An innovative biotrickling filter for H_2S removal from biogas

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ABSTRACT

A novel biotrickling filter system was developed to remove H_2S from biogas. The aim was to remove 2000 ppmv of H_2S to less than 3 ppmv in order to use biogas in combination with fuel cells, as vehicle fuel or inject it in the natural gas grid. It was found that for H_2S inlet concentrations up to 1000 ppmv the H_2S outlet concentration was < 3 ppm with efficiencies > 99%. The maximum practical elimination capacity was 32.5 g-H_2S. m^{-3}_{filter}. h^{-1}. For 2000 ppmv H_2S inlet concentrations the outlet concentrations were up to 75 ppmv and the elimination capacity was 55 g-H_2S. m^{-3}_{filter}. h^{-1}. The H_2S removal efficiency never dropped below 93.5% in all the concentration range tested.

1 INTRODUCTION

Biogas, produced by the digestion of organic materials in landfills and sewage treatment plants, is a potentially important renewable energy source. It has a high content of methane and its use is highly encouraged by the need of reducing greenhouse gas emissions. Nowadays it is mainly utilized to obtain electrical and thermal energy in combustion engines, but a more efficient and widespread use can be reach by introducing it in the natural gas grid or using it in fuel cells or as automobile fuel.

Hydrogen sulphide, which is always present in the biogas, normally at concentrations between 80 - 4000 ppmv, is one of the most problematic contaminants in order to use digested gas as energy source because is toxic and corrosive to most equipment. Moreover, its combustion leads to sulphur dioxide emissions. In the case of the fuel cells, very low concentration of H_2S can damage the FCs' catalyst. The requirements are also rather strict when injecting upgraded biogas into the natural gas grids or using it as vehicle fuel (Table 1).

In general, H_2S removal methods can be classified in two big groups, the physical-chemicals, which are the traditional ones and currently still dominate the market, and the biotechnological. In the past two decades increasing attention has been paid to the biotechnological methods because having the same or even more efficiency than the physical-chemical ones are generally cheaper, avoid the use of catalysts, and do not generally originate secondary contaminant streams (Sublette *et al*., 1988; Gadre, 1989; Deshusses and Cox, 2000).

Table 1.
H_2S requirements for different biogas utilization technologies
(Wellinger and Lindberg, 2000; Trogisch *et al*., 2004).

Technology	**H_2S tolerance (ppmv)**	**Remarks**
Boilers and stirling engines	< 1000	
Kitchen stoves	< 10	
Internal Combustion Engines	< 1000	Otto engines more susceptible than diesel
Turbines	< 10000	
Microturbines	< 70000	
Fuel Cells: MCFC	< 10 in fuel	<0.1-0.5 at the anode
Natural Gas Upgrade/Vehicle fuel	< 4	Depends on the country

A large variety of aerobic and aerobic bacteria are capable of H_2S oxidation and hence serve as potential candidates for gas desulphurisation technology (Syed *et al*., 2006). Biogas has a very low content of oxygen so, the use of anaerobic bacteria seems a logical option. Several studies with phototrophic bacteria and anaerobic chemotrophic bacteria have been done (Cork *et al*., 1985; Sublette and Sylvester, 1987; Kim and Chang, 1991). Important disadvantages for the application of photosynthetic bacteria is their requirement of radiant energy and their very slow growth rate (Syed *et al*., 2006). In the case of facultative anaerobic chemotrophic bacteria, like *Thiobacillus denitrificans,* there are two main drawbacks. The lower H_2S degradation capacity under anaerobic conditions and the fact that air can be supplied to bioreactors more economically than nitrate (Sublette, 1987). Aerobic bacteria like *Thiobacilli* present several advantages as low nutritional requirements, usually high H_2S affinity and slow biomass growth (Cho *et al*., 1995; Chung *et al*., 1996; Jin *et al*., 2005). In this respect, Profactor GmbH has patented a novel biotrickling filter for the removal of H_2S from biogas using autotrophic aerobic bacteria. In this article the performance of this system is presented.

2 MATERIALS AND METHODS

2.1 Bacteria and medium

The biotrickling filter (BTF) was inoculated with a biomass suspension harvested from a BTF that was eliminating H_2S for several months. Originally this BTF was inoculated with bacteria isolated from activated sludge taken from a wastewater treatment plant in Asten (Austria). A 16S-rDNA sequencing was performed on a sample from the biofilm of the new BTF after 2 months of operation. The dominant bacterial band obtained by single strand conformation polymorphism was identified as *Thiobacillus denitrificans*. The identification was commissioned to the Natural Science University of Graz (Austria).

The medium used in the BTFs contained per litre of distilled water: 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 $CaCl_2.2H_2O$ and 0.8 g of NH_4Cl.

2.2 Novel Biotrickling filter

To determinate the performance of our novel biotrickling filter and to find the optimal operational conditions a co-current laboratory system was set-up (Figure 1). The filter was divided into 3 packed beds. Oxygen saturated medium was introduced at the inlet of each bed, it flowed from that bed to the next ones and finally left the system at the bottom of the third bed.

The conventional way of supply oxygen into a biofilter, when working with biogas, is injecting directly air into the gas stream. When doing this, a safety system is required to avoid explosive mixtures in case of compressor failure. Moreover, the quality of the biogas decreases when nitrogen is added and when not all the oxygen is consumed. This is a problem if the biogas is used as a vehicle fuel or injected in the natural gas grid because of the strict biogas quality requirements. When working with fuel cells oxygen is also a problem because the anode of the fuel cells is damaged with very low concentrations of this compound. By introducing oxygen through the liquid medium the use of a safety system is avoided and the quality problems minimized.

The filter column, of 0.07 m of diameter and 0.6 m of total height, was made of plexiglass. Each of the beds had a height of 0.1 m. A total working volume of 1.15 dm^3 was filled with glass Raschig rings. The liquid distribution system consisted of perforated plates on the top and bottom of each bed with 3 and 4.5 mm holes. The bubble column had a diameter of 0.07 m and a length of 0.5 m. It was made of plexiglass and the air was introduced in the liquid through a horizontal perforated pipe on the bottom of the column, obtaining dispersed bubbles.

Instead of using biogas, due to safety reasons, a mixture of N_2 (65%), CO_2 (35%) and H_2S (traces) was utilized. The H_2S was supplied from a gas cylinder containing 2000 or 4000 ppm of H_2S with N_2 as a diluted gas. The inlet loads were

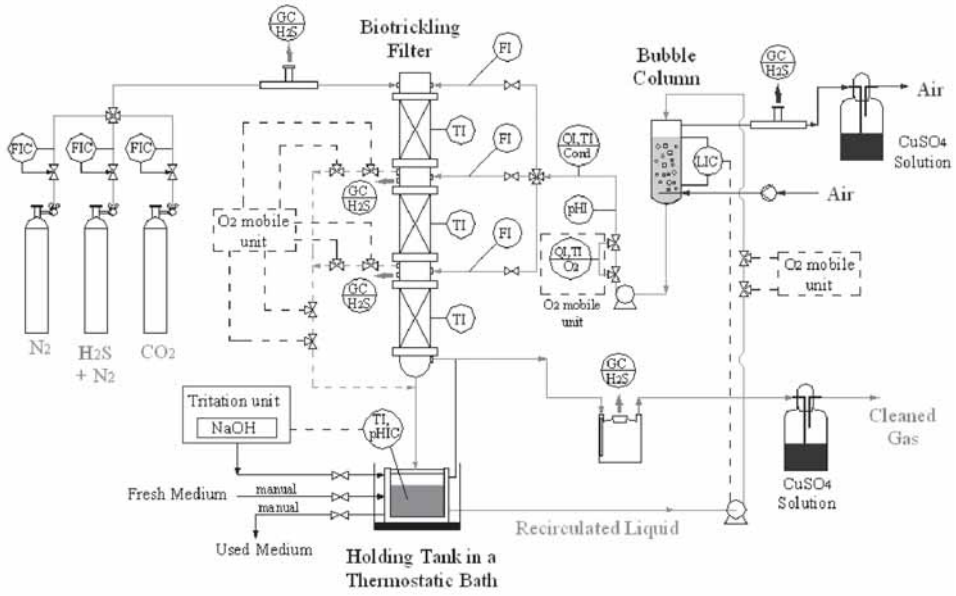

Figure 1. Scheme of the biotrickling filter system.

controlled by changing the effluent flow rates of the gas cylinders utilizing Bronkhorst HI-TEC electronic mass flow controllers.

Control parameters were the temperature, kept at 30ºC through a thermal bath; the pH, adding NaOH 2N as neutralized agent of the formed sulphate (Titroline Alpha Plus, Schott) and the conductivity by adding or/and removing manually medium. In daily bases 10% of the total recirculated medium was lost by evaporation, mainly at the bubble column. The same amount of fresh medium was added, in order to keep the nutrient concentrations sufficiently high and to prevent sulphate accumulation. When conductivity was near to 30 $mS.cm^{-2}$ approximately half of the recirculated medium was replaced by fresh one.

The H_2S concentration on the gas phase was determined at the inlet gas stream, at the gas outlets of the three beds and at the air outlet of the bubble column. Hydrogen sulphide was analysed using a gas chromatograph (Perkin-Elmer Autosystem XL) equipped with a flame photometric detector.

The whole system was placed inside of a hood extractor and the outlet gas and air streams were forced to pass through a $CuSO_4$ solution to retain as CuS the possible no degraded H_2S.

The operational parameters are given in Table 2.

Table 2.
Standard operating conditions of the biotrickling filter.

Operating parameters	**Value**
Inlet H_2S concentration (ppmv)	200 – 2000
Gas flow rate ($m^3.h^{-1}$)	0.020
Fresh liquid inlet medium rate per bed ($m^3.h^{-1}$)	$7.7.10^{-3}$
Empty bed retention time per bed (min)	1.15
Air flow rate at the bubble column ($m^3.\ h^{-1}$)	0.34
pH	7
Temperature (°C)	29 – 31
Liquid oxygen concentration at the BTF inlets ($mg.l^{-1}$)	~ 6-6.5

The packed division of the biotrickling filter, as well as the general design, was performed taking into account the results obtained from two previous biotrickling filter prototypes. The first one worked with a single packed bed and it was running in a biogas plant at the University of Nitra, Slovakia, during 18 months. Good results where achieved for relatively low H_2S concentrations but for concentrations higher than 450 ppmv the H_2S outlet concentrations were much higher than 3 ppmv. It was observed that the oxygen was mainly consumed at the top part of the filter bed. Consequently, the biodegradation in the lower part was reduced, leading to less bacterial efficiency and a not optimal H_2S reduction. To try to solve this problem a laboratory biotrickling filter divided in 3 sections was set-up. At this filter equal amounts of oxygen saturated medium was introduced at the beginning of each bed leaving the system at the end of that bed. In this way more flexibility and a higher elimination capacity was expected by optimising the oxygen transference. With this system the oxygen transference limitation was partially solved as for H_2S inlet concentrations up to 900 ppmv the outlet values were inferior to 3 ppmv. Nevertheless, H_2S was stripped in the air stream leaving the bubble column. This is not affecting the quality of the cleaned gas but could produce odour and healthy problems if the system is in a close environment. The H_2S stripping is produced because not all the H_2S that is dissolved in the liquid phase is degraded by the bacteria. Part of it remains in the recycled liquid and past to the air when reaching the equilibrium at the bubble column. The largest source of dissolved H_2S come from the first and second bed liquid exists. To solve the stripping problem the new configuration here presented, where all the liquid medium is drained at the filter bottom, was tested.

3 RESULTS AND DISCUSSION

Increasing H_2S concentrations were fed to the filter at the standard operational parameters (Table 2) and the H_2S concentration was measured at the different bed outlets. When reaching 2000 ppmv decreasing H_2S concentrations were introduced to evaluate if there was any difference in the performance of the system due to the adaptation of the microorganisms to high H_2S concentrations (Figure 2).

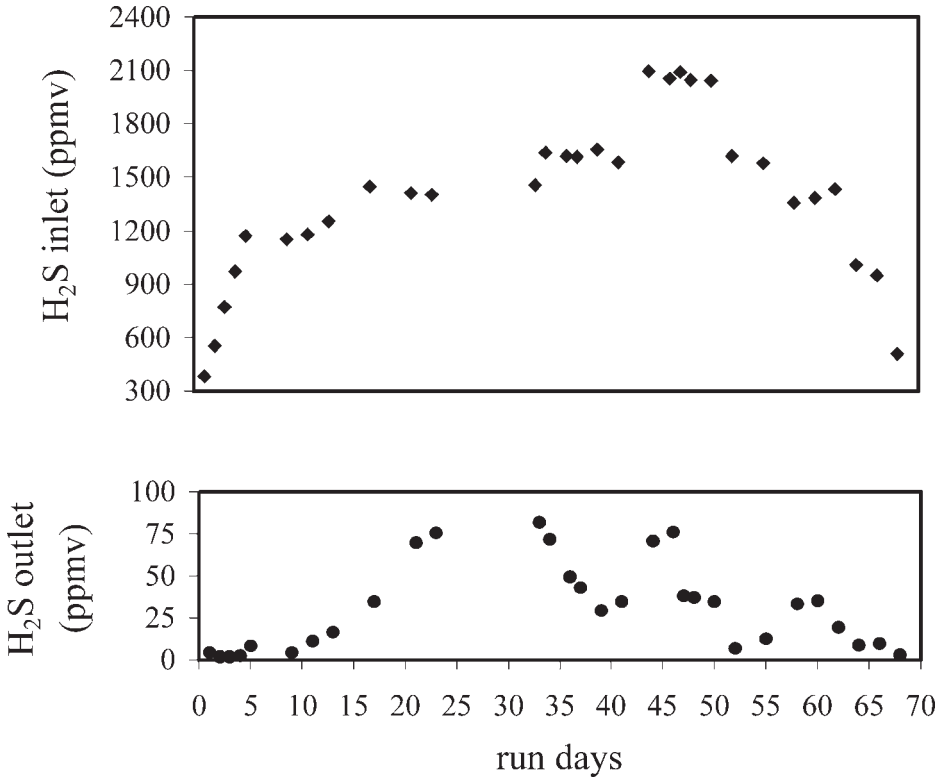

Figure 2. Relationship between the inlet and outlet H_2S.

In standard operational conditions the system was able to remove 1,000 ppmv of H_2S to less than 3 ppmv with efficiencies >99%. The maximum practical elimination capacity was 32.5 g-H_2S. m^{-3}_{filter}. h^{-1}. For 2000 ppmv H_2S inlet concentration, outlet concentrations of 34 to 75 ppmv were found. RE of H_2S never dropped below 93.5% in the tested concentration range (Figure 3). At the highest concentration applied, 2,100 ppmv, the elimination capacity was 55 g-H_2S. m^{-3}_{filter}. h^{-1}.

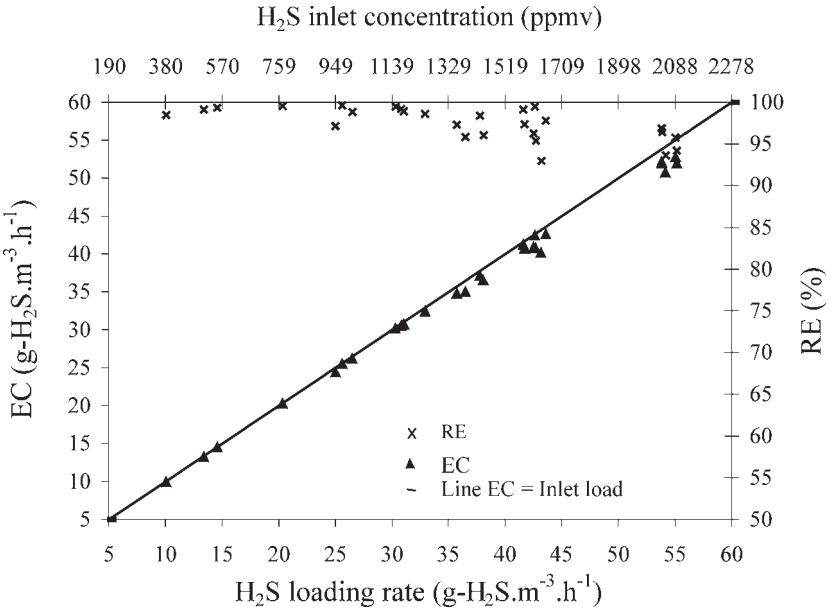

Figure 3. Relationship between H_2S elimination capacity, removal efficiency and H_2S inlet loading rate.

There were not significant differences in the performance of the biotrickling filter for increasing or decreasing H_2S inlet concentrations, which suggests that the bacteria are easily adaptable to different H_2S loads.

In this system the amount of H_2S stripped was always lower than 1.3 $mg.h^{-1}$ (3.3 ppmv) (Figure 4). The new liquid configuration was a good solution to the stripping problem. Moreover the new liquid and therefore oxygen distribution did not have negative effect in the performance of the system as the EC and RE were slightly better than in the previous one.

Referring to the performance of the different beds, the contribution of each of them to the overall removal efficiency is presented in Figure 5.

The removal efficiency at each bed has been calculated as the ratio of the difference between the inlet and outlet concentrations of H_2S in every bed to the concentration at the entrance of the filter. Around 70% of the H_2S is removed in the 1 bed, 25% in the 2 bed and 5% in the last one. For the highest loadings the percentage of H_2S removed on the 1 bed decreases and on the 2 and 3 increases but very slightly. It can be possible that in the 1 bed the H_2S were not totally degraded by the bacteria but just dissolved and degraded afterwards in the other beds. However, when working with just 2 beds the contribution of each of them is quite similar than when working

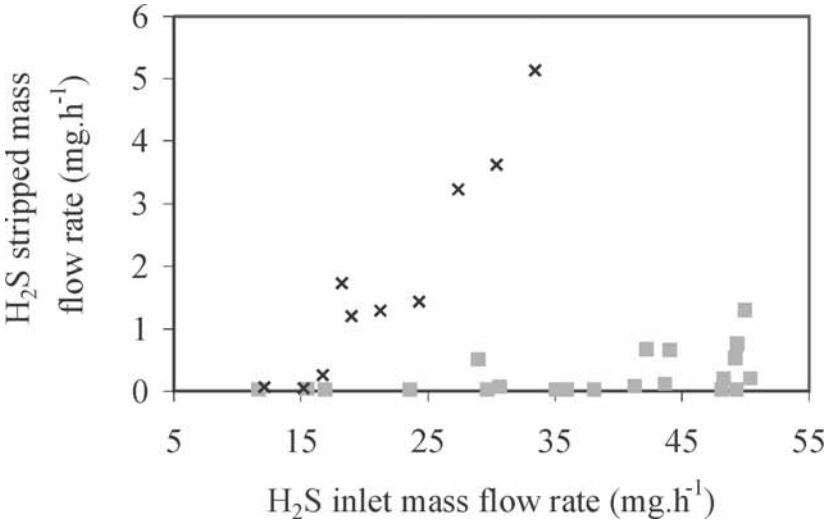

Figure 4. H_2S stripped through the bubble column at different H_2S inlets in the old (x) and new (■) BTF configuration.

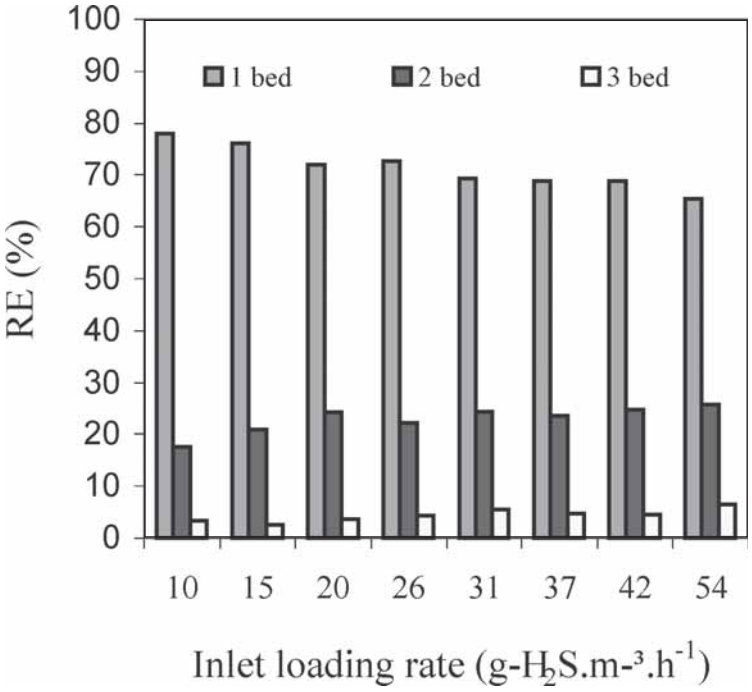

Figure 5. Removal efficiency profiles in the different beds.

with 3 (results not shown) and with almost no H_2S stripping, which means that the amount of H_2S dissolved on the liquid phase is very low.

According to the obtained results it seems that the BTF should have more capacity for removing H_2S. The fact that for H_2S inlet concentrations of 1000 ppmv more than 3 ppmv are detected in the outlet could be due to oxygen limitations or to H_2S mass transfer limitations.

To check this air was directly introduced in the system through the gas stream (flow rate of 50% vol. air of the gas stream). In these conditions for an inlet 2000 ppmv H_2S the outlet was lower than ~3 ppmv. This indicates that the system is oxygen limited. The presence of oxygen in the gas phase specially benefits the areas in the biofilm with low water content because of the small diffusion barrier and the lower availability of oxygen through the liquid phase. This means a higher active biofilm layer. The large availability of oxygen in the liquid phase implies as well a higher microbiological activity. Oxygen concentration in the liquid phase highly influences the bacterial degradation rate (Jaworska and Urbanek, 1998).

There are two basic possibilities of increasing the amount of oxygen introduced in our BTF. The simplest would be to raise the recycled liquid flow rate. In this way the oxygen liquid concentration remains constant. The other would be to use in the bubble column, instead of air, pure oxygen or a mixture of air and oxygen. Doing this higher oxygen saturation concentrations would be reached at the liquid.

The effect of an increase in the liquid flow was studied by doubling it respect to standard operation conditions. After an adaptation period of 11 days with double liquid flow rate, 46.2 $l.h^{-1}$, the RE of the system increased. For example, for an inlet H_2S concentration of 2000 ppmv the H_2S outlet was 16 ppmv, the RE 99.23 % and the stripped H_2S 1 ppmv.

The improvement in the performance of the system with double liquid flow rate could be due apart from a more availability of oxygen to a better liquid distribution. It is likely that the biotrickling filter was limited by liquid channelling and partial wetting of the carrier material. Other studies with a higher oxygen saturation concentration should be done.

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