



Research article

Biogas trace compound removal with ashes using proton transfer reaction time-of-flight mass spectrometry as innovative detection tool



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ABSTRACT

The feasibility of reusing waste materials as an inexpensive sorbent to remove volatile organic compounds from gaseous waste streams has been demonstrated. Ashes from wood-chips were tested as sorbent materials for VOCs removal with a PTR-ToF-MS instrument. Both scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) and BET analysis were used to identify the structural characteristics, elemental composition and surface area of the tested ashes respectively.

Most of the tentatively identified compounds were less strongly adsorbed by wet ash: thiols, siloxanes, carbonyl compounds and terpenes. Hydrogen sulfide and alcohols show improving removal performance in wet conditions. These results are related to the water solubility properties. Siloxanes were tentatively identified and monitored with PTR-ToF-MS. This demonstrates how this instrument is a suitable tool for simultaneously providing a multitude of analysis for rapid in situ monitoring of fuel contaminants.

Considering the low cost, and the recycling of environmental pollutants, wood ashes are a possible choice for VOCs removal from biogas.

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1. Introduction

In recent years, anaerobic digestion has emerged as one of the technologies of high interest because of its potential usefulness as an alternative to fossil fuel energy. Anaerobic digestion is a biological process in which biodegradable matter, e.g. OFMSW is degraded or decomposed by the activity of specific microorganisms in the absence of oxygen. The resulting biogas (mainly methane and carbon dioxide) can be used for electricity generation [1]. Organic fraction of municipal solid waste (OFMSW) offers the possibility to obtain a valuable bio-fuel from a waste that otherwise would be disposed in landfill. Typically, the biogas produced by anaerobic digestion of OFMSW is comprised of 50–70% v/v methane, 30–50% v/v carbon dioxide and trace volatile compounds [2–4]. Aside from the main components, methane and carbon dioxide, biogas from the organic sources can contain a large number of other trace compounds, e.g., sulfurs, terpenes, aromatics and hydrocarbons, carbonyls and carboxyls, siloxanes and alcohols [2,5,6]. In addition, these trace gases can include other odorous compounds such as hydrogen sulfide and ammonia [7]. Biogas from anaerobic digestion of

OFMSW could be adopted as renewable fuel for several energy generators, e.g. internal combustion engines, fuel cells, and micro-turbines. Among these technologies solid oxide fuel cells (SOFCs) are the most promising in terms of overall efficiency. SOFCs have an advantage over the fuel cell technologies with its carbon dioxide tolerance [8–10]. The direct use of biogas containing trace contaminants may lead to cell anode damage after few hours of operation due to the carbon deposition and catalyst deactivation [9,10]. These contaminants need to be removed by the proper choice of a reforming agent and a gas cleaning method [8–11]. Sulfur and siloxane compounds are probably the trace constituents of most concern that strongly affect the SOFC anode activity [12,13] [9,10]. In particular, exposure to more than 1–2 ppm(v) of H₂S SOFC performance decreases strongly and irreversibly. The decrease caused by surface adsorption of sulfur to produce nickel sulfides, reduce the catalyst activity [9,10,13]. The presence of siloxanes can cause deposition-type degradation. A study by Haga et al., (2008) reveals a strong cell voltage decrease. Hydrogen with 10 ppm(v) of decamethylcyclopentasiloxane (D5), contained in a biogas from waste water treatment plant (WWTP), induces cell voltage decrease and fatal degradation after 50 h of the test at 800 °C due to the formation of SiO₂(s) [14]. Madi et al., (2015) investigated the siloxane impact on SOFC single cells. High degradation rates are observed already at ppb(v) level of contaminant in the fuel stream [11].

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Nomenclature

a1	15th day of digestion process with an ash dry filter
a2	16th day of digestion process with an ash wet filter
AD	Anaerobic digestion
BET	Brunauer–Emmett–Teller
C/C ₀	Pass through ratio of an organic compound; final/initial concentrations
C ₀	Concentration detected before the filter
FEM	Fondazione Edmund Mach Research and Innovation Center
GHSV	Gaseous hourly space velocity, h ⁻¹
OFMSW	Organic fraction of municipal solid waste
m/z	Mass to charge of ionic compound
ppb(v)	Parts per billion volume
ppm(v)	Parts per million volume
PTR-ToF-MS	Proton transfer reaction-time of flight-mass spectrometry
SEM	Scanning electrode microscopy
SOFC	Solid oxide fuel cell
VOC	Volatile organic compound
VOSC	Volatile organic sulfur compound
WWTP	Waste water treatment plant
% v/v	Volume concentration in percent

To be technically viable methods are required to reduce the impurity concentrations to tolerable levels, if not to eliminate the impurities entirely. These methods represent the cleaning section for fuel cell applications. Contaminant removal increases the complexity of the system, raising the capital and operating costs [15]. Potential technologies for removal of the trace compounds in biogases include various adsorbents [16], absorbents [17] and biofilters [18]. Generally, activated carbons are used as sorbent materials, when impregnated with metals, such as iron, copper or chromium [19,20]. For reasons related to technical, environmental and economic aspects we decided to investigate the VOC removal with ashes obtained from a wood boiler. Considering the low cost, and the possible recycling of environmental pollutants, wood ash is an attractive choice for VOCs capture. The fly ash from biomass or from municipal solid waste incineration is investigated to remove organic compounds from biogas stream [21–23]. Previously Kastner et al., (2003) [24] investigated sulfur compound removal using wood and coal fly ash. Wood fly ash demonstrated a lower removal capacity for H₂S and CH₄S compared to activated carbon. However, no literature studies were found with wood ash used to remove VOCs from biogas. In general, there is a need for sensitive and robust methods of real-time analysis of the volatile trace compounds to protect public health and welfare and to allow optimal process control. In this context, one alternative for contaminant analysis is direct injection mass spectrometry (DIMS). DIMS offers advantages in terms of rapidity and sensitivity

without the need for pretreatments [2,19,20,25]. In particular, the recent introduction of time of flight (ToF) mass analyzers coupled with proton transfer reaction mass spectrometry (PTR-ToF-MS, [26]) indicates the possibility of maintaining high sensitivity with improved time resolution (0.1 s), mass range (virtually not limited) and mass resolution (better than 4000). This improved mass resolution allows the separation of isobaric compounds and the identification of the chemical formula of the spectrometric peaks. Regarding problems related with the use of PTR-ToF-MS data analysis (handling of large data sets (giga-byte/h), spectra alignment, peak extraction) represent a crucial point. Recent literature describes how these problems can be overcome to make PTR-ToF-MS a routine technique for monitoring of VOCs [27,28].

The aim of the present study is twofold: a) to investigate the potential of the recently developed analysis technique of PTR-ToF-MS as a tool for the rapid, direct and high sensitivity monitoring of VOCs emitted from the anaerobic digestion of OFMSW and b) to investigate the removal of VOCs with a potentially, economic and ecologically safe material; ashes from wood-chips for SOFCs' related applications.

2. Materials and methods

2.1. Anaerobic digestion plant

OFMSW was adopted as organic source to produce biogas with an anaerobic digester pilot plant, located at Foundation Edmund Mach (S. Michele a/A, Italy) (FEM). Biowaste was obtained from selected sources to avoid undesired components (such as stones, paper, plastic, glass) in the organic fraction. The biomass comes from the local organic waste (San Michele a/A (TN), Italy). The plant is based on a barrel shape design with a working volume of 16 m³ with frontal loading. The digester is composed of resin sealed rectangular reinforced concrete modules. Before digester loading, OFMSW at a volume ratio from 0.6 to 0.7 was mixed with chipped wood to achieve a suitable biomass porosity. Before the anaerobic digestion phase, biomass was subjected to a four day pre-oxidation process. The temperature increased 35 °C and released significant amounts of carbon dioxide and other VOCs. After the aerobic phase, the digester was isolated to transition from aerobic to anaerobic conditions. The biomass temperature was thermostatically controlled by fixed floor and wall coils and by leachate sprinkling as needed. Under these conditions the anaerobic digestion was accomplished in approximately 30 days. The biomass was subjected to a further aerobic composting treatment for 20 days before final use as fertilizer. Table 1 summarizes the composition and physicochemical characteristics of the OFMSW batch used in this study.

2.2. Experimental sorbent characterization and VOC removal section

Ashes from a forestry wood-chips boiler (3.3 MW, Viessman, Allendorf Germany) were tested in a glass reactor filter of 340 ml. Two different VOCs removal tests were performed with ashes; the

Table 1

Starting values of digestion cycle – initial biomass parameters.

	Volume (m ³)	Mass (t)	Water content (%)	Volatile solids (%)	pH in	pH out
Digestate from previous batch	7.33 [±0.43]	6.67 [±0.52]	61.6 [±1.02]	55.3 [±3.1]	8.7 [±0.2]	
OFMSW + wood	9.29 [±0.51]	5.34 [±0.53]	59.5 [±0.75]	82 [±3.2]	5.8 [±0.2]	
Mix	14.95 [±0.52]	12.01 [±0.46]	58.8 [±1.19]	59.8 [±3.3]	7.8 [±0.2]	8.3 [±0.2]

Where:

- pH in: pH measured at the beginning of loading into the digester;
- pH out: pH at end of digestion process;
- Mix: total biomass loaded into the digester; and
- Square brackets indicate the standard deviation of measurements.

*Mix was left at ambient temperature for 4 days prior to loading into the digester, thereby probably changing the pH e.g. via CO₂ escaping into the atmosphere.

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