



Contents lists available at ScienceDirect

## Waste Management

journal homepage: [www.elsevier.com/locate/wasman](http://www.elsevier.com/locate/wasman)

## Biogas from the organic fraction of municipal solid waste: Dealing with contaminants for a solid oxide fuel cell energy generator

Davide Papurello<sup>a,b,\*</sup>, Andrea Lanzini<sup>a</sup>, Pierluigi Leone<sup>a</sup>, Massimo Santarelli<sup>a</sup>, Silvia Silvestri<sup>b</sup>

<sup>a</sup> Department of Energy (DENERG), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

<sup>b</sup> Fondazione Edmund Mach, Biomass and Renewable Energy Group, Via E. Mach, 1, 38010 San Michele a/A, Italy

## ARTICLE INFO

## Article history:

Received 13 August 2013

Accepted 17 June 2014

Available online xxxxx

## Keywords:

Direct biogas reforming

SOFC

Volatile Organic Compounds (VOCs) monitoring

Partial oxidation (POx)

Anaerobic digestion (AD)

Proton Transfer Reaction – Mass

Spectrometry (PTR-MS)

## ABSTRACT

The present work investigates electricity production using a high efficiency electrochemical generator that employs as fuel a biogas from the dry anaerobic digestion of the organic fraction of municipal solid waste (OFMSW).

The as-produced biogas contains several contaminants (sulfur, halogen, organic silicon and aromatic compounds) that can be harmful for the fuel cell: these were monitored via an innovative mass spectrometry technique that enables for in-line and real-time quantification.

A cleaning trap with activated carbons for the removal of sulfur and other VOCs contained in the biogas was also tested and monitored by observing the different breakthrough times of studied contaminants.

The electrochemical generator was a commercial Ni anode-supported planar Solid Oxide Fuel Cell (SOFC), tested for more than 300 h with a simulated biogas mixture (CH<sub>4</sub> 60 vol.%, CO<sub>2</sub> 40 vol.%), directly fed to the anode electrode. Air was added to promote the direct internal conversion of CH<sub>4</sub> to H<sub>2</sub> and CO via partial oxidation (POx).

The initial breakthrough of H<sub>2</sub>S from the cleaning section was also simulated and tested by adding ~1 ppm(v) of sulfur in the anode feed; a full recovery of the fuel cell performance after 24 h of sulfur exposure (~1 ppm(v)) was observed upon its removal, indicating the reliable time of anode exposure to sulfur in case of exhausted guard bed.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

The Kyoto protocol identifies several key points to curb greenhouse gas emissions (GHG), among which is the production of renewable fuels from organic waste (De Boer, 2008; IEA, 2008). Anaerobic digestion (AD) is not only able to recover energy from different biowaste substrates in the form of biogas, but it also avoids the emission of pollutants and GHG emissions into the atmosphere (Porrizzo et al., 2012; Mata-Alvarez et al., 2000; Smith et al., 2001).

AD is a biological process that takes place in sealed vessels in the complete absence of air. Given the physical properties of OFMSW (Mata-Alvarez et al., 2000), dry digestion seems to be more advantageous than wet processes as it minimizes the required reactor volume, water and thermal demands, and finally losses of organic matter during pre-processing operations. It also requires a lower number of biomass pre-treatment steps (Forster-Carneiro, 2009). The biogas produced through the anaero-

bic digestion of OFMSW is comprised of 50–70 vol.% methane, 30–50 vol.% carbon dioxide and trace volatile compounds (Mata-Alvarez et al., 2000; Khalid et al., 2011). The volume-reduced solid residue (digestate) can be used as compost after an adequate period of maturation.

#### 1.1. The effect of contaminant in biogas-to-electricity

The as-produced biogas, after a cleaning stage, can be used to produce electricity (and recovered heat in CHP plants): generally internal combustion engines or gas turbines are employed (Balat and Balat, 2009; Luke Murray et al., 2007; Guzowski and Recalde, 2010; Duerr et al., 2007). The efficiency of ICEs (Diesel or Otto engines) ranges from 30% to 40%, depending mostly on size.

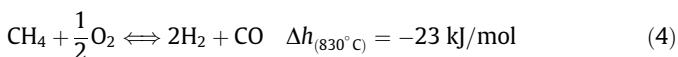
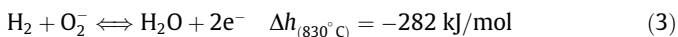
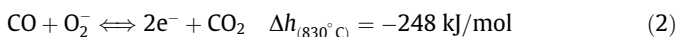
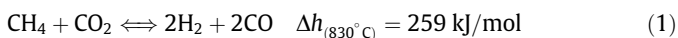
In terms of contaminants, especially siloxanes are dangerous and must be removed from the biogas when used in these thermal engines. In fact, siloxanes are not decomposed in the activated sludge process and partly concentrate in the sludge. During anaerobic digestion of the sludge, they volatilize into the formed biogas. Combustion of silicon containing gases in thermal engines produces, however, the abrasive microcrystalline silica that has chemical and physical properties similar to those of glass and

\* Corresponding author at: Department of Energy (DENERG), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy. Tel.: +39 3402351692.

E-mail address: [davide.papurello@polito.it](mailto:davide.papurello@polito.it) (D. Papurello).

causes serious damage to the engines, heat exchangers and catalytic exhaust gas treatment systems (Dewil et al., 2006).

An interesting alternative pathway, due to their high biogas-to-electricity conversion efficiency (around 50–60% on a LHV basis), can be based on Solid Oxide Fuel Cells (SOFCs). Conversely to thermal engines, the SOFC can operate with diluted biogas (while ICE cannot if the CH<sub>4</sub> content in biogas falls below 40–45%). Essentially, two main concerns come from direct biogas feeding in an SOFC generator: carbon deposition and the detrimental effects of contaminants on the Ni anode electrode (Rasmussen et al., 2011; Lanzini and Leone, 2010; Shiratori et al., 2010; Sasaki et al., 2011). Carbon deposition can be easily managed provided that a proper steam-to-carbon or oxygen-to-carbon ratio is guaranteed at the SOFC inlet so that C build-up is thermodynamically unfeasible. Carbon deposition phenomena has been investigated experimentally by Lanzini and Leone (2010), through direct feeding of clean biogas. Different reforming agents, such as steam, oxygen and carbon dioxide were tested for at least 50 h each. No degradation was observed. Similarly, Shiratori et al. (2010) have studied the direct feeding of biogas in an SOFC button cell for even longer periods. Direct reforming processes also have effects on the energy balance around an SOFC stack running on biogas. In fact, the thermochemical conversion of methane to hydrogen and carbon monoxide, via endothermic reforming reactions (Eqs. (1) and (5)) (i.e., by mixing biogas with either steam or carbon dioxide), could be used to counter-balance the exothermic electrochemical reactions (Eqs. (2)–(4)) relative to the hydrogen and carbon monoxide oxidation.



Nevertheless, the resulting thermal balance is not satisfying, as it results in an endothermic operating condition. Therefore, Takahashi et al. (2012) have studied the feasibility of a Ni-YSZ anode supported cell (ASC) running on biogas with air addition to promote POx. This kind of exothermic reforming reaction can counter-balance the endothermic reforming of methane. By controlling the amount of air in the anode compartment, the thermal gradient and the related thermo-mechanical stresses across the SOFC can be relaxed.

On the contaminants side, in a previous work (Papurello et al., 2012) it was shown that the as-produced biogas from the AD of the OFMSW contained several VOCs (sulfur, aromatic, siloxane and halogenated compounds) that can in principle affect the SOFC performance and the electrode stability. Sulfur compounds are present in the range from tens to thousands of ppm(v) (sulfur), while halogens and siloxanes vary from 0.1 to 10 ppm(v). Hence biogas requires a gas cleaning section before feeding it to an SOFC. Sulfur compounds, which decompose to H<sub>2</sub>S at the SOFC operating temperature (600–800 °C), are generally the most abundant VOCs in biogas. Moreover, H<sub>2</sub>S is a well-known poison for Ni-based ceramic cells (Rasmussen et al., 2011; Cheng et al., 2011). Sulfur compounds decomposed to H<sub>2</sub>S at the SOFC operating temperature as shown from equilibrium thermodynamic calculations. H<sub>2</sub>S adsorbs on the Ni active sites preventing H<sub>2</sub> (and CO) oxidation as well as also methane reforming (Rostrup-Nielsen et al., 2006). The effect of Chlorine compounds generally decomposed to HCl in the H<sub>2</sub>-rich anode environment is less understood. However a de-activation

mechanism similar to that of sulfur (i.e., dissociative chemisorption on the Ni surface with contaminant adsorption consequently blocking reactive sites), but less severe was generally observed (Bao et al., 2009; Tremblay et al., 2007). Aromatic compounds are probably the less dangerous ones as they are catalytically converted to H<sub>2</sub> and CO within the SOFC.

Once again, siloxanes are instead the most critical ones for durability of the fuel cell. For instance, a study by Ruokomäki et al. (2009) showed how siloxane compounds already affect the SOFC performance at 10 ppb(v), whereas for chlorine compounds concentrations above 5000 ppb(v) are required. Haga et al. (2008) also showed how an amount of 10 ppm(v) of D5 in the H<sub>2</sub> feed quickly (within few hours) led to a cell failure.

Therefore, a proper gas cleaning unit is required for biogas conversion to electricity, especially if fuel cell devices such SOFC are used.

### 1.2. Contaminants removal

Several AD biogas cleaning systems exist and varies according to the size of the plant (gas volume flows). However, for a thorough cleaning, a guard bed is always present, often based on activated carbons. In fact, as reported in Yang (1987), the adsorption process is a combination of physical and chemical adsorption, involving weak Van der Waals forces or covalent bonds. Sulfur compounds, in fact, are polar substances with a dipole moment higher than 1 Debye. In order to remove polar substances using carbon particles, metal salts (cations) such as Fe<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O/CuO are added. Several authors (Hernandez et al., 2008; Hernandez et al., 2011; Cosoli et al., 2008) have investigated the removal performance of activated carbons for VOCs contained in a biogas feed. Sulfur and chlorine compounds removal has been investigated also relying on zeolites and advanced activated carbons (Hernandez et al., 2008).

### 1.3. Detection of biogas trace compounds

In general, it is a difficult task to detect the whole range of VOCs in a biogas, either before or after filtration, while it is important to exactly analyze the breakthrough time of different contaminants in order to correctly design the cleaning system and to fix the time of switching off the cleaning beds. Previous tests have exploited the combined gas chromatography/mass spectrometry (GC–MS) technique as a detection method that allows for a highly detailed analysis to be conducted (Orzi et al., 2010). However, it is too slow in the case of rapid VOC formation during anaerobic digestion. Besides, the Proton Transfer Reaction – Mass Spectrometry (PTR-MS) technique allows in-line real-time monitoring to be carried out. This technique does not involve laborious preparation procedures, and offers high sensitivity and high temporal resolution throughout the entire test (De Gouw and Warneke, 2007).

In the described context, the aim of the present work is a thorough assessment on the energy utilization of biogas from dry anaerobic digestion of OFMSW. Our analysis includes an investigation on the removal of harmful contaminants with activated carbon beds. The monitoring of VOCs before and after the cleaning stage with an innovative and powerful instrument (the PTR-MS). The effect of sulfur in an SOFC running on biogas with direct internal reforming (autothermal POx).

## 2. Materials and methods

### 2.1. Dry anaerobic digestion of OFMSW

The dry anaerobic digestion of the OFMSW was carried out in a pilot plant located at the Edmund Mach Foundation (S. Michele a/

Download English Version:

<https://daneshyari.com/en/article/6354768>

Download Persian Version:

<https://daneshyari.com/article/6354768>

[Daneshyari.com](https://daneshyari.com)