₂. The change of absorption behavior due to

Table 1
Operating parameters of the stirred tank reactor. Specifications of liquid and gas compositions are given as the initial conditions for each experiment.

System volume (without bag)	6.9 L
Bag volume	7 L
Liquid volume	1 L
CO ₂ content (gas)	50% (v/v)
H ₂ S content (gas)	1040 ppmv
NaHCO ₃ concentration (liq.)	0–90 kg/m ³
NaOH concentration (liq.)	0.15 kg/m ³
H ₂ O ₂ concentration (liq.)	0.15 kg/m ³
Gas–liquid contact area	0.07 m ²
Operating temperature	298 K
Operating absolute pressure	≈10 ⁵ Pa

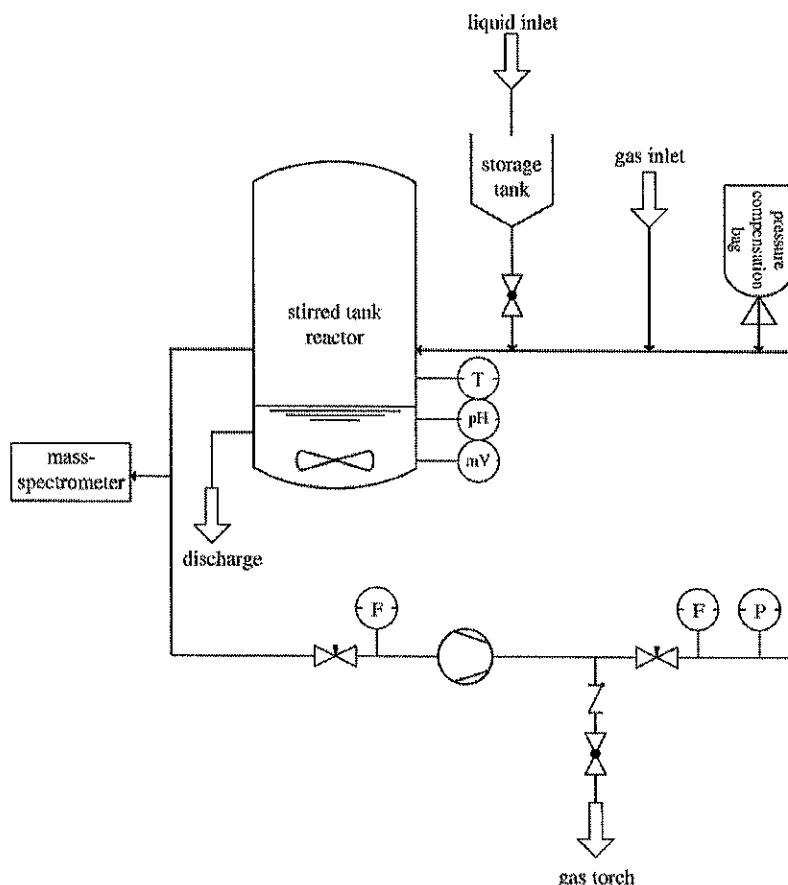


Fig. 1. Flowsheet of the stirred tank reactor.

increasing concentrations of sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) ions with the aging of the liquid was also investigated. Therefore, the scrubbing solution was reused for all experiments. The absorption capacity was restored after each run by adding a new amount of NaOH and H_2O_2 in order to reach the respective starting condition of 0.15 kg/m^3 in the scrubbing solution (see Table 1). The electrical conductivity of the solution was measured (with a GMH 3430 sensor from GREISINGER electronic) previously to each experiment, as a criterion for the total ion concentration. For some experiments, additional amounts of sodium bicarbonate (NaHCO_3) and sodium sulfate (Na_2SO_4) were added in order to test the absorption at higher values of electrical conductivities (up to 74.4 mS/cm), as they are possible to occur during a continuous process without a frequent exchange of the scrubbing solution. It could be observed that the aging of the scrubbing solution lead to a better absorption behavior due to the increasing buffer capacity with increasing concentration of NaHCO_3 , which forms carbonic acid (H_2CO_3) by taking up protons (backward reaction in Eq. (6)). This phenomenon will be further discussed in Section 3.

2.2. Laboratory scrubbing column

The second set of experiments was done on a continuous packed scrubbing column in laboratory-scale. In these experiments the same gas mixture was used as in the experiments on the stirred tank reactor. The gas stream passed through the column continuously and was subsequently burned in a gas torch. The scrubbing solution circulated in a closed loop through the column and the storage tank. Eventually, H_2O_2 was added with a syringe, while an

equal amount of liquid was discharged. The analytic devices were the same as in the experiments on the stirred tank reactor. The mass spectrometer was used to analyze the outlet gas. Redox potential, pH and electrical conductivity were measured in the storage tank. Fig. 2 shows the flowsheet of the process. The operating parameters are shown in Table 2.

The aim of the experiments on the continuous absorber was to obtain process control parameters that can ensure an effective H_2S absorption while keeping the consumption of chemicals low. At the beginning of the experiments, the scrubbing solution had a concentration of 80 kg/m^3 NaHCO_3 and an electrical conductivity of about 45 mS/cm . This value was chosen based on the results from the stirred tank reactor. It was assumed to be close to the values reached in a large-scale absorber at continuous operation. In order

Table 2

Operating parameters of the scrubbing column. The NaHCO_3 concentration is given as the initial concentration of each experiment. The H_2O_2 concentration refers to the amount periodically added to the scrubbing solution.

Gas flow rate	$0.48 \text{ m}^3_{\text{STP}}/\text{h}$
Liquid flow rate	$0.02 \text{ m}^3/\text{h}$
Column diameter	0.1 m
Active height	0.4 m
CO_2 content (crude gas)	50% (v/v)
H_2S content (crude gas)	1040 ppmv
NaHCO_3 concentration (liq.)	80 kg/m^3
NaOH concentration (liq.)	Not used
H_2O_2 concentration (liq.)	$0.1\text{--}1.4 \text{ kg/m}^3$
Specific area (packing material)	$300 \text{ m}^2/\text{m}^3$
Operating temperature	298 K
Operating absolute pressure	$\approx 10^5 \text{ Pa}$

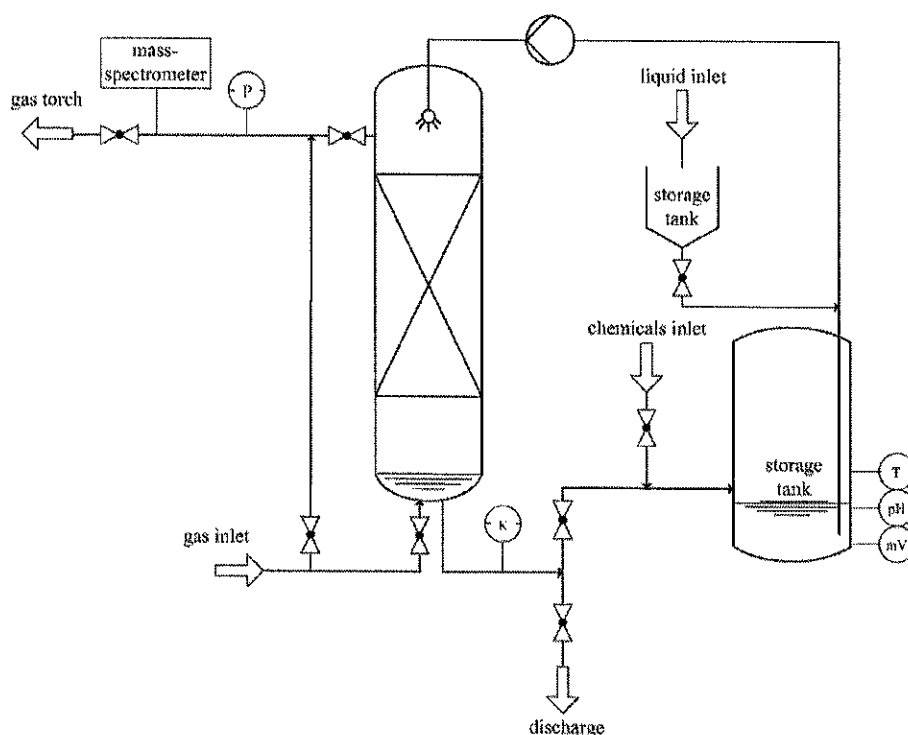


Fig. 2. Flowsheet of the laboratory plant.

to investigate the influence of the H_2O_2 concentration on the H_2S absorption, different amounts of H_2O_2 were added periodically by injection, whenever a complete H_2S absorption no longer occurred, i.e. the H_2O_2 became depleted. There was no need to add NaOH , as the solution was strongly buffered by NaHCO_3 and the pH value was constant on approximately the same level within 8 hours of experiment.

2.3. Pilot plant

The industrial-scale pilot plant was constructed at an existing biogas upgrading plant for the desulfurization of $180 \text{ m}^3/\text{h}$ of raw biogas. Fig. 3 shows the flowsheet of the absorber. The operating parameters are shown in Table 3. The criteria of similarity considered during the process of scale-up were the residence time of the gas in the column, the ratio between gas and liquid flow rate, the ratio between column diameter and column height as well as the specific surface area of the packing material. The dosage of NaOH and H_2O_2 is carried out through a regulation of pH and redox potential, respectively. The electrical conductivity of the scrubbing solution is controlled by a periodical discharge of scrubbing solution and replacement with fresh water through level control.

In order to obtain some data on the separation efficiency of the pilot plant, the contents of H_2S at the inlet and the outlet of the

plant were measured by the plant operators for several months. The measurements were performed using a portable gas analyzer BM2000 provided by GSI. Due to technical reasons the collection of data at the pilot plant was done irregularly. The collected values for the consumption of chemicals are hourly averages, while the H_2S content was measured at certain time instants. The separation efficiency is defined as the difference in H_2S content between the inlet and the outlet divided by the H_2S content at the inlet of the scrubber. The specific consumption of chemicals is defined as the molar amount of the consumed pure reagent divided by the molar amount of the separated H_2S .

The constructed pilot plant is used as a desulfurization step in connection with the biogas upgrading process based on membrane gas permeation technology [2]. The task of this process combination is the production of natural gas substitute and supply to a public gas grid.

3. Results and discussions

3.1. General behavior

Exemplary results obtained in an absorption process on the laboratory column are shown in Fig. 4. At the beginning of the experiment the H_2S content in the sweetened gas was zero because of an alkaline absorption into the NaHCO_3 solution as shown in Eqs. (1)–(3). At the same time CO_2 was absorbed into the liquid, which could be observed by the lowered CO_2 content of about 49% (v/v). This led to a decrease of pH due to Eq. (4)–(7). After about 10 minutes the equilibrium was reached and no more H_2S or CO_2 could be absorbed. As a result, H_2S could be observed in the sweetened gas. The subsequent addition of H_2O_2 resulted in the oxidation of HS^- ions as shown in Eqs. (8)–(10). At this point, the H_2S content in the sweetened gas began to decrease rapidly. The increased oxidation potential of the scrubbing solution was indicated by the redox signal, which peaked from approximately -390 mV to

Table 3
Operating parameters of the pilot plant.

Gas flow rate	$180 \text{ m}^3_{\text{TP}}/\text{h}$
Liquid flow rate	$7.9 \text{ m}^3/\text{h}$
Column diameter	0.71 m
Active height	3 m
CO_2 content (gas)	30–50% (v/v)
H_2S content (gas)	$\leq 3000 \text{ ppmv}$
Specific area (packing material)	$300 \text{ m}^2/\text{m}^3$
Operating temperature	298–313 K
Operating absolute pressure	$\approx 10^5 \text{ Pa}$

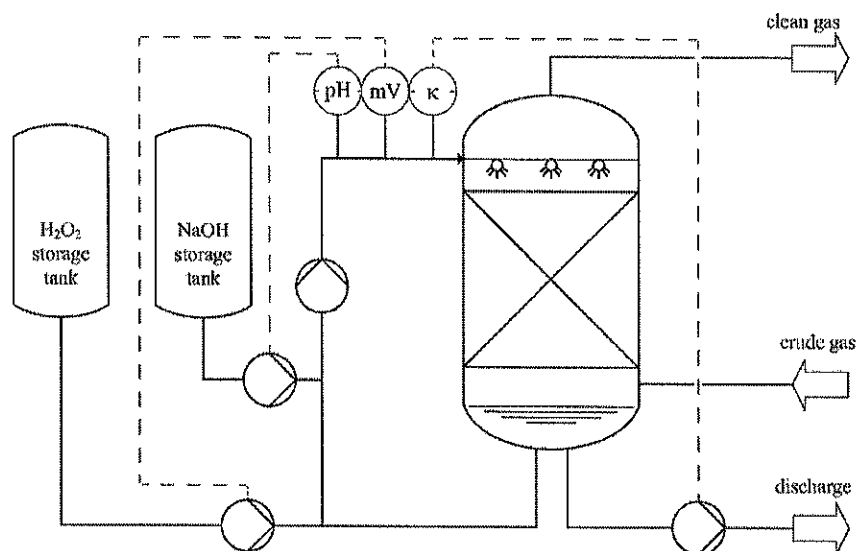


Fig. 3. Flowsheet of the pilot plant.

higher values depending on the added amount of H_2O_2 . As the absorption proceeded, H_2O_2 was consumed and the redox potential gradually decreased. If higher amounts of H_2O_2 were added, the redox potential remained at the saturation value of approximately 180 mV, as in Fig. 4 at process times of 6000 s and above. The continuous absorption of H_2S caused a gradual decrease of redox potential down to a value of about 90 mV, then a rapid decrease started, indicating that the H_2O_2 became depleted. A minimum value between -370 and -390 mV was reached when there was no H_2O_2 present in the solution. H_2S absorption still occurred until the equilibrium of Eqs. (1)–(3) was reached. Then the H_2S content in the sweetened gas began to increase. This behavior proves a correlation between the redox potential and H_2S absorption of the solution. For a better visualization of this correlation, Fig. 5 shows the column volume specific H_2S absorption rate $r''_{\text{H}_2\text{S}}$ and the redox potential over the course of the process. The maximum rate of $4.4 \times 10^{-5} \text{ m}^3/\text{m}^3\text{s}$ was achieved independently of the exact amount of H_2O_2 , as long as the redox potential was above around 100 mV.

The CO_2 absorption, on the other hand, is not influenced by the redox potential. As one can see in Fig. 4, the CO_2 content in the sweetened gas levels off at 50% (v/v) in the course of the process.

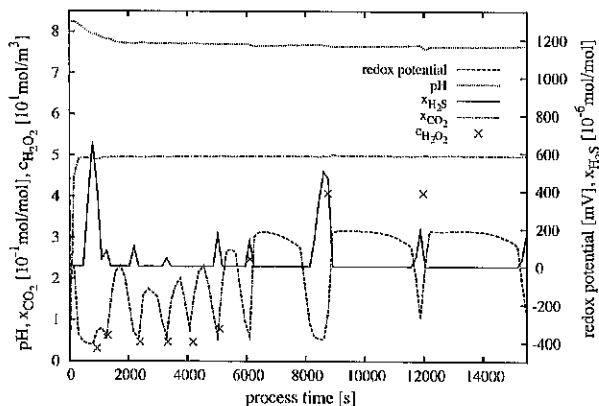
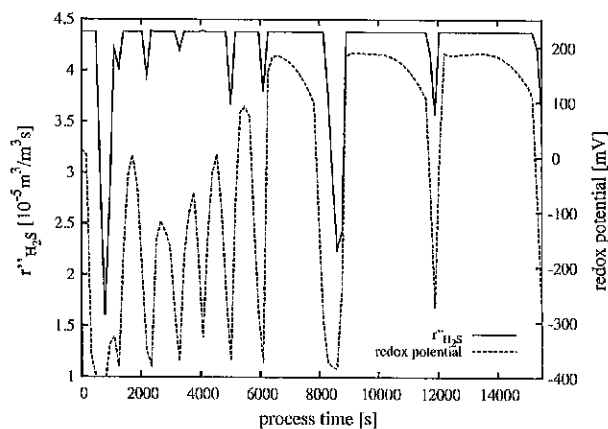


Fig. 4. Absorption behavior on the laboratory column.

HCO_3^- ions cannot be further oxidized and are not removed from the dissociation equilibrium. Therefore, the problem of strong pH decrease and high NaOH consumption due to CO_2 absorption occurs only at the beginning of the experiment until the chemical equilibrium is reached. Then the decrease in pH is mainly caused by the H_2S absorption, which results in a much smaller slope. This behavior provides the main advantage of the proposed method. By adjusting the pH just high enough for H_2S to dissolve and by constantly removing the sulfide ions from the equilibrium with H_2O_2 , a high selectivity can be achieved without a reduction of the absorption efficiency.

3.2. Influence of solution aging

The influence of solution aging on the absorption behavior was mainly studied during the experiments on the stirred tank reactor. At the start of each experiment, the same amounts of NaOH and H_2O_2 were added to the reused scrubbing solution. The contents of Na_2SO_4 and NaHCO_3 increased from run to run, the latter providing a pH buffer with increasing strength. This is shown in Fig. 6, where the change of pH during the progress of different runs

Fig. 5. Correlation between the redox potential and the H_2S absorption rate.

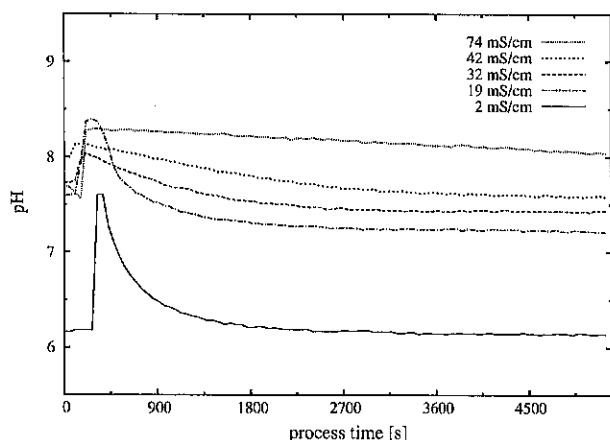


Fig. 6. Change of pH during the progress of selected experiments on the stirred tank reactor.

Table 4

H₂S absorption velocities for scrubbing solutions with different electrical conductivities.

κ [mS/cm]	pH	$r'_{\text{H}_2\text{S}}$ [m ³ /m ² s]
2.1	6.1	4.0×10^{-8}
18.8	7.4	1.0×10^{-7}
31.8	7.6	2.0×10^{-7}
42.0	7.9	4.4×10^{-7}
74.4	8.2	2.5×10^{-7}

is displayed. Both the rapid increase with the addition of freshly recovered solution and the decline due to H₂S and CO₂ absorption were damped by increasing NaHCO₃ concentrations (increasing electrical conductivities in Fig. 6). Also, the average operating pH increased with the electrical conductivity of the scrubbing solution, as shown in Fig. 7. This behavior illustrates the advantage of adjusting the pH with NaHCO₃ instead of NaOH, as NaOH is quickly consumed by reaction with CO₂, while NaHCO₃, as the product of CO₂ dissociation, shifts Eq. (6) to the left and counteracts CO₂ absorption.

Table 4 shows the average electrical conductivities of experiments performed with different amounts of added NaHCO₃ and Na₂SO₄, the respective average pH and the respective average H₂S absorption velocities based on the interfacial area $r'_{\text{H}_2\text{S}}$. The absorption velocities were calculated from the time needed for

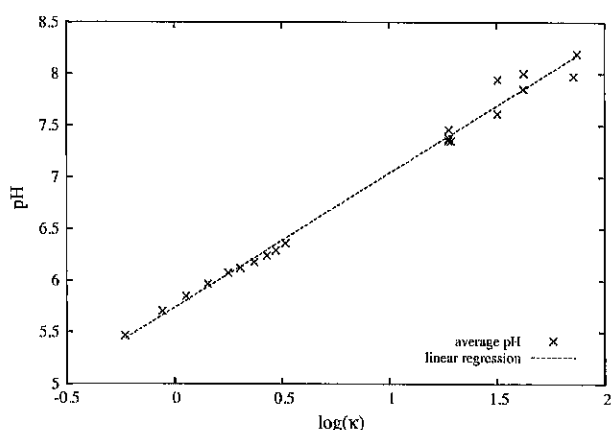


Fig. 7. Correlation between the average pH and the electrical conductivity of the scrubbing solution.

a defined volume of H₂S to be absorbed into the scrubbing solution. Generally, an increase of the H₂S absorption rate with increasing electrical conductivity (and, therefore, increasing average pH) could be observed. This phenomenon was to be expected, as the equilibria of Eqs. (1)–(3) are shifted to the right with increasing pH (see Section 1). However, a lower absorption rate was observed during the experiments performed at an average electrical conductivity of 74.4 mS/cm. This might be caused by a limitation in mass transfer because of the high ionic strength of the liquid. The highest absorption rates were achieved with electrical conductivities of the scrubbing solution between 40 and 45 mS/cm. Therefore, this range of electrical conductivity was chosen for the experiments on the laboratory scrubbing column.

3.3. Process control parameters

From the experiments on the stirred tank reactor and the laboratory column, the following conclusions considering H₂S absorption could be drawn:

- Reasonable H₂S absorption could be observed for all tested pH values from 6.1 to 8.2.
- Higher concentrations of NaHCO₃ in the solution buffer the pH, which leads to higher absorption rates and a lower consumption of base.
- As long as there is enough H₂O₂ in the solution, the redox potential has a value of above 100 mV. When H₂O₂ becomes depleted, the redox potential rapidly drops below zero.
- This rapid decline, which starts reproducibly around 90 mV, is always coupled with the shortage of H₂O₂ and the termination of H₂S absorption.

Therefore, the approach for the second set of experiments on the laboratory column was to ensure complete H₂S absorption at any time by keeping the pH above 6.1 and the redox potential above 100 mV. The scrubbing solution used was again a NaHCO₃ solution with an electrical conductivity in the range of 45 mS/cm. This buffer was strong enough to keep the pH above 7.7 for the whole period of continuous absorption (more than 8 h). Different amounts of H₂O₂ were injected, whenever the redox potential dropped down to 100 mV. With this method, virtually complete H₂S absorption could, in fact, be ensured at any time. The H₂S content in the sweetened gas remained below the limit of detection during the whole process, i.e. in ppb range.

3.4. H₂O₂ consumption

In the experiments on the laboratory column, different amounts of H₂O₂ were added at a time. This affected the specific H₂O₂ consumption, i.e. the amount of H₂O₂ consumed per amount of H₂S absorbed. Fig. 8 shows the specific uptake averaged between the injection points ($\nu_{\text{H}_2\text{O}_2}$) plotted over the initial H₂O₂ concentration, i.e. the concentration at the time of injection. It is clearly noticeable that the specific H₂O₂ consumption increases with the initial concentrations of H₂O₂.

This can be explained by the different possible oxidation states of sulfur during the oxidation of the HS⁻ ion, as explained by means of Eqs. (8)–(11) in Section 1. Apparently, if the concentration of H₂O₂ is very low, Eq. (8), where one equivalent of H₂O₂ is consumed, predominates and elemental sulfur is the main oxidation product. With increasing amounts of H₂O₂ the formations of sulfite and sulfate, that consume three or four equivalents of H₂O₂, respectively, become more prevalent, which leads to a higher consumption of H₂O₂. This issue was discussed and experimentally verified by Couvert et al. [17].

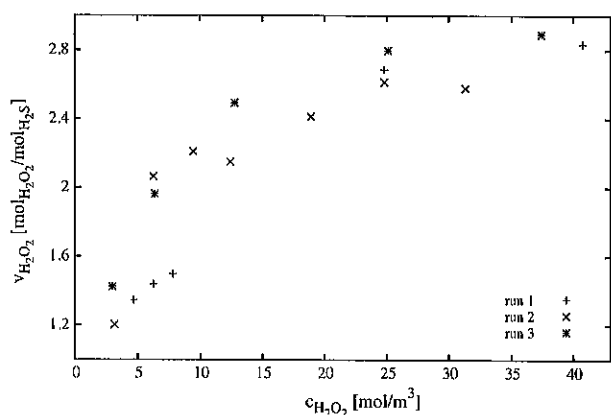


Fig. 8. Correlation between the consumption of H_2O_2 and its concentration.

The lowest consumption of H_2O_2 is theoretically obtained if only elemental sulfur is produced. Also, as can be seen in Eq. (8), the byproduct of sulfur formation is the hydroxide ion, which helps to stabilize the pH and, therefore, reduces the consumption of base. For the formation of sulfite and sulfate, the consumption of H_2O_2 is three and four times higher, respectively. Besides, in Eq. (9) protons are produced, which leads to a higher consumption of base. On the other hand, elemental sulfur is hardly soluble in water and precipitates in pipes and on the packing material. The process time on the laboratory column was not long enough to observe problems related to these precipitations, like an increasing pressure drop due to plugging. Nevertheless, their occurrence can be expected at continuous operation of a large-scale plant and is also reported for other processes where elemental sulfur is produced [24]. The consequences are high predicted maintenance costs for emptying and cleaning pipes and packing material. Thiosulfate and sulfate have a better solubility in water. They can be discharged with the waste water and, therefore, are not likely to cause such precipitations.

It should be noted that H_2O_2 decomposition, as described by Charron et al. [22] and Spalek et al. [23], can also be a possible explanation for the higher H_2O_2 consumption at higher initial H_2O_2 concentrations, as the use of a stabilizer cannot guarantee a complete inhibition of H_2O_2 decomposition.

3.5. Pilot plant

The pilot plant was constructed and tested at a cofermentation biogas plant that utilized substrates of great variety. Therefore,

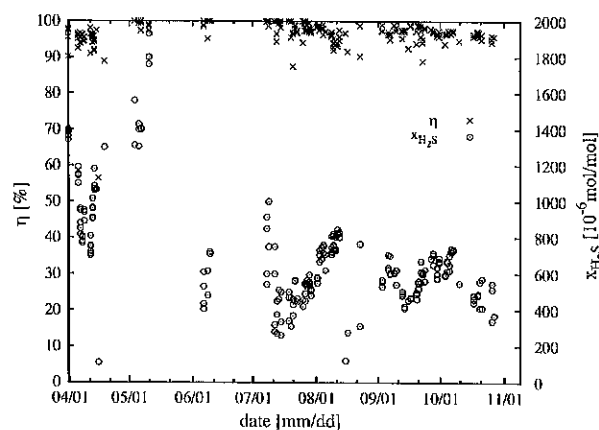


Fig. 9. H_2S content in the raw biogas and the separation efficiency of the pilot plant in a long-term test.

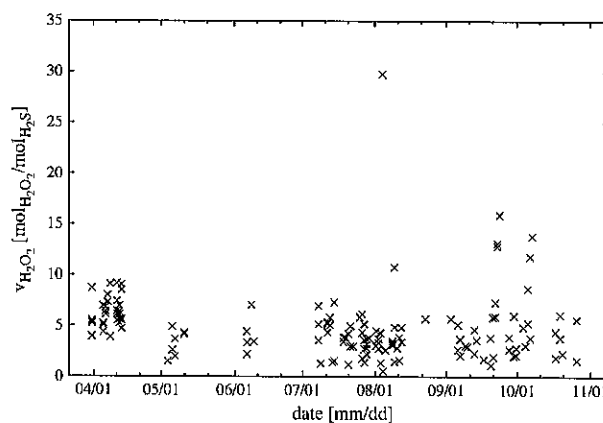


Fig. 10. Specific H_2O_2 consumption in a long-term test on the pilot plant.

daily and monthly fluctuations in the H_2S content in the produced biogas were expected. Fig. 9 shows the collected data points on the separation efficiency η and the H_2S content in the raw biogas within a period of several months. It is noticeable that the plant was able to achieve high separation efficiencies, even if relatively high H_2S contents of up to 2000 ppmv were present in the raw biogas. Also, high fluctuations in the H_2S content did not influence the separation efficiency. The average separation efficiency calculated from the documented data points equals 97%.

Figs. 10 and 11 present the collected data points on the specific consumption of H_2O_2 and NaOH , respectively. The majority of the points representing the H_2O_2 consumption can be found in the range of up to $10 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$. The average consumption calculated from the data points from the test period is equal to $4.8 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$. This value is higher than the values reported in the laboratory experiments (see Fig. 8). It is also higher than the maximum possible stoichiometric amount of H_2O_2 that is consumed if all HS^- is converted to SO_4^{2-} (i.e. $4 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$). The overconsumption might be caused by the loss of H_2O_2 during the periodical exchange of the scrubbing solution or to the oxidation of other trace components present in the biogas (typical trace components in biogas are given in [25,26]). Also, H_2O_2 decomposition can be a possible explanation, as described in Section 3.4. The average specific consumption of NaOH calculated from the collected data points equals $6 \text{ mol}_{\text{NaOH}}/\text{mol}_{\text{H}_2\text{S}}$.

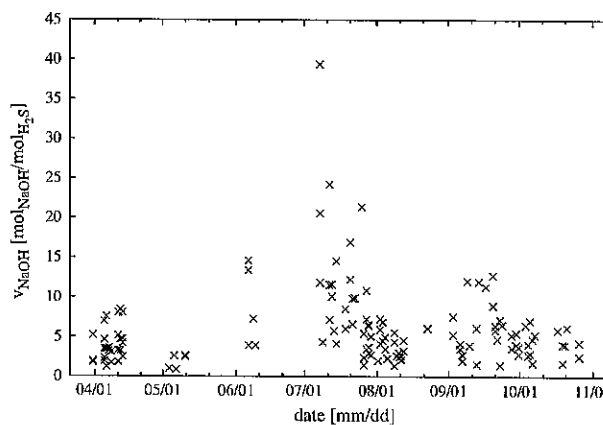


Fig. 11. Specific NaOH consumption in a long-term test on the pilot plant.

4. Conclusions

Chemical oxidative absorption is a promising method for the H₂S removal in the biogas upgrading process, since the irreversible oxidation reactions can guarantee constant and effective H₂S removal, even at relatively high and strongly fluctuating H₂S contents in the crude gas, while the CO₂ absorption and thus the consumption of base is kept low. Also, no harmful substances are produced during oxidation, thus the remnant liquid can be fed back into the fermenter and discharged with the digestate.

In the laboratory experiments, virtually complete H₂S absorption could be ensured at any time by maintaining the pH above 7.7 and the redox potential above 100 mV. Investigations on the solution aging showed that the increasing content of HCO₃⁻ ions, which were formed by the previously absorbed CO₂, provided a pH buffer with increasing strength. Therefore, the aging of the solution had a positive effect on H₂S absorption and NaOH consumption. However, at high ionic strength a decrease in absorption rates was observed, which can be attributed to limitations in mass transfer.

The H₂O₂ consumption is directly proportional to the H₂S content in the crude gas, but it can also be negatively influenced by the overdosage of H₂O₂. High concentrations of H₂O₂ present in the solution lead to a higher specific uptake because the dissociated H₂S is oxidized all the way to SO₄²⁻, while for low concentrations of H₂O₂ in the solution elemental sulfur is the final oxidation product.

In the experiments on the pilot plant, high separation efficiencies (with an average of 97%) could be reached, despite strongly fluctuating H₂S contents in the crude gas. The average H₂O₂ consumption equaled 4.8 mol_{H₂O₂}/mol_{H₂S}, which is higher than the values reported for the laboratory column (1.2–2.9 mol_{H₂O₂}/mol_{H₂S}). It is also higher than the maximum theoretical consumption (4 mol_{H₂O₂}/mol_{H₂S}). This overconsumption can be attributed to the oxidation of other trace components that are present in biogas, to the loss of the oxidizing agent during the periodical exchange of the scrubbing solution, or to a decomposition of H₂O₂. Future work includes the reduction of the specific H₂O₂ consumption in the pilot plant through an optimized control system as well as optimization efforts in process design.

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