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SORBENT MATERIALS FOR THE CLEANING OF SEWAGE BIOGAS IN HIGH TEMPERATURE FUEL CELL PLANTS

Extended abstract

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Background

A good solution to reduce greenhouse gas emissions is represented by the micro-cogeneration locally distributed with fuel cell systems. Fuel cells directly transform efficiently fuel into electrical energy by electro-chemical reactions. Amongst fuel cells, SOFCs achieve the highest electrical conversion efficiencies (Buono and Simeone, 2010; Cresson, 1999) with wide fuel flexibility. Extensive research has been performed on fuel cells (Andujar and Segura, 2009; Austergard et al., 2006; Caserini et al., 2004). The integration between SOFCs in domestic and locally distributed systems however represents in theory and in practice a possible solution to reduce pollutant emissions improving also the fuel exploitability. One of the main challenges with SOFCs is the low tolerability with contaminants (VOCs) contained in biogenous fuel, such as biogas from the anaerobic digestion of waste water treatment plant sludge. Main compounds found in this biogas are methane and carbon dioxide, while trace compounds are sulphur, chlorine and higher hydrocarbon compounds (from tens to hundreds ppm(v)).

Mainly cell voltage decreases, cell power drop and fuel cell degradation are the main consequences of fuel impurities for the anode compartment (Lanzini et al., 2013) as well as carbon deposition phenomena (Lanzini and Leone, 2010). The problem of VOCs tolerability is addressed by making fuel cells more tolerant against these compounds (Wu and Liu, 2002), or by reducing the amount of VOCs in the fuels (Song, 2002). The most relevant volatile contaminants are sulfur, aromatic, carbonyl and chloro-compounds (Papurello et al., 2012; Sasaki et al., 2006), and siloxanes. The latter two groups are derived from the starting biomass loaded into the digester (Papurello et al., 2012). Hence, it is necessary to implement a cleaning section which effectively removes at ultra-low level VOCs from the biogas in order to feed SOFC systems. To achieve such stringent requirements, commercial sorbent materials are investigated in laboratory conditions.

Objectives

The main objective of this work was to investigate on the effectiveness of commercial filter: ZnO, RST3 and Carb-ox activated carbon. The effect of biogas water content was tested according to measurements done in a real waste water treatment plant (WWTP) (around 7.28 %vol.). At SMAT site H_2S contained in the biogas is one of the main pollutant compounds. Contaminant concentrations, GHSV values and water percentages affect the breakthrough time decreasing the filter removal performance. To know in which way these performances are affected was developed this preliminary work. Especially water content on equal terms affect strongly the removal performance of the sorbent filters, as previously described by Hernandez et al. (2008). In this work we focused on the water content effect on the sulfur removal performance of sorbent materials for SOFC applications. Preliminary considerations on the filter optimization are also reported in order to design a real scale gas cleaning unit for a SOFC stack (SOFCOM project). SOFCOM is an applied research project devoted to demonstrate the technical feasibility,

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the efficiency and environmental advantages of CCHP plants based on SOFC fed by different typologies of biogenous primary fuels (locally produced) also integrated by a process for the CO_2 separation from the anode exhaust gases.

Outline of the work

This work is divided in two main parts:

- The first part covers the biogas characterization made at SMAT waste water treatment plant site.
- The second part covers the investigation on the gas cleaning section at the laboratory conditions, controlling the methane, carbon dioxide volume percentage, the hydrogen sulfide concentration and the water content.

Methods

This paper presents the experimental results achieved for three different sorbent materials for the biogas cleaning for SOFC applications. Characteristics of sorbent materials adopted are indicated in Table 1.

Gas analysis of the biogas produced from the SMAT site, adopting waste derived biomass, was registered monthly (from January to July). For the chlorine, fluorine and bromine compounds it was adopted a method published on DM 25/08/2000 All.2; for the siloxanes and mercaptanes the EPA-TO-15-1999 method; for the sulfur it was adopted the adsorption on an activated carbon cartridge following the EPA 9056A 2007 method with the Mahler bomb. The experimental set-up adopted for the sorbent material test with simulated biogas (CH_4/CO_2 = 1.5), H_2S at 30.72 ppm(v) and demineralized water at 7.28% vol. is reported in Fig. 1. The biogas mixture and pollutant compound were inserted to the experimental set-up with mass flow controllers (Bronkhorst, The Netherlands) whereas the cylinder gas are prepared from (Siad spa, Italy). The demineralized water was added to the main stream using a liquid mass flow controller and a controlled evaporator mixer (Bronkhorst, The Netherlands). Fig. 1 depicts the experimental set-up adopted, red color represents the heated lines at 50°C with heater strings (isopad Thermocoax, Germany) controlled via a PID regulator (Horst, Germany). A PDMS (20 μm) membrane filter, to protect the mass spectrometer from the carbon particles, was inserted between the filter line and the heated trap before the capillary line of the mass spectrometer HPR 20 (Hiden Ltd., UK). The sorbent materials were grounded up to 100-180 μm with a vibratory sieve shaker (Fritsch, Germany). The filter cartridges were prepared with Teflon tubes with around 0,12 g of sorbent material.

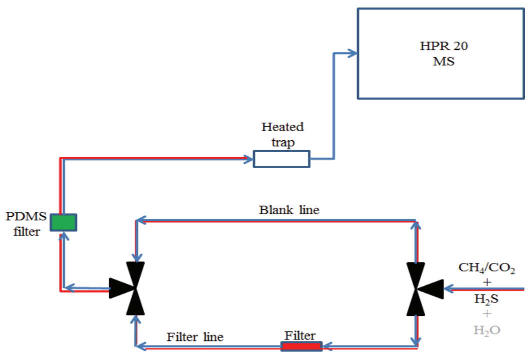

Fig. 1. Experimental set-up

Table 1. Characteristics of sorbent materials tested

Sorbent material	*Apparent density ($kg\ m^{-3}$)*	*Relative density ($kg\ m^{-3}$)*	*Note*
Activated carbon, RST3 Norit	200-600	2100	
Zinc oxide, Actisorb S2 ZnO Clariant		1090	
Activated carbon, Carb-OX Air dep	520	1650	The best performance are achieved with low fraction of oxygen and water – manufacturer

Results and discussion

This paper presents results of the gas cleaning removal with commercial sorbent materials. This work was focused in particular on the sulfur compound removal with and without the contemporary presence of water.

Biogenous gas from the anaerobic digestion of sewage sludge from a waste water treatment plant (SMAT spa), showed the principal contaminants: sulfur, chlorine, siloxane compounds and hydrocarbons. Fig. 2 depicts the concentration for siloxanes (2.a) and halogens (2.b). Organic silicon compounds are in the range of 2.5 and 10 mg/Nm^3 with a highest concentration of D5, D4, D3. Halogen (namely HCl) concentration is around 0.25 mg/Nm^3. Halocarbon concentration is around 1 mg/Nm^3 with dicholoroethylene being the most abundant compound. Total sulfur, not reported in Fig. 2, has on average a total concentration below 120 ppm(v) in the as produced biogas.

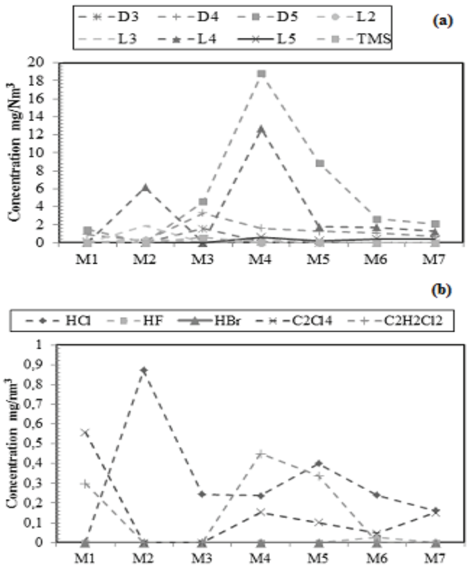

Fig. 2. Siloxanes (a) and Chlorine compounds in the as produced biogas from the SMAT WWTP plant

Considering the H_2S as the principal sulfur compound its concentration trend is reported below, with the maximum concentration around 100 ppm(v).

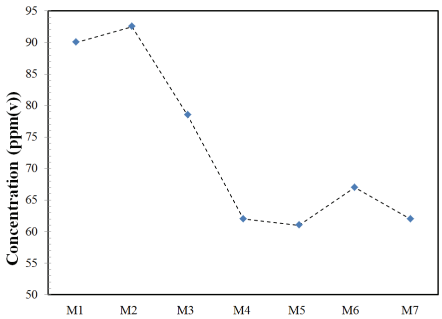

Fig. 3. Hydrogen sulfide in the as produced biogas from the SMAT WWTP plant

Resuming the maximum concentration monitored are: H_2S 95 ppm(v), HCl 0.6 ppm(v), D5 1.25 ppm(v) and D4 0.33 ppm(v). These concentrations are extremely detrimental for fuel cells as reported by Sasaki et al., 2011. For this reason further work is needed especially on the siloxane removal with sorbent materials, due to the low limits for SOFCs detrimental effect is reported around 100 ppb(v) (Sasaki et al., 2011).

Three different sorbent materials were tested for the H_2S removal with simulated biogas mixture CH_4/CO_2. Fig. 4 depicts the removal performance as the ratio between the outlet concentration (C) and the inlet concentration (C_0) of the filter cartridge. The best performance are achieved by ZnO and RST3 activated carbon for the sulfur removal. Carb-ox activated carbon decreases the filer performance around 9% in dry conditions. At stationary conditions this material removes only 30% whereas the other two sorbents 60%.

The impact of the biogas water content on the H_2S removal was investigated for the three different sorbent materials. At the SMAT plant the water contained in the biogas was monitored, a mean value was registered around 7% vol. Considering a humid biogas the filter performance trend changes accordingly to Fig. 4. Zinc oxide and RST3 still show a similar trend even if after the removal of 70% the ZnO allows to have better performance. Carb-ox with water content (7.28 %vol.) shows the best performance for the sulfur removal. An increasing of 50% on the removal performance respect to RST3 at 80% of the concentration removed is depicted in Fig. 4. Under humid conditions the filter performance decrease for RST3 and ZnO around 36% and 28% respectively, whereas in case of Carb-ox they improve of +17%.

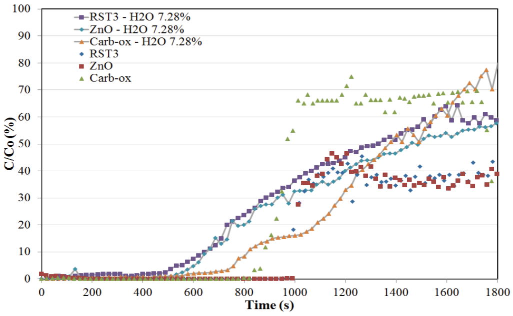

Fig. 4. Hydrogen sulfide removal for sorbent materials in dry and humid conditions

Concluding remarks

This paper describes the removal performance of different sorbent materials for SOFC applications. A biogas mixture and a sulfur pollutant compound was considered for the filter performance in dry and humid conditions according to the measurements done in a real WWTP (SMAT site). According to experimental results, Zinc Oxide and RST3 activated carbon show the best performance in dry conditions. Considering the presence of water in the biogas, the filter performance would decrease with around 30%. A new activated carbon made from air-dep shows a performance increases, around 17% in humid conditions even if in dry conditions presents the worst performance. For a gas cleaning section not only considerations on the biogas water content has to be done, but also on the other pollutant compound concentrations. An our previous study, results not reported here, showed how even only 1 ppm(v) of co-vapors concentration affect the filter performance.

A decreasing in the performance around 30-40% was reported. Co-vapors considered were: aromatic (toluene, xylene) carbonyl (2-butanone) and chlorine (chloroethane) compounds. In conclusion, to design a proper gas cleaning section for SOFC related applications, further work on the pollutants removal is needed, especially considering chlorine and siloxane compounds effect and the contemporary presence of water.

Keywords: biogas, cleaning sorbent material, hydrogen sulfide, SOFC

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