Development of a biotrickling filter for the removal of H_2S from biogas

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ABSTRACT. One of the most important obstacles to widespread the use of biogas by injecting it on the natural gas grid or using it in fuel cells is related to the strict requirements concerning gas quality, as some detrimental compounds like hydrogen sulphide must be almost completely removed for these uses. Nowadays H_2S is mainly removed by expensive physical-chemical methods. The objetive of this study is the devolpment of a cost-effective biotrickling filter for treating biogas containing high concentrations of H_2S (2000 ppmv) in order to reduce it to less than 3 ppmv. With this intention a laboratory trickle bed filter was set up. It was found that for H_2S inlet concentrations up to 900 ppmv the H_2S outlet concentration was < 3 ppm with an efficiency > 99%.

1 INTRODUCTION

Biogas, produced by the digestion of organic materials in landfills and sewage treatment plants, is a potentially important renewable energy source. Nowadays it is mainly used to obtain electrical and thermal energy in cogeneration systems, but a more efficient and widespread use can be reached by introducing it in the natural gas grid for a more effective distribution or using it in fuel cells for a more efficient energy conversion. An important drawback of these applications is that the biogas has to have a high purity and therefore it is necessary to remove almost completely some trace detrimental compounds. Specific contaminants for biogas utilization are hydrogen sulphide, halides and silicon containing compounds. Hydrogen sulphide, which is always present in the biogas, normally at concentrations between 80 - 4000 ppmv, is one of the most problematic contaminants as being toxic and corrosive to most equipment. Moreover, its combustion leads to sulphur dioxide emissions, which have harmful environmental effects. In the case of the fuel cells, very low concentration of H_2S can damage the FCs' catalyst, e.g. at Molten Carbonate Fuel Cell (MCFC) the requirements are < 10 ppmv H_2S in the fuel and < 0.1-0.5 ppmv at the anode (Trogish *et al*., 2004). In case of injecting upgraded biogas into natural gas grids the requirements are also rather strict, e.g. in Austria < 5 mg H_2S/m^3 (approx. 3 ppmv)

At the present time, H_2S is mainly removed by expensive physical-chemical methods, mostly adsorption and absorption, so the objective of our work is to develop a cost effective biological biogas H_2S cleaning system. Concretely we have focused our attention on the biotrickling filter technology. Biotrickling filters (BTFs) were initially developed for air pollution control in order to treat odorous off-gases from wastewater treatment plants and other sources (Groenestijn *et al*., 1993; Wani *et al*., 1997). To test the use of this kind of system for removing H_2S from biogas Profactor has developed a prototype laboratory biotrickling filter. The aim is to reduce the concentration of H_2S to less than natural gas levels, that is from about 2000 ppmv to 3 ppmv.

2 MATERIALS AND METHODS

2.1 Bacteria and medium

Bacteria, tentatively identified as *Thiobacillus* were isolated from activated sludge taken from a waste water treatment plant in Asten (Austria). The isolation and generation of biomass was done aerobically in liquid culture using 250 ml Erlenmeyer flasks. Each flask was filled with 100 ml of general *Thiobacillus* medium and 2 ml of centrifuged sewage sludge (at 4000 rpm during 10 minutes) and set to thrive on a rotating shaker at 150 rpm at room temperature. The composition of the mineral medium used was: 1,5 g of KH_2PO_4; 8,58 g of $K_2HPO_4.3H_2O$; 0,1 g of $MgCl_2.6H_2O$; 0,055 g of $CaCl_2.2H_2O$; 0,8 g of NH_4Cl and 1 l of distilled water (pH~7). The cultures were periodically shock-loaded with sulphur substrate ($Na_2S.9H_2O$) at 4 mM of Na_2S, keeping the pH at 7. This same medium was used as recirculated liquid on the biotrickling filter. The inmovilization of the bacteria on the filter was done by recirculating effluent trickled filter enriched with the bacteria culture through the carrier material.

2.2 Biotrickling filter

A scheme of the cocurrent laboratory-scale biotrickling filter is shown in Figure 1. The filter column, of 0.07 m of diameter and 0.6 m of total height, was made of plexiglas and divided into 3 beds, each of them of 0.1 m height. A total working volume of 1.16 dm^3 was filled with glass rings of 8 mm external diameter and the liquid distribution system consists of perforated plates with 4 mm holes.

To provide oxygen to the bacteria, as working with biogas, the liquid medium is forcing through a bubble column were is saturated with oxygen approximately at 7 mg O_2/l. The introduction of oxygen in the liquid medium instead of injecting directly air in the gas stream, which is the normal method, is the main differential characteristic of our system. In this way the quality of the biogas is better because it is not diluted with the N_2 from the added air. Moreover, if the biogas is used in high temperature fuel cells the mixture of methane and air, which can lead to explosive conditions, is avoided, as well as the damage of the anode due to the presence of oxygen. The division of the filter in 3 packed beds provides more flexibility and a higher elimination capacity by optimizing the oxygen transference. The bubble column has a diameter of 0.07 m and a length of 0.5 m. It was made of plexiglass and the air is introduced in the liquid through a horizontal perforated pipe obtaining dispersed bubbles.

The packed division, as well as the general BTF design, has been performed taking into account the results obtained from a previous Profactor BTF prototype which worked with a single packed bed. This filter, developed in the European Union RTD project EFFECTIVE, was running in the biogas plant at the University of Nitra, Slovakia, for 18 months.

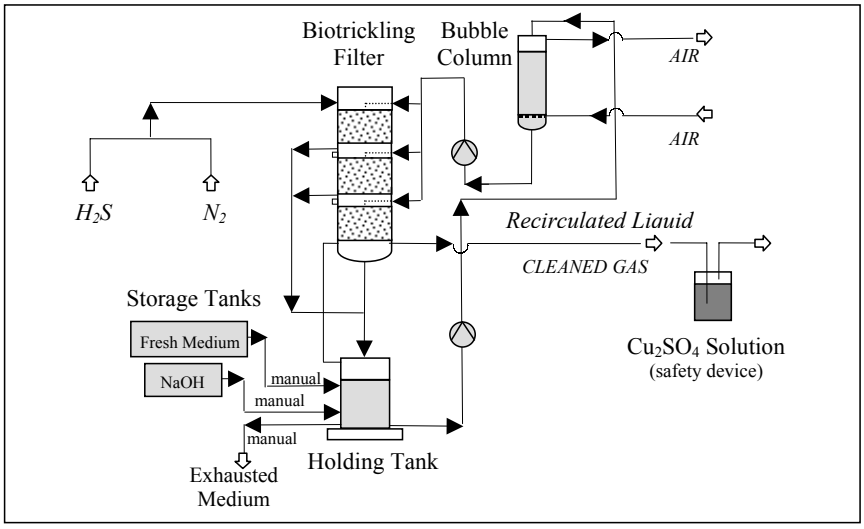

Figure 1. Scheme of the laboratory biotrickling filter system.

Instead of utilizating biogas, due to safety reasons, a mixture of nitrogen and hydrogen sulphide was used. The operational parameters of the BTF are given in Table 1.
Control parameters were temperature through a heating plate, pH by adding NaOH 2N to the recirculated liquid and conductivity by removing or/and adding medium. The gas flow rates for H_2S and N_2 were adjusted utilizing Bronkhorst HI-TEC electronic mass flow controllers and the liquid rate through a Prominent gamma/L solenoid dosing pump. Temperature was measured in each bed using Eutech EcoScan Temp 6 with PT100RTD Temperature Sensors. Conductivity and pH in the recirculated liquid were determined after the bubble column with a WTW-Inolab pH/Cond Level 3 with Schott in Labor pH-Elektrode BlueLine 18 pH and WTW conductivity sensor Tetracon 325. Dissolved oxygen concentration was measured before and after the biotrickling filter with two WTW-Inolab Oxi Level 2 with WTW Oxygen-sensor CellOx 325. Hydrogen sulphide was analysed using a gas chromatograph (Perkin-Elmer Autosystem XL) equipped with a flame photometric detector.

Table 1. Operating conditions of the biotrickling filter.

Operating parameters	Value
Inlet H_2S concentration (ppmv)	100 - 2000
Gas flow rate (m^3/h)	0.020
Gas velocity (m/h)	5.20
Liquid recirculation rate per bed (m^3/h)	0.006
Liquid recirculation velocity per bed (m/h)	1.62
Gas retention time per bed (min)	1.15
pH of recirculation solution	7
Temperature (°C)	28 – 30

3 RESULTS AND DISCUSSION

Figures 2 and 3 show the performance of the system for different inlet H_2S concentrations.

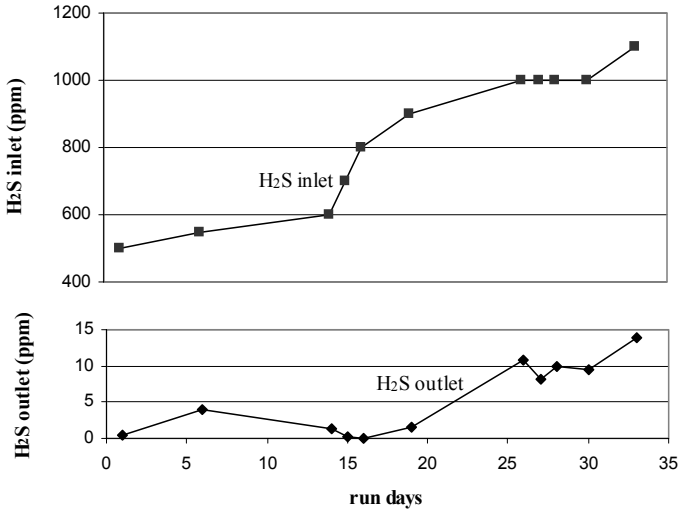

Figure 2. Relationship between the inlet and outlet H_2S concentration.

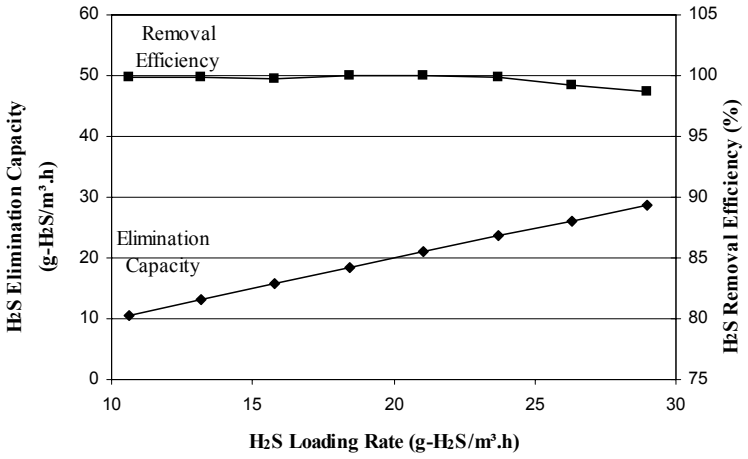

Figure 3. Relationship between H_2S elimination capacity, removal efficiency and H_2S loading rate.

After one month of operation it was proved that the system is able to remove 900 ppmv of H_2S to less than 3 ppmv with an efficiency > 99%, but for higher H_2S inlet concentrations the outlet is superior to 10 ppmv. The H_2S elimination capacity at that inlet concentration is 23,7 g $H_2S/m^3.h$.

During the tests it was also observed that a small amount of H_2S was stripped with the air in the bubble column, which could produce odour and health problems if the system is in a close environment.

One of the possibilities of not having reached the reduction of 2000 ppmv of H_2S to 3 ppmv could be that the system was kinetically limited from the availability of oxygen. To check this, in a short term experiment, air was directly introduced in the system (flow rate of 5% vol. O_2 of the gas stream). In these conditions, the biotrickling filter was able to remove beyond detection limit 2000 ppmv of H_2S. Chemical oxidation could have taken place, but according to Buisman (1989) at sulphide effluent concentrations below 2 mg/l the chemical oxidation is found to be less than 1% of the total oxidation; and at 10 mg/l of sulphide the chemical oxidation is below 2% of the biological oxidation. Nevertheless further tests without inoculum will be carried out to verify this. Moreover, to have a better understanding of the system biologically as well as physically (kinetic and mass transfer limitations) a model of the system is being developed using the Modelica language, and will be implemented in the Dymola simulation program. Several mathematical models have been developed for the removal of pollulants in biotrickling filters. Most of them deal with volatile organic compounds (Alonso *et al*., 1999; Baltzis *et al*., 2001; Barton *et al*., 1999; Diks *et al*., 1991; Hartmans *et al*., 1991; Mpanias *et al*., 1998). Besides, the few ones that treat specifically with H_2S removal do not account for potential kinetic limitations from the availability of oxygen in the biofilm, as working with air gas stream (Deshusses *et al*., 2003; Li *et al*., 2002; Lobo *et al*., 1999). In our model the oxygen is an important parameter. The objetive is for the model to be capable of predicting H_2S and oxygen concentrations in the gas stream, the trickling liquid and the biofilm.

Another aspect to take into consideration in our laboraty system is the carbon source. It could have been possible that it was acting like limiting substrate. In our system the amount of $CO_{2(aq)}$ is 0.40 mg/l; which corresponds to the saturation concentration of liquid in contact with air (~0.03% CO_2) at the bubble column. But, even if the carbon is not a limiting substrate, considering the results of Jaworska (1997), the degradation of sulphur has an important dependency of CO_2 concentration. In his experiments the sulphur bioxidation rate was 45 mg $S/m^2.h$ when the CO_2 concentration in the culture medium corresponded to saturation with air; a maximum rate of 360 mg $S/m^2.h$ was reached for approximately 5.9% CO_2 in the gas phase in contact with the liquid medium and then it decreased and reached a constant value of 160 mg $S/m^2.h$ for more than 9.8% CO_2 in the gas phase, which would be the conditions in a system where the gas were biogas.

Due to these first results, the system has been optimized. In this: a) the gas phase of the system is a mixture of N_2 65 %, CO_2 35% and traces of H_2S, instead of just N_2 and H_2S, in order to avoid the possibility of carbon being a limiting substrate and to get more similar conditions to a real system with biogas; and b) the intermediate liquid outlets of the biotrickling filter have been eliminated leaving all the liquid flow through the beds to avoid the H_2S stripping at the bubble column. In a preliminary study of this action no washing of the microorganisms was detected when increasing the liquid flow.

In this first optimization phase the oxygen concentration will not be increased in order to verify the new conditions with the introduction of CO_2. And again the performance

curve of the system will be determinated and data will be collected in certain operational conditions for the validation of our model.
The model will also be tested with the data coming from two pilot plant units of the system, with respective capacities of 1 and 10 Nm^3/h, which have been just installed in Upper Austria in combination with other biogas upgrading processes.

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