



Proton transfer reaction mass spectrometry technique for the monitoring of volatile sulfur compounds in a fuel cell quality clean-up system



Davide Papurello^{a,b,*}, Lorenzo Tognana^c, Andrea Lanzini^a, Federico Smeacetto^e, Massimo Santarelli^a, Ilaria Belcari^b, Silvia Silvestri^b, Franco Biasioli^d

^a Department of Energy (DENERG), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Turin, Italy

^b Fondazione Edmund Mach, Biomass and Renewable Energy Unit, Via E. Mach, 1, 38010 San Michele a/A, Italy

^c SOFCpower S.P.A., Viale Trento, 115/117, c/o BIC, I-38017 Mezzolombardo, TN, Italy

^d IASMA Research and Innovation Centre, Fondazione Edmund Mach, Food Quality and Nutrition Area, Via E. Mach 1, 38010 S Michele a/A, TN, Italy

^e Applied Science and Technology Department (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Turin, Italy

ARTICLE INFO

Article history:

Received 13 June 2014

Received in revised form 25 September 2014

Accepted 28 September 2014

Available online 20 October 2014

Keywords:

Volatile sulfur compounds (VSCs)

Biogas

Solid oxide fuel cell (SOFC)

Organic fraction of municipal solid waste (OFMSW)

Proton transfer reaction-mass spectrometry (PTR-MS)

ABSTRACT

Biogas from the dry anaerobic digestion of OFMSW from a pilot plant was analyzed in terms of sulfur compound removal through a gas cleaning section based on activated carbons, from lab. scale to real plant. In general, even the presence of sub-ppm(v) of selected biogas contaminants can hamper the life-time of SOFC systems. For this reason, stringent fuel cell quality requirements apply. The challenge of real-time monitoring of the performance and quality of the fuel feeding the SOFC can be solved through the use of PTR-MS. This technique – once properly and preliminarily calibrated as shown in this study – has the capability of rapidly resolving the wide spectrum of contaminants slipping from the clean-up section. A commercial sorbent material was adopted to remove sulfur compounds and was tested for 80 h in a pilot gas cleaning system. H₂S, the main sulfur compound detected (99.36% of total sulfurs) was removed to a satisfactory level. The sulfur compounds elute from the cleaning section in the following order: CH₃SH, CH₃SCH₃, CH₃CH₂CH₂SH, CH₃(CH₂)₃SH, CS₂ and H₂S. The filter section was able to provide a clean biogas (1 ppm(v)) throughout the whole experimental trial (almost 450 h) with an average H₂S inlet concentration of 52 ppm(v).

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1. Introduction

Amongst the various biogas production sources, the anaerobic digestion of organic fraction of municipal solid waste (OFMSW) offers the possibility to obtain a valuable bio-fuel thus recovering the energy content of a waste that would be otherwise disposed in landfill contributing to atmospheric, soil and water pollution. Several applications of biogas have been investigated, mostly for combined heat and power systems (CHP) with internal combustion engines (ICEs) [1]. A growing interest in the field of energy production was more recently gained by micro-turbines or by high temperature fuel cells systems, i.e., molten carbonate technology fuel cells (MCFCS) or solid oxide fuel cells (SOFCs) [2].

At present, fuel cell systems suffer from still very high investment costs. However the potential for higher electric power generation efficiency remains, which means increased fuel saving [3], while at the same time reducing atmospheric emissions (nitrogen oxides (NOx),

sulfur oxides (SOx), carbon monoxide (CO) and volatile organic compounds (VOCs)). In addition, the carbon capture storage or re-use option in fuel cell systems can be achieved more readily than with conventional combustion power systems [4–7], mostly thanks to the absence of nitrogen in the fuel exhaust. One of the main problems related with the energy production with SOFC systems is the biofuels reforming into hydrogen, e.g. biogas and the trace compounds impact on cell performance. Lanzini and Leone [6] investigated on the performances of SOFC fed by simulated biogas mixtures comparing different direct reforming options [8,9].

So far studies with real biogas feeding on SOFC generators have been few. The importance of investigating real biogas feeds is essentially related to the presence of micro-contaminants and their removal to meet the stringent fuel cell requirements [10] for the SOFC anode. In addition to the main biogas constituents (methane and carbon dioxide), trace compounds can seriously affect SOFC systems including the reforming section [11]. Sulfur and chlorine compounds, as shown by Sasaki et al. [8], affect the fuel cells and the reforming section through nickel deactivation, being sulfur far more deleterious than chlorine. Our studies demonstrate how siloxane compounds affect preferentially the interconnectors, limiting the fuel flow to reach the nickel active sites. The subsequent detrimental action of siloxanes concerns the

* Corresponding author at: Department of Energy (DENERG), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Turin, Italy. Tel.: +39 3402351692.
E-mail address: davide.papurello@polito.it (D. Papurello).

Nomenclature

AD	anaerobic digester
ACFs	activated carbon filters
CAR	carboxen fiber
C/C ₀	removal performance efficiency, ratio between actual concentration (C) and starting concentration (C ₀)
CHP	combined heat and power system
DIMS	direct injection mass spectrometry
DPM	dew point mirror
DVB	divinylbenzene fiber
EDS	energy-dispersive X-ray spectroscopy
FC	fuel cell
GC-MS	gas chromatography mass spectrometry
GCU	gas calibration unit
GHSV	gas hourly space velocity
ICE	internal combustion engine
MCFC	molten carbonate fuel cells
MFC	mass flow controller
m/z	mass over
OFMSW	organic fraction of municipal solid waste
PA	proton affinity
PDMS	polymeric dimethylsiloxane membrane
PEG	polyethylene glycol fiber
PEEK	polyether ether ketone
PFA	perfluoroether
PM	polymeric membrane
ppb(v)	parts per billion (volume)
ppm(v)	parts per million (volume)
ppq(v)	parts per quadrillion (volume)
ppt(v)	parts per trillion (volume)
PTR-MS	proton transfer reaction-mass spectrometry
QMS	quadrupole mass analyzer
SEM	scanning electrode microscopy
SOFC	solid oxide fuel cell
SPME	solid phase micro extraction
Td	Townsend, unit for measuring E/N, 1 Townsend (1 Td) = 10 ⁻¹⁷ Vcm ² mol ⁻¹
THT	tetrahydrothiophene
ToF	time-of-flight (analyzer type of mass spectrometers)
VMRs	volatile mixing ratios
VOCs	volatile organic compounds
VSCs	volatile sulfur compounds
ZnO	zinc oxide sorbent material

three phase boundary obstruction with the consequent electrochemical active site reduction [9]. As a conclusion, the most detrimental and abundant biogas trace compound for the nickel anode deactivation is hydrogen sulfide as reported in literature studies [7,8,11]. Nevertheless, Papurello et al. [12,13] have shown that other biogas trace compounds besides hydrogen sulfide could have a role. These are for instance methanethiol, dimethylsulfide, carbon disulfide, propanethiol and butanethiol, which are all detected in the biogas from OFMSW anaerobic digestion.

Studies from Hernandez et al. (2008–2011) reported that a proper gas clean-up section is essential to feed SOFC energy generators [14, 15]. The effectiveness of micro-contaminant removal widely depends on the biogas trace compounds' variability. So there are no standard solutions; a rather specific combination of impurity removal methods must be used to ensure a fuel gas of the quality that meets the fuel cell tolerance thresholds as given by the manufacturer [16]. Several authors [17–19] indicate that the following steps are required: a primary clean-up step, in which a condenser and a first sorbent bed are inserted,

followed by a fine guard bed before delivery of the biogas to the fuel cell system.

A condenser is useful in removing water because of its competitive adsorption behavior towards other contaminants in the downstream guard beds. Siloxanes are generally heavier than other biogas trace compounds and thus easily removed from biogas by water condensation. Nevertheless, according to results by Haggmann et al. [20] on siloxane compounds, the removal through a condenser section achieves only a 26vol.% degree of separation at –25 °C, whereas at –70 °C the removal ratio increased up to 99vol.%. Schweigkofler and Niessner [21] pointed out that, by cooling the gas to 5 °C, approximately 12vol.% of siloxane compounds are removed. Therefore, these results show how the removal of VOCs by a condenser section is not significant, but only strictly necessary to remove water from the biogas stream in order to protect the activated carbon guard bed lifetime [15]. Activated commercial carbons, impregnated with metal oxides such as iron, copper and silver, are widely used mainly to remove sulfur compounds [15–17]. Other sorbent materials such as Zinc Oxide (ZnO) are also used to remove volatile organic compounds as reported by Hernandez et al. [14]. Nano particle zinc oxide has a higher adsorption capacity with respect to the commercial activated carbon for H₂S removal. In Papurello et al. [13] it is shown how the breakthrough fraction and the breakthrough time are affected by the type of the sulfur compounds that have to be removed, by the gas hourly space velocity (GHSV) in the gas cleaning section and finally by the presence of vapors of organic compounds besides sulfur ones. It was demonstrated that even only 1 ppm(v) of aromatic, carbonyl and Cl compounds can reduce the removal filter efficiency by 11% of the expected value [13]. It is evident that further investigation of the efficiency obtainable by cleaning filter in fuel cell related applications is necessary especially under real working conditions, as those in the coupling with an anaerobic digester pilot plant.

High-sensitivity and robust methods for the real-time analysis of the volatile compounds released by OFMSW digestion are a valuable tool to better understand and support the development of better industrial procedures for biogas exploitation. In this context, direct Injection Mass Spectrometry (DIMS) offers interesting performances in terms of rapidity, sensitivity and absence of pre-treatments [22]. One of the most promising DIMS techniques is certainly PTR-MS. It is based on an efficient implementation of chemical ionization based on proton transfer from hydronium ions [22] and allows the rapid and on-line monitoring of most volatile compounds. It has been applied in many situations ranging from breath analysis to environmental monitoring and, recently, also to issues related to waste management and odorant emission control [23–27].

In this study, the monitoring of contaminants contained in a biogas produced from a pilot plant loaded with OFMSW is assessed before and after a gas cleaning section. The as-produced biogas from the digester first passed through a condenser and then through an activated carbon filter bed. Trace compounds contained in such a biogas were analyzed by PTR. A gas calibration unit was adopted in combination with the PTR-MS instrument in order to confirm the quantification obtained by PTR-MS.

2. Material and methods

2.1. Gas cleaning section – pilot plant

The dry anaerobic digestion of OFMSW was conducted in a pilot plant located at Fondazione Edmund Mach (FEM) (S. Michele a/A, Italy). A detailed description of the pilot plant digester can be found in [12]. A gas cleaning section was built according to the scheme in Fig. 1. The biogas line was connected to a condenser filled by plastic rings with an overall capacity of 54 L. Two filter reactors are connected in series after the condenser. The first filter reactor was filled with plastic rings to entrain small water drops, while the second one with commercial Sulfatrap R8 activated carbons (TDA research Inc., USA). The

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