Real time monitoring of removal of trace compounds with PTR-MS: Biochar experimental investigation.

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Abstract

The removal of trace compounds contained in a biogas from the dry anaerobic digestion of organic waste was accomplished. The resulting data were monitored online with a direct injection mass spectrometry technique. Biochar from the pyrolysis of recovered wood waste was adopted as sorbent material. This material was selected to demonstrate the usefulness of recovered waste for the energy production purposes. In fact, considering a highly efficient energy generation system, such as Solid Oxide Fuel Cell, the fuel requirements are stringent in terms of trace compounds concentration. Material characterization of biochar was accomplished using scanning electron microscopy, energy dispersive X-ray analysis and nitrogen adsorption. The performance achieved with this material is comparable with performances achieved by reference commercial carbons, even if some more optimized and selective materials show better results. The main expense that weighs on the service life time of biochar is the electricity consumed followed by the costs required for material replacement.

Keywords: Adsorption, VOCs removal, Biogas, Solid Oxide Fuel Cell (SOFC), Carbon, PTRMS.

Nomenclature

CHO, carbonyl and carboxyl compounds;

D3, hexamethylcyclotrisiloxane;

D4, octamethylcyclotetrasiloxane;

D5, decamethylcyclopentasiloxane;

EDS, Energy Dispersive X-ray Spectroscopy;

GHSV, Gas Hourly Space Velocity;

ICE, Internal Combustion Engine;

L2 MM, hexamethyldisiloxane;

MIEC, Mixed Ionic Electronic Conducting ceramic material;

MSW, Municipal Solid Waste;

OFMSW, Organic Fraction of Municipal Solid Waste;

OW, Organic Waste;

PTR-MS, Proton Transfer Reaction Mass Spectrometer;

PTR-ToF-MS, Proton Transfer Reaction Time of Flight Mass Spectrometer;

SEM, Scanning Electron Microscopy;

SOFC, Solid Oxide Fuel Cell;

VOCs, Volatile Organic Compounds.

1. Introduction

The management of solid waste is a global issue due to population growth and environmental and energy related problems. Organic waste could have an added value if considered as feedstock for energy production. Advantages are related to energy production and to the reduction of pollutant emissions into air, soil and water. Biogas produced from this waste can be adopted in several energy generators, usually using a mechanical or an electrochemical approach to generate clean energy. Carnot cycle is the key limitation of this approach in terms of efficiency and exploitability. Among electrochemical systems, solid oxide fuel cells (SOFC) currently receive much attention (Papurello et al., 2014; Papurello et al., 2014a; Papurello et al., 2015a; Shiratori et al., 2010; Van Herle et al., 2004). SOFCs present several advantages compared to mechanical competitors for electricity production (ICE, mTurbine, Rankine cycles,etc). Advantages of these systems are mainly their high efficiency, low noise levels, low pollutant emissions, the availability of a wide range of suitable fuels, , and the possibility to be scaled up with practically no variation in the efficiency value. (Maghanki et al., 2013). Their main drawback is their low resistance to trace compounds (Blum et al., 2016; Facci et al., 2016; Davide Papurello et al., 2016a, 2016b, 2016c; Torii et al., 2016; Turco et al., 2016). Literature studies focus mainly on gas cleaning or on SOFC material tolerability against these compounds.

The removal of trace compounds with sorbent materials was investigated considering the effect of temperature, relative humidity and contemporary removal of several compounds to simulate real conditions (Papurello et al., 2015b, 2015c, 2013). Papurello et al., (2016) showed the temperature dependency on the removal performance of commercial carbons (D. Papurello et al., 2016). Another parameter that affects removal performance is the relative humidity content (Barelli et al., 2017; D. Papurello et al., 2016). In fact, depending on whether basic active sites are present or absent, the water humidity content could have a positive or negative impact. It was demonstrated that, for carbons activated with KOH and KI, the formation of water film around activated carbon pores, which favors H_2S molecules dissociation. Conversely, humidity could be a problem for carbons activated with metals, such as Cu or Fe. Here, the interaction between H_2S and metals loaded on carbon surface results in metal sulfide (MeS) and water production. The water contained in the gas matrix disadvantages the sulfur removal. As reported in literature, a relative humidity value above 50% lead the adsorption capacity to zero mg/g (D. Papurello et al., 2016). Finally, the multiple removal of trace compounds has to be considered. This condition is crucial for the industrialization of the direct biogas to energy production systems with SOFCs. Preliminary results carried out in laboratory highlighted how the contemporary presence of more than one single compound, usually H_2S, causes the strong removal performance to decrease (Davide Papurello et al., 2014b). All of these factors can be present at the same time in a real plant. Considering a more realistic case, an experimental pilot plant for gas cleaning with ashes was investigated (Davide Papurello et al., 2016d). Results showed the higher efficiency of ashes in removing H_2S, alcohols and some terpenes, while the removal of thiols, siloxanes and carbonyl compounds was less succesful. Results obtained at the end of the experiments demonstrated that ashes are not economically and technically exploitable to work with SOFC energy generators. This is due to the stringent gas concentration requirements. The low cost of activated carbons and the low sulfur capacity of ashes are also involved in this process. In this work, considering the philosophy of circular economy, we want to prove how another waste material can be adopted for the gas cleaning for SOFC applications. Biochar from the wood pyrolysis chain was selected for the removal of trace compounds. Biochar has a relative structure carbon matrix with a high specific surface area and high degree of porosity able to act as a surface sorbent. These features are similar to optimized commercial activated carbons. Char material was tested elsewhere for the removal of only sulfur compounds (Shang et al., 2016, 2013). The adsorption characteristics of biochar are a function of the raw material, the production process and the temperature adopted. Ahmad et al., (2012) showed how in a pyrolysis process the temperature reached for the char production is crucial for the increase of surface area and porosity (Ahmad et al., 2012). Both, surface area and porosity are linked to the adsorption capacity of trace compounds as reported in literature (Shang et al., 2016). To the best of our knowledge, this paper is the first attempt to monitor online the removal of biogas trace compounds, using a recoverable waste as a sorbent material with PTR-MS instrument.

2. Experimental and methods

2.1. Anaerobic digestion pilot plant

The organic fraction of municipal solid waste was selected as substrate for biogas production. These wastes where treated in a pilot plant placed at Foundation Edmund Mach - S. Michele a/A, Italy (TN). Bio-wastes were pretreated in a cylindrical sieve to avoid undesired components, such as stones, papers, plastics and glasses. The rectangular digester is made by concrete (16 m^3) and it is sealed with resin . Before the waste loading, OFMSW was mixed with chipped wood, at a volume ratio of 0.6 – 0.7 to achieve suitable biomass porosity. To rapidly initiate the methane production, the biomass was subjected to a four day preoxidation process. Consequently, the initial lag phase was reduced. The temperature increased at 35 °C and a significant release of carbon dioxide and other VOCs was recorded. After the aerobic phase, the digester was sealed for the transition from aerobic to anaerobic condition. The biomass temperature was thermostatically controlled by fixed floor, 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 composting treatment for 20 days before final use as fertilizer. Table 1 summarizes the composition and physicochemical characteristics of the OFSMW batch used in this study.

Table 1 – Composition and physicochemical characteristics of the OFSMW batch

	Volume (m^3)	Mass (t)	Water content (%)	Volatile Solids (%)	pH in	pH out
Digestate from previous batch	7.38 [±0.31]	6.75 [±0.51]	61.7 [±1.1]	55.8 [±3.1]	8.5 [±0.15]	
OFSMW + Wood	9.08 [±0.39]	5.34 [±0.45]	59.1 [±0.72]	83.2 [±3.0]	5.7 [±0.18]	

Mix	14.84 [±0.45]	11.85 [±0.48]	58.9 [±1.05]	56.7 [±3.2]	7.8 [±0.19]	8.2 [±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
- 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 CO_2 escaping into the atmosphere.

2.2. Sorbent material characterization and experimental settings

Biochar from the pyrolysis of wood was produced by Gruppo RM Impianti srl. (Italy), in a 200 kWe reactor at low temperature (150 °C). This sorbent sample was tested in a glass reactor filter of 340 ml. The experimental set-up is described in Figure 1. The blower coupled with the digester flushes an average flow rate of 0.3 Nm^3/h with a gas hourly space velocity (GHSV) of 882 h^{-1}, at ambient temperature and pressure around 80 mbar. The value chosen for the GHSV parameter is compatible with space velocities expected for 1 kWel SOFC micro-CHP application (Barelli et al., 2015).

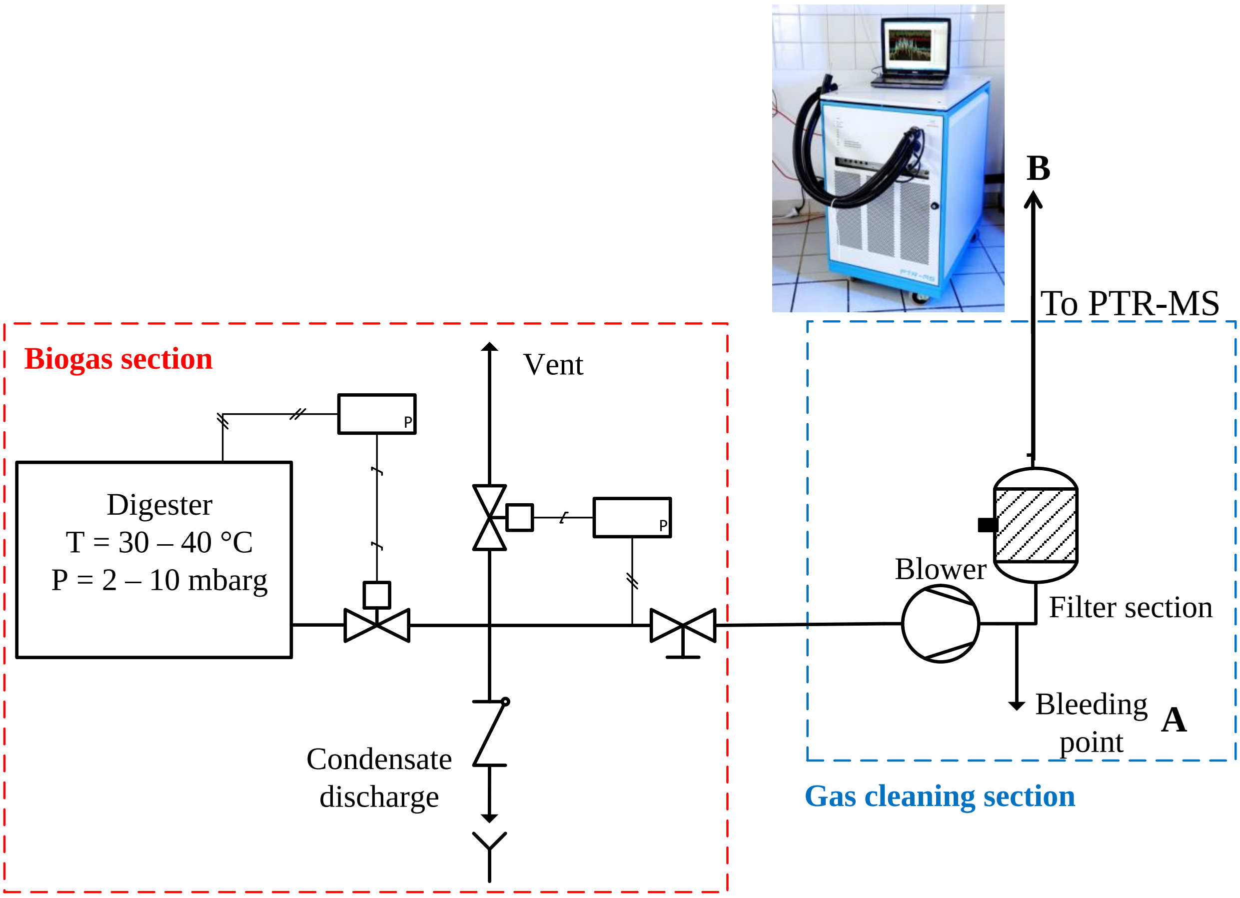

Figure 1 – Biogas to gas cleaning section – experimental set up for biochar testing

Adsorption isotherms for N_2 at 77 K were determined using a Quantachrome Autosorb 1 (Boynton Beach, Florida, USA). These measurements were able to characterize the sample in terms of specific surface area. Samples were outgassed at 423 K overnight prior to the adsorption measurements. The equipment allows measurement of relative pressure of 10^{-6} bar. Specific surface areas have been calculated by Langmuir model. Langmuir surface area resulted to be 75 m^2/g (average value of 3 samples). This value, although lower than activated carbons (typically 1500 m^2/g), is significantly higher than ashes (~1 m^2/g) (Davide Papurello et al., 2016d). The porosity was evaluated indirectly considering the mass of sample, the micro, meso and total pore volume of the filter. The porosity was about 4%. Figure 2 shows the FESEM images for the biochar sample.

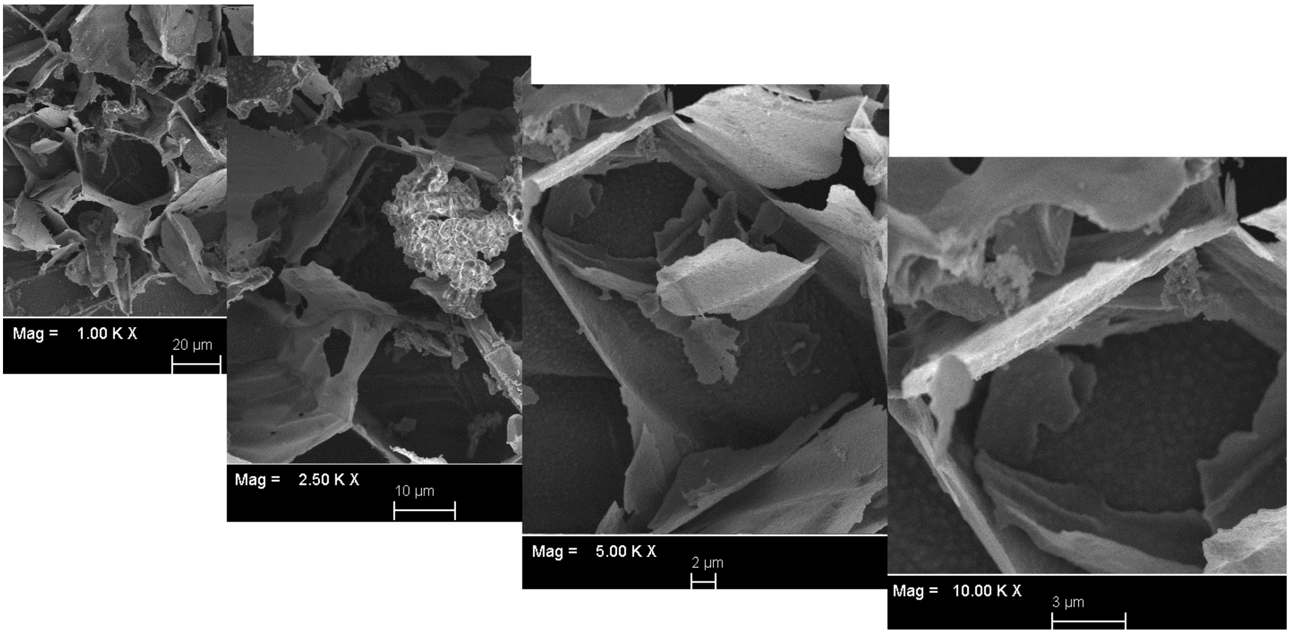

Figure 2 – FESEM biochar characterization

Elemental composition measurements were performed by scanning electron microscopy (SEM) (FEI Inspect, Philips 525 M) coupled with EDS (SW9100 EDAX) analysis. The results are reported in the following table.

Table 2 – Elements identified with SEM-EDS analysis in the biochar sample

Element	Atomic % virgin	Atomic % tested
C	98.85	98.95
K	0.34	0.30
Ca	0.81	0.37
Mn	0	0
S	0	0.38
Total:	100.00	100.00

The most abundant element is carbon followed by calcium, potassium, manganese. Only for the tested sample also elemental sulfur is detected. The concentrations of K and Ca are important for the removal of sulfur compounds, as reported by Tepper and Richardson et al., (2002) (Richardson J., Bjorheden R., Hakkala P., Lowe AT., 2002; Tepper, n.d.). It was difficult to correlate the elements before and after the experimental test. A potassium and calcium decrease could be related to the reactions between metals and trace compounds, such as sulfur compounds.

2.3. Online monitoring technique – PTR-MS

Trace compounds were monitored using a PTR-QMS 500 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) connected directly to the gas cleaning section (Figure 1). Biogas was sampled in two points: before the filter (point (A)) and after the filter (point (B)). All the lines were made in Teflon. This has been done to guarantee the trace compounds stability along the lines. Several studies have investigated the suitability of different materials for VOC gas sample storage (Beauchamp et al., 2008). Pet'ka et al., (2000) found that tedlar and saran bags were two unsuitable material for storage applications due to high levels of contaminant compounds emanating from the bag materials (Pet’ka et al., 2000). Focusing on the teflon material it was reported a compound losses over time, function of the trace compound type (Pet’ka et al., 2000). Van Harreveld (2003) investigated nalophan bags and found that samples remained relatively stable between 4 and 12 h after sampling. Concentration decreases after 30 h of storage to about half of their initial levels: This was attributed to diffusion effects (van Harreveld, 2003). In our case, contrarily to the common literature studies, VOCs analysis was performed in real time (B). Here, the information losses related to the concentration diffusion are limited to the minimum. The concentration from point (A) was monitored once a day, for at least one hour, to find the breakthrough of clean gas. The clean biogas, point (B) was monitored continuously 23 h per day. The concentrated sample (A) was diluted with nitrogen at a ratio of 1:10. This procedure is required to maintain the instrument linearity, between 300 pptv and 10 ppm(v). PTR-QMS 500 is able to detect compounds from 1 – 300 amu, with a resolution close to 1 amu, a response time of 100 ms and a linearity range of 300 ppt(v) – 10 ppm(v) (Ionicon datasheet). Detail investigation on the instrument settings was reported elsewhere (Boschetti et al., 1999; Papurello et al., 2015a). The sample was directly injected into the drift tube of the instrument via a heated PEEK line (110 °C). Table 3 lists a selection of the mass peaks which are the subject of this paper. Each compound is characterized by its nominal mass (m/z), protonated chemical formula, and tentative identification based on the previous studies.

Table 3 – Mass peaks which were used in this study along with their experimental and expected m/z values, their chemical formula and tentative identification supported also by available literature

Nominal m/z	**Protonated chemical formula**	**Tentative identification**	**References for PTR-MS spectra**	**References for biogas from waste management**
31	CH_3O^+	Formaldehyde	(Buhr et al., 2002)	(Font et al., 2011; Mata-Alvarez et al., 2000)
34	H_3S^+	Hydrogen sulfide	(Papurello et al., 2012; Singer et al., 2011)	(Font et al., 2011; Lomans et al., 2002; Mata-Alvarez et al., 2000)
41	$C_3H_5^+$	Alkylic fragment	(Knighton et al., 2012; Morozova et al., 2016)	(Papadias et al., 2012)
45	$C_2H_5O^+$	Acetaldehyde	(Buhr et al., 2002; Jordan et al., 2009)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011; Wang and Wu, 2008)
47	$CH_3O_2^+$	Formic acid	(Jordan et al., 2009)	(Papadias et al., 2012)
49	CH_5S^+	Methanethiol	(Papurello et al., 2012)	(Font et al., 2011; Lomans et al., 2002; Orzi et al., 2010)
55	$C_4H_7^+$	Butadiene	(Knighton et al., 2012)	(Papadias et al., 2012)
59	$C_3H_7O^+$	Acetone	(Buhr et al., 2002)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
61	$C_2H_5O_2^+$	Acetic acid	(Aprea et al., 2007; Buhr et al., 2002)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
63	$C_2H_7S^+$	Dimethylsulfide (DMS)	(Biasioli et al., 2011)	(Font et al., 2011; Lomans et al., 2002)
67	$C_5H_7^+$	Cyclopentadiene	(Brilli et al., 2014)	(Demirbas, 2007)

69	$C_4H_5O^+$	Isoprene	(Biasioli et al., 2011)	(Font et al., 2011)
71	$C_5H_{11}^+$	Cyclopentane	(Yuan et al., 2013)	(Papurello et al., 2012)
73	$C_3H_5O_2^+$	Acrylic acid	(Brilli et al., 2014)	(Demirbas, 2007)
75	$C_3H_7O_2^+$	Propionic acid/propanoates	(Aprea et al., 2007; Buhr et al., 2002)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
77	$C_3H_9S^+$	Propanethiol	(Papurello et al., 2012)	(Vairavamurthy and Mopper, 1987)
79	$C_6H_7^+$	Benzene	(Biasioli et al., 2011)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
81	$C_6H_9^+$	Cyclohexadiene		(Papadias et al., 2012)
83	$C_5H_7O^+$	Cyclopentenone		(Demirbas, 2007)
87	$C_5H_{11}O^+$	2-Pentanone/Pentanal	(Buhr et al., 2002)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
89	$C_4H_9O_2^+$	Butyric acid/butyrates	(Aprea et al., 2007; Buhr et al., 2002)	(Font et al., 2011)
91	$C_4H_{11}S^+$	Butanethiol	(Papurello et al., 2012)	(Vairavamurthy and Mopper, 1987)
93	$C_7H_9^+$	Toluene	(Biasioli et al., 2011; Jordan et al., 2009)	(Font et al., 2011; Staley et al., 2006)
101	$C_6H_{13}O^+$	2-Hexanone/hexanal	(Buhr et al., 2002)	(Scaglia et al., 2011)
105	$C_8H_9^+$	Styrene	(Biasioli et al., 2011)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
107	$C_8H_{11}^+$	Xylene	(Biasioli et al., 2011)	(Font et al., 2011; Orzi et al., 2010; Scaglia et al., 2011)
109	$C_7H_9O^+$	Benzyl alcohol	(Brilli et al., 2014)	(Demirbas, 2007)
115	$C_7H_{15}O^+$	2-Heptanone/heptanal	(Buhr et al., 2002)	(Scaglia et al., 2011)
119	$C_9H_{11}^+$	Methylstyrene	(Yuan et al., 2013)	(Demirbas, 2007)
121	$C_9H_{13}^+$	Cumene	(Jordan et al., 2009)	(Mata-Alvarez et al., 2000; Scaglia et al., 2011)
135	$C_{10}H_{15}^+$	p-Cymene	(Biasioli et al., 2011)	(Font et al., 2011; Mata-Alvarez et al., 2000; Orzi et al., 2010; Scaglia et al., 2011)
137	$C_{10}H_{17}^+$	Monoterpenes	(Biasioli et al., 2011)	(Font et al., 2011; Mata-Alvarez et al., 2000; Orzi et al., 2010; Scaglia et al., 2011)
143	$C_9H_{19}O^+$	2-Nonanone/nonanal	(Buhr et al., 2002)	(Mata-Alvarez et al., 2000; Scaglia et al., 2011)
205	$C_{15}H_{25}^+$	Sesquiterpenes	(Biasioli et al., 2011; Jordan et al., 2009)	(Demirbas, 2007; Mata-Alvarez et al., 2000)

223	$C_6H_{18}O_3Si_3H^+$	D3, hexamethylcyclotrisiloxane	(Singer et al., 2011)	(Papadias et al., 2012)

3. Results

3.1. Biogas composition of trace compounds

Commonly, the biogas composition of trace compounds was monitored using a bag collection system, as reported from literature (Davide Papurello et al., 2016d, 2014a, 2014b, Papurello et al., 2015b, 2015c, 2013, 2012). The discontinuous monitoring system shows some lacks due to the instability of some compounds. This instability was studied and results suggest to improve the collecting system, as reported elsewhere (Arnold, 2009; Beghi and Guillot, 2008). To the best of our knowledge this research was the first attempt to build a direct connection from the biogas anaerobic digester, to the monitoring system. Rapid and reliable results were achieved in real time, as demonstrated from the comparison between the monitored and tentative identification compounds reported in literature (Table 3). The effectiveness of an OFMSW anaerobic digestion process for large-scale application depends to a great extent on the quantity and quality of the produced biogas. In all the experimental tests, the initial lag phase in which carbon dioxide production predominated, was reduced using aerobic and alkaline pre-treatments. The anaerobic digestion process lasted about three weeks after the first stage of loading. For the first week, the process produced mainly carbon dioxide (max 70% and average flow rate 3 m^3/h) with a low fraction of methane (min 5-6% and average flow rate 0.01 m^3/h), as reported in our previous studies (Papurello et al., 2015a, 2012). The amount of CO_2-rich biogas produced in the first phase is not useful for the energy purposes. After this period of time, the methane production phase starts and it lasted for the remaining two weeks with a concentration of CH_4 around 60/65 %vol. with an average flow rate value around 0.5 m^3/h. Trace compounds monitored along the digestion process are collected in Table 4. These data are an average value of the trace compounds monitored. Standard deviations of these data are also reported. The spread of experimental points is short. The variability of these points range from +/- 11%.

It is possible to group the trace compounds into the following families: terpene, siloxane, hydrocarbon, sulfur, carbonyl, carboxyl and aromatic compounds. Taking in consideration the average value, the biogas composition can be divided as follows: siloxanes 1%, sulfur compounds 6%, higher hydrocarbons 9%, terpenes 13%, carbonyl-carboxyl and aromatic compounds 35% and 37%, respectively.

Siloxanes can be found in a non-perfect separate collection because they are included in many industrial processes and consumer products (Arnold, 2009), such as soaps and cosmetics. Siloxanes were tentatively identified in Papurello et al., (2016) in a biogas produced from dry anaerobic digestion of OFMWS (Davide Papurello et al., 2016d). They come from silicon released from the mass treated inside the digester (Rasi et al., 2011). The release of organosilicon compounds from the biomass to the biogas, in general, is dependent on the T, p and digestion process. At present, there is no standard method for the analysis of volatile siloxanes in a gaseous mixture. In this batch the only siloxanes detected is D3 (m/z 223).

Sulfur compounds, mainly H_2S is dependent on the aerobic to anaerobic transition phase (Papurello et al., 2012). As reported elsewhere, H_2S represents the main sulfur compound (Orzi et al., 2010; Papurello et al., 2012; Scaglia et al., 2011). H_2S represents 76% of the total sulfur compounds detected. The remaining contribution derives from butanethiol (m/z 91) (21%), dimethylsulfide (m/z 63) (2%) and metanethiol (m/z 49) (1%). These thiols are mainly produced at the end of the digestion process. As reported in other testing campaigns the production of sulfur compounds occur mainly at the beginning and at the end of the digestion process (Davide Papurello et al., 2014a; Papurello et al., 2015a, 2012).

Terpenes originate from the inherited organic matter, fruits and vegetables contained in the OFMSW and they are released into the gas matrix. Terpenes have been reported to be stripped during the first stage of aerobic process (Pierucci et al., 2005). The main terpene compound detected is p-cymene (m/z 135) with 48%, followed by limonene (m/z 137) with 41%. The remaining contribution derives from sesquiterpene (m/z 205) (6%) and isoprene (m/z 69) (5%). The high levels of p-cymene in the biogas suggests the occurrence of d-limonene transformation by the anaerobic bacteria, as reported by (Orzi et al., 2010).

Aromatic compounds can be detected in organic material decomposition. In fact, Eitzer (1995), reported during unsorted MSW-composting, the high presence of terpenes, but also the high presence of aromatic hydrocarbons (Eitzer, 1995). In another study, Komilis et al., (2004) indicated that aromatic hydrocarbons were emitted even if only food waste were composted (Komilis et al., 2004). In Orzi et al., (2010) the aromatic hydrocarbons detected were mainly, toluene and various alky-benzene that probably suggested a non-biogenic origin (Orzi et al., 2010). In the present study aromatic hydrocarbons detected are toluene (m/z 93) (80%), cyclohexadiene (m/z 81) (14%) followed by cyclopentane (m/z 71) and propyne (m/z 41).

Carbonyl and carboxyl compounds can be detected in the biogas due to the decomposition of OFMSW. Two different mechanistic approaches could be adopted in order to explain the release of carbonyl compounds: (a) direct oxidation of alcohols in the presence of oxygen – formation of 2-ketones during the acetogenesis and (b) formation of 2-ketones through methanogens induced oxidative reactions under alkaline conditions (Papurello et al., 2012; Scaglia et al., 2011). Generally, the carbonyl compound levels remain remarkably high throughout the dry anaerobic digestion, which is in accordance with the findings of Orzi et al. (2010) (Orzi et al., 2010). Formic (m/z 47.012), acetic (m/z 61.027), propionic (m/z 75.044), and butyric (m/z 89.059) acid are detected along the anaerobic digestion process. The emissions of carboxylic acids are strongly dependent on pH. The initial pH at the beginning of the digestion is neutral to basic, and the final pH at the end of digestion is alkaline. This is confirmed by the increase of CO_2 production. Carboxylic acids formation is generally related to the inherited organic matter. In fact, derives from the lipids breakdown and also from acidogenic bacteria action on the carbohydrate substrate derived from the hydrolysis of starch and cellulosic biopolymers.

Table 4 – Biogas trace compounds composition from dry Anaerobic Digestion process of organic waste from local municipality. (ppb(v))

Time (h)	31		34		41		45		47		49		55	
	CH_2O		H_2S		C_3H_4		C_2H_4O		C_2H_6O		CH_4S		C_4H_6	
	formaldehyde	**std.dev.**	**hydrogen sulfide**	**std.dev.**	**propyne**	**std.dev.**	**acetaldehyde**	**std.dev.**	**formic acid**	**std.dev.**	**methanethiol**	**std.dev.**	**butadiene**	**std.dev.**
129	1376	5.2	23425	925.6	522	40.7	141	16.8	53	16.8	21	0.9	201	30.7
159	1379	3.6	22966	876.4	530	49.9	163	13.3	48	13.3	23	1.4	209	4.7
161	1085	12.5	26430	948.9	564	46.2	154	14.3	64	14.3	19	1.7	225	17.2
175	1412	3.9	23511	1058.1	540	72.4	158	23.1	64	23.1	26	2.8	228	23.6
183	1274	7.2	27353	1752.1	567	56.1	172	5.8	61	5.8	21	2.4	201	26.5
199	1256	8.8	21393	969.9	504	70.4	137	6.2	54	6.2	24	2.9	214	18.4
206	1522	14.3	26353	1342.0	503	37.6	186	13.5	69	13.5	32	1.5	294	9.2
222	101	12.4	2892	187.8	956	67.0	711	76.6	193	76.6	2	0.2	698	54.3
230	1143	15.0	30571	1123.7	566	51.7	170	13.7	61	13.7	17	0.8	207	15.2
246	1344	13.4	25222	1134.7	435	40.9	150	8.3	61	8.3	23	2.5	226	5.5
269	1269	8.9	26928	995.8	493	13.9	164	19.4	64	19.4	22	1.5	233	28.9
293	1393	13.7	24845	1188.4	467	55.7	148	18.1	61	18.1	24	2.4	246	19.2
301	1144	9.2	26151	1114.5	507	31.6	156	18.5	60	18.5	19	1.8	219	27.6
313	1292	12.9	25741	1443.3	462	38.3	154	10.8	55	10.8	21	2.2	216	29.2
325	939	12.3	27913	829.8	534	28.1	171	26.6	61	26.6	15	1.2	219	8.1
Min (ppm(v))	0.1		2.9		0.4		0.1		0		0		0.2	
Max (ppm(v))	1.5		30.6		1		0.7		0.2		0.03		0.7	

Time (h)	59		61		63		67		69		71		73	
	C_3H_6O		CH_3COOH		C_2H_6S		C_5H_6		C_5H_8		C_5H_{10}		C_4H_8O	
	acetone	**std.dev.**	**acetic acid**	**std.dev.**	**dimethylsulfide**	**std.dev.**	**ciclobutadiene**	**std.dev.**	**isoprene**	**std.dev.**	**cyclopentane**	**std.dev.**	**2-butanone**	**std.dev.**
129	2529	201.0	55	7.0	84	8.9	99	4.8	535	38.0	515	52.8	12310	1422.8
159	2339	283.6	58	6.0	74	7.1	86	8.8	415	21.8	440	46.6	10633	1137.1

161	2286	197.5	29	2.1	70	5.6	136	13.2	606	58.3	454	64.7	16761	2172.2
175	2658	340.4	82	6.9	85	12.9	93	11.0	480	41.1	557	26.8	11081	1189.9
183	2550	267.0	41	4.0	62	7.1	99	9.4	496	50.1	445	36.5	16559	1367.9
199	2335	259.2	53	5.8	89	9.1	81	3.0	431	25.4	495	22.9	12189	1052.4
206	2671	249.9	69	8.4	95	7.7	78	6.8	404	45.4	477	39.5	12215	961.3
222	1765	130.7	230	27.6	3	0.3	27	2.5	69	6.4	98	13.7	5889	762.4
230	2098	211.0	35	4.4	55	5.6	116	14.8	500	54.6	404	46.0	11629	1157.9
246	2096	173.4	60	5.8	73	4.5	72	6.9	352	35.6	372	11.3	8889	687.2
269	2474	287.6	46	4.6	67	2.8	84	7.7	427	44.9	391	38.2	15721	1103.5
293	2346	162.4	53	5.8	84	8.4	71	6.8	353	26.0	409	45.1	12478	702.0
301	2447	249.6	34	1.0	61	4.0	96	7.4	509	47.4	397	24.1	19059	1025.6
313	3035	190.4	187	24.6	68	6.7	77	9.1	270	22.4	481	44.4	12786	1261.3
325	2231	150.9	23	0.6	57	4.2	100	13.8	200	27.7	401	35.2	20817	2051.5
Min (ppm(v))	1.8		0		0		0		0.1		0		6	
Max (ppm(v))	3		0.2		0.1		0.1		0.6		1		21	

Time (h)	**75**		**77**		**79**		**81**		**83**		**87**		**89**	
	$C_3H_6O_2$		**C_3H_8S**		**C_6H_6**		**C_6H_8**		**C_5H_6O**		**$C_5H_{10}O$**		**$C_4H_8O_2$**	
	propionic acid	**std.dev.**	**propanethiol**	**std.dev.**	**benzene**	**std.dev.**	**cyclohexadiene**	**std.dev.**	**methylfuran**	**std.dev.**	**2pentanone**	**std.dev.**	**butyric acid**	**std.dev.**
129	51	6.3	9	0.7	22	1.7	3767	251.3	1414	115.2	524	32.7	9	0.8
159	43	3.9	8	0.8	22	1.1	3346	233.3	1181	127.7	415	44.4	8	0.4
161	66	1.3	12	0.4	24	2.9	5534	430.8	1764	61.6	587	42.4	9	0.7
175	51	2.2	7	0.6	7	0.7	3743	571.6	1242	137.3	458	51.5	14	1.9
183	65	6.0	7	0.7	7	0.7	4251	288.5	1464	78.4	659	66.3	11	1.5
199	50	3.0	8	0.2	8	1.0	3587	435.2	1289	99.3	490	19.5	8	1.1
206	52	4.9	23	1.6	22	1.5	3475	335.6	1382	123.0	519	54.9	11	1.2
222	36	5.6	25	3.3	16	1.1	591	70.3	136	7.8	121	17.0	10	0.9
230	49	3.1	6	0.1	6	0.2	4676	175.7	1457	107.7	258	10.4	4	0.5

246	40	3.0	5	0.8	5	0.5	2857	192.2	1031	92.1	192	17.4	4	0.5
269	64	2.4	6	0.5	6	0.5	3320	317.7	1166	55.2	256	9.4	3	0.3
293	40	4.2	4	0.4	4	0.3	2937	272.3	1115	90.7	191	16.5	2	0.3
301	75	1.4	5	0.4	5	0.5	4151	191.2	1489	84.8	250	27.0	3	0.4
313	45	5.9	4	0.5	4	0.4	2898	211.1	932	66.9	205	18.3	2	0.3
325	50	3.2	5	0.6	5	0.5	5296	271.9	1811	116.3	385	41.2	3	0.2
Min (ppm(v))	0		0		0		1		0		0		0	
Max (ppm(v))	0		0		0		6		2		1		0	

Time (h)	**91**		**93**		**101**		**105**		**107**		**109**		**115**	
	$C_4H_{10}S$		**C_7H_8**		**$C_6H_{12}O$**		**C_8H_8**		**C_8H_{10}**		**C_7H_8O**		**$C_7H_{14}O$**	
	butanethiol	**std.dev.**	**toluene**	**std.dev.**	**2-hexanone**	**std.dev.**	**styrene**	**std.dev.**	**xylene**	**std.dev.**	**benzilic acid**	**std.dev.**	**2-heptanone**	**std.dev.**
129	523	58.8	17745	1193.3	145	12.4	47	4.5	36	4.6	69	6.7	88	8.5
159	506	55.3	17497	1293.6	115	13.3	36	4.2	32	3.5	65	2.2	74	5.6
161	1046	47.9	30423	3533.0	140	21.5	163	9.5	50	6.4	85	3.6	132	11.6
175	548	34.3	18741	431.0	137	16.0	42	5.2	36	3.1	69	3.3	79	6.2
183	867	41.9	27046	3425.5	160	19.1	75	5.6	37	2.3	65	2.4	103	10.7
199	500	55.2	17481	874.4	127	13.9	32	1.4	28	3.2	51	4.8	71	7.7
206	545	47.9	18819	1832.6	139	17.0	29	2.4	30	4.1	62	6.7	76	9.9
222	486	50.6	11019	590.8	49	2.9	14	1.1	15	2.0	47	4.4	31	1.7
230	1150	110.3	31000	3109.0	123	2.7	134	13.2	46	5.9	77	7.9	105	10.1
246	381	35.6	13852	1809.2	116	13.2	21	3.1	29	1.9	64	2.1	62	5.4
269	599	61.9	18511	1897.3	161	24.7	41	2.2	31	2.3	58	4.6	78	8.7
293	423	45.9	15002	1558.8	128	13.9	24	1.9	26	1.3	52	4.5	66	3.6
301	839	64.5	26972	2305.7	166	17.5	80	11.8	33	1.4	60	6.4	112	16.8
313	555	52.4	17875	936.8	164	15.9	34	1.5	33	1.6	93	5.0	98	9.9
325	1083	123.7	30433	2431.1	200	22.8	152	5.2	47	3.8	75	6.2	158	23.7
Min (ppm(v))	0		11		0		0		0		0		0	

Max (ppm(v))	1	31	0.2	0.2	0	0.1	0.2

Time (h)	**119**		**121**		**135**		**137**		**143**		**205**		**223**	
	C_9H_{10}		**C_9H_{12}**		**$C_{10}H_{14}$**		**$C_{10}H_{16}$**		**$C_9H_{18}O$**		**$C_{15}H_{24}$**		**C6H18O3Si3**	
	methylstyrene	**std.dev.**	**cumene**	**std.dev.**	**p-cymene**	**std.dev.**	**limonene**	**std.dev.**	**2-nonanone**	**std.dev.**	**sesquiterpene**	**std.dev.**	**hexamethylcyclotrisiloxane**	**std.dev.**
129	123	14.4	25	1.0	4114	221.3	3586	218.9	33	3.8	535	48.2	535	53.5
159	103	12.6	21	1.5	3682	331.6	3170	440.4	29	2.5	421	57.6	421	43.8
161	324	48.1	47	4.1	4889	153.6	4880	271.0	39	3.8	597	64.0	597	19.2
175	109	10.5	23	3.5	3864	302.9	3367	351.8	33	3.5	490	18.1	490	25.7
183	168	18.4	26	1.3	4345	264.1	3437	342.6	29	1.8	496	20.0	496	70.2
199	83	3.5	18	2.5	3725	510.4	3066	156.6	23	3.0	437	27.7	437	28.5
206	74	4.7	17	2.1	3409	330.4	2729	313.4	29	2.6	412	25.4	412	46.9
222	246	27.4	10	1.2	1091	112.1	372	15.5	14	1.4	69	8.7	69	1.4
230	255	22.0	35	2.1	4229	349.1	3524	270.1	30	3.7	500	49.1	500	61.5
246	61	3.0	15	1.5	2585	232.9	2412	267.6	24	3.5	358	34.3	358	32.6
269	99	6.4	18	1.9	3203	311.5	2574	281.1	25	2.3	427	25.9	427	32.2
293	63	6.0	14	1.4	3041	195.8	2405	280.8	23	2.8	360	22.9	360	23.4
301	173	8.3	26	1.7	3793	187.0	3087	344.4	25	1.5	509	18.4	509	29.5
313	90	8.1	18	1.5	2886	178.7	2385	263.0	50	7.1	380	11.8	150	3.9
325	265	36.0	40	4.3	3508	319.2	3913	156.4	33	3.1	360	43.6	150	18.0
Min (ppm(v))	0.1		0		1.1		0.4		0		0.1		0.1	
Max (ppm(v))	0.3		0		4.9		4.9		0		0.6		0.6	

3.2. Adsorption capacity evaluation

The adsorption capacity is inversely correlated to the breakthrough capacity for a given sorbent material. The adsorption capacity estimation is often the major determinant of service life time for an adsorbent. The adsorption capacity was evaluated considering the following equation, (Sisani et al., 2014):

$$C_{ads} = \frac{\dot{Q} \cdot MW \cdot \left(C_{in} \cdot t_1 - \left(t_1 - t_0\right) \cdot 0.5\right)}{Vm \cdot m \cdot 10^3} \qquad (1)$$

Where:

Q, total gas flow rate (Nl/h);

MW, molecular weight (H_2S 34 g/mol);

C_{in}, inlet H_2S concentration (ppm(v));

t_1, breakthrough time when the outlet H_2S concentration is 1 ppm(v) (h);

t_0, breakthrough time at the last detection of 0 ppm(v) (h);

Vm, molar volume (24.414 Nl/mol);

m, mass of adsorbent material (g).

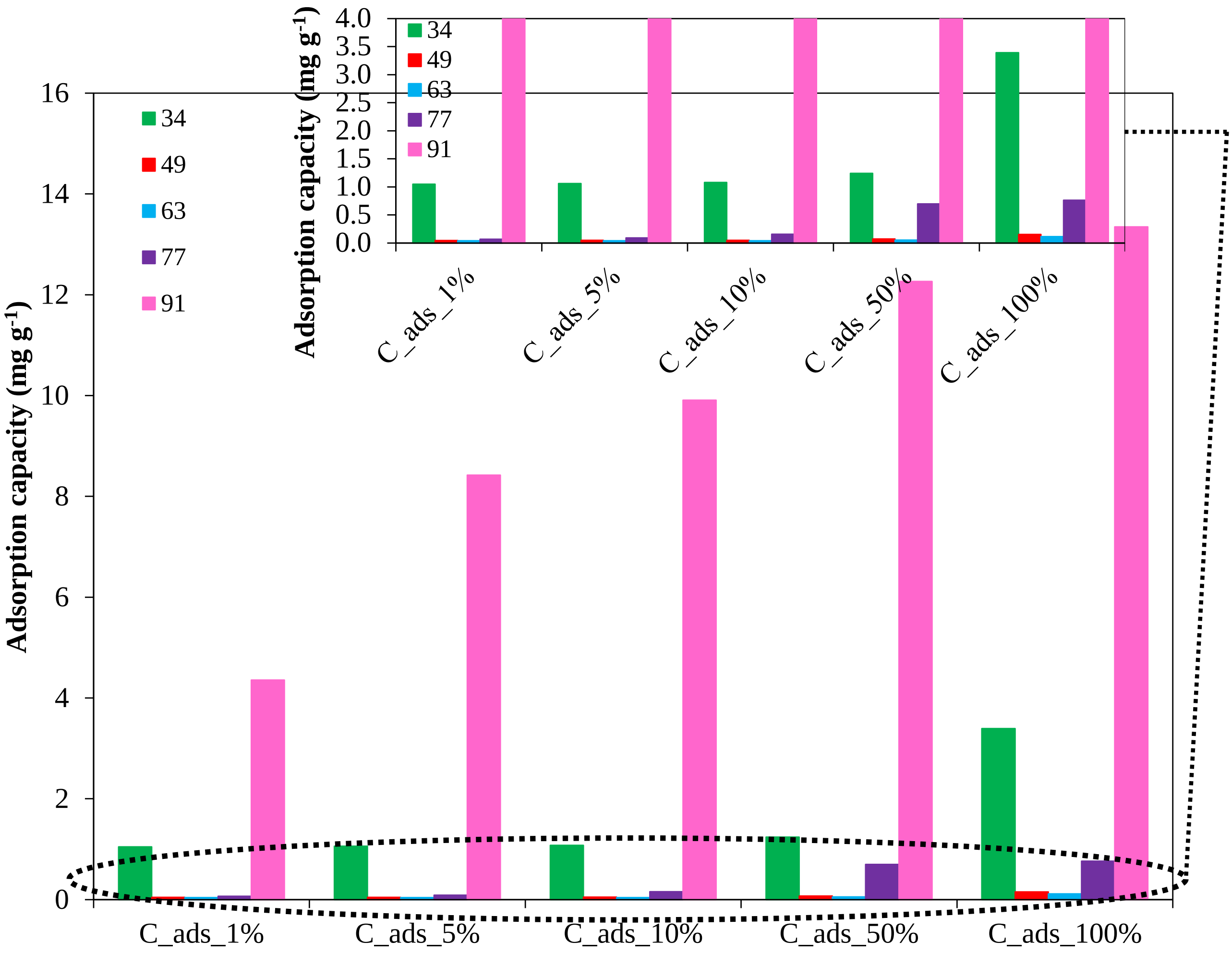

Figure 3 – Adsorption capacity for sulfur compounds

The adsorption capacity for sulfur compounds evaluated with equation 1, is reported in Table 5 and in Figure 3. It is crucial the initial breakthrough time for the SOFC feeding system and to plan a maintenance operation process for the sorbent replacement. In fact, as reported in literature, the tolerable levels of trace compounds contained in the biogas fuel are low (Hagen et al., 2011; D. Papurello et al., 2014; Davide Papurello et al., 2014a; Sasaki et al., 2011). The adsorption capacity achieved to remove H_2S was about 1.05 mg/g when it was achieved 1% of the starting H_2S concentration (limit fixed for the initial breakthrough value for SOFC requirements). This adsorption capacity value increased to 3.39 mg/g when the saturation of filter is reached. As reported in Papurello et al., (2016) simulated biogas with only H_2S, using two different commercial activated carbons showed an adsorption capacity that ranged from 3 – 6 mg/g. In this study biochar was selected as sorbent material in a real biogas pilot plant. Results achieved are comparable with literature results for H_2S removal. The second sulfur compound in terms of abundance was butanethiol. Biochar showed an adsorption capacity value, at the initial breakthrough around 4.4 mg/g up to achieve 13.3 mg/g at the saturation of the filter. Considering the other sulfur compounds, due to their lower concentration showed an adsorption capacity relatively low. Values achieved ranged from 0.04 mg/g to 0.76 mg/g, from initial breakthrough to saturation. As reported elsewhere, (D. Papurello et al., 2016) when the pollutant concentration increases also the adsorption capacity increases. This is due to the driving force increasing; up to achieve a limit value above which the adsorption capacity remains constant. The effectiveness of the adsorption treatment is determined also by the type of substance to be removed. Substances with a high molecular weight and low water solubility are better adsorbed with active carbon. In fact, H_2S showed a lower adsorption capacity than butanethiol even with higher concentration values.

Commercial activated carbons, properly prepared for siloxanes removal have an adsorption capacity that ranged around 100-200 mg/g in the single removal test (laboratory conditions). Biochar showed an adsorption capacity of 1.28 mg/g at 1% of the starting D3 concentration, limit for the initial breakthrough value. This adsorption capacity increased up to achieve, at 50% of the initial concentration, 12.28 mg/g and at the saturation of the filter, remains quite stable with 13.15 mg/g.

The adsorption capacity for the removal of terpenes is reported in Table 5 and in Figure 4. The most abundant terpene compound was p-cymene, followed by limonene. For these compounds the adsorption capacity started from 35 mg/g and 64 mg/g, respectively. The trend for p-cymene showed a significant increase from 1% to 5% of initial concentration of more than 50% up to achieve, at the saturation condition 97.6 mg/g. The adsorption capacity increased significantly up to 102 mg/g at saturation conditions for limonene. Cumene and isoprene showed a lower adsorption capacity due to pollutant concentration contained in the biogas.

Among aromatic compounds: benzene, toluene, styrene and xylene were detected. The most abundant aromatic compound is toluene with an average value around 21 ppm(v), while benzene, styrene and xylene showed a concentration below 10 ppb(v). The adsorption capacity of toluene, at the starting condition showed a value above 140 mg/g up to achieve, rapidly the maximum capacity at the saturation conditions (40% by weight of the carbon), see Figure 4 and Table 5.

The most common CHO compound detected in the biogas mixture was 2-butanone and the adsorption capacity calculated ranged from 160 mg/g to 270 mg/g from initial to saturation condition. Acetone and methylfuran show lower adsorption capacity values. The remaining aromatic compounds, due to their lower concentration showed an adsorption capacity value below the unity of mg/g.

Table 5 – Adsorption capacity from the initial breakthrough (1%) to saturation (100%) level

Cads (mg/g)	**31** **CH_2O** **formaldehyde**	**34** **H_2S** **hydrogen sulfide**	**41** **C_3H_4** **propyne**	**45** **C_2H_4O** **acetaldehyde**	**47** **C_2H_6O** **ethanol**	**49** **CH_4S** **methanethiol**	**55** **C_4H_6** **butadiene**	**59** **C_3H_6O** **acetone**	**61** **CH_3COOH** **acetic acid**	**63** **C_2H_6S** **dimethylsulfide**	**67** **C_5H_6** **ciclobutadiene**	
1%	0.24	1.05	0.24	0.09	0.01	0.05	0.08	0.85	0.04	0.04	0.51	
5%	0.26	1.06	0.24	0.10	0.01	0.05	0.09	2.29	0.04	0.04	0.71	
10%	0.29	1.08	0.25	0.10	0.01	0.05	0.10	22.65	0.05	0.04	0.74	
50%	0.57	1.24	0.30	0.11	0.02	0.07	0.20	26.40	0.20	0.05	0.82	
100%	1.46	3.39	0.83	0.13	0.06	0.15	1.10	28.24	0.22	0.11	0.87	
Cads (mg/g)	**69** **C_5H_8** **isoprene**	**71** **C_4H_6O** **crotonaldehyde**	**73** **C_4H_8O** **2-butanone**	**75** **$C_3H_6O_2$** **propionic acid**	**77** **C_3H_8S** **propanethiol**	**79** **C_6H_6** **benzene**	**81** **C_6H_8** **ciclohexadiene**	**83** **C_5H_6O** **methylfuran**	**87** **$C_5H_{10}O$** **2pentanone**	**89** **$C_4H_8O_2$** **butyric acid**	**91** **$C_4H_{10}S$** **butanethiol**	**93** **C7H8** **toluene**
1%	0.44	2.36	158.84	0.02	0.07	0.12	31.93	7.18	2.35	0.05	4.36	140.10
5%	1.69	4.67	191.31	0.02	0.09	0.15	57.14	16.71	4.78	0.09	8.42	302.80
10%	3.38	5.01	206.13	0.02	0.16	0.35	61.20	17.89	5.11	0.37	9.91	334.78
50%	4.05	5.91	248.84	0.05	0.70	0.66	73.01	20.82	5.90	0.72	12.27	400.80
100%	4.32	6.39	272.01	0.05	0.76	0.71	79.46	22.37	6.32	0.81	13.35	433.83
Cads (mg/g)	**101** **$C_6H_{12}O$** **2-hexanone**	**105** **C_8H_8** **styrene**	**107** **C_8H_{10}** **xylene**	**109** **C_7H_8O** **benzilic acid**	**115** **$C_7H_{14}O$** **2-heptanone**	**119** **C_9H_{10}** **methylstyrene**	**121** **C_9H_{12}** **cumene**	**135** **$C_{10}H_{14}$** **p-cymene**	**137** **$C_{10}H_{16}$** **limonene**	**143** **$C_9H_{18}O$** **2-nonanone**	**205** **$C_{15}H_{24}$** **sesquiterpene**	**223** **$C_6H_{18}O_3Si_3$** **hexamethylcyclotrisiloxane**
1%	0.77	0.65	0.13	0.06	0.59	1.67	0.19	34.92	64.05	0.92	1.26	1.28
5%	1.67	0.76	0.29	0.11	0.95	2.75	0.26	72.75	74.41	1.52	5.45	5.36
10%	1.79	0.77	0.30	0.32	1.03	2.91	0.57	77.17	79.31	1.61	11.08	10.09
50%	2.08	0.83	0.33	0.44	1.15	3.36	1.16	90.66	93.69	1.79	13.65	12.28
100%	2.22	0.86	0.35	0.48	1.21	3.60	1.25	97.58	101.59	1.89	14.62	13.15

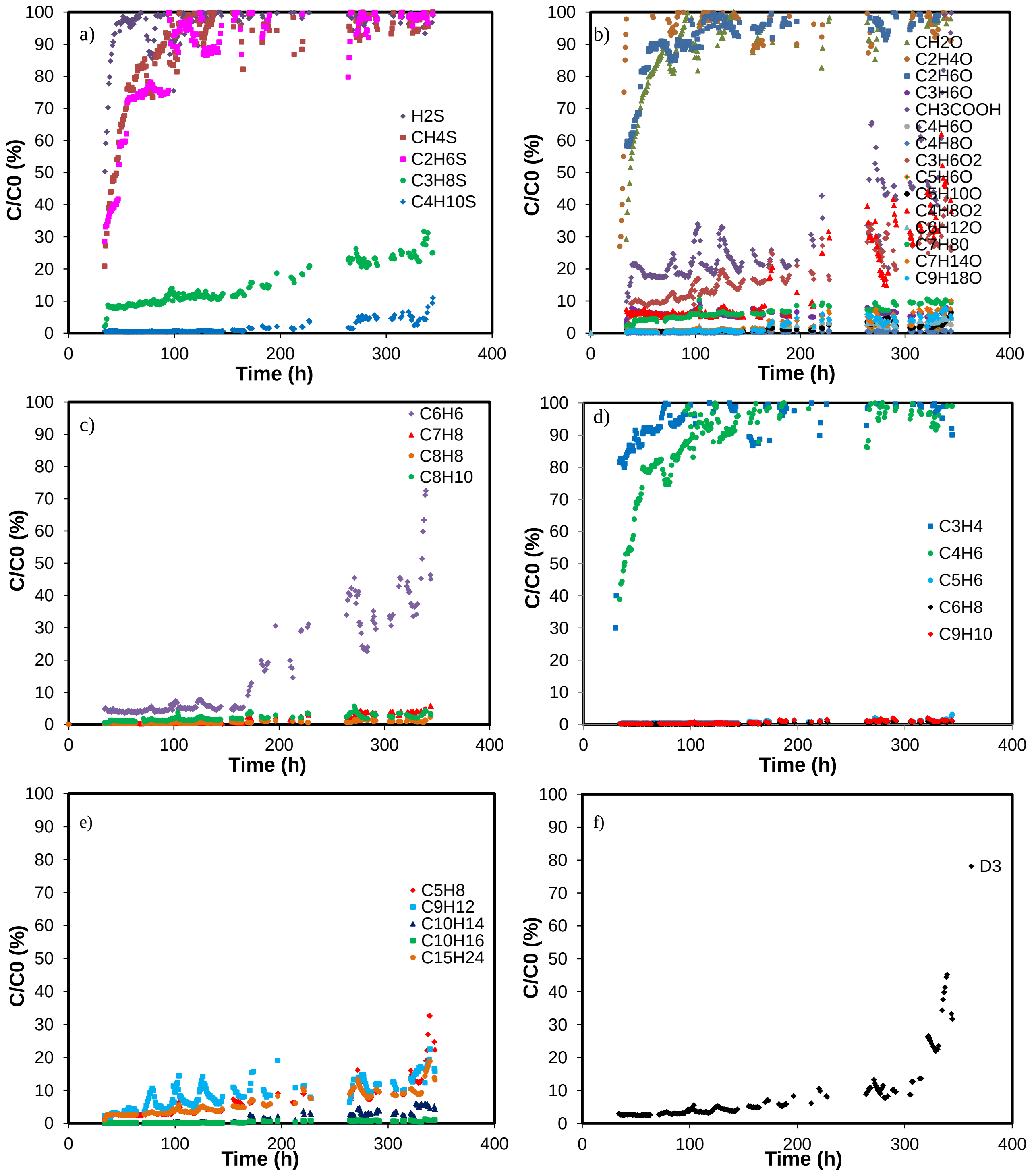

Figure 4 – Removal performance for trace compounds: a) sulfur compounds, b) carbonyl and carboxyl compounds, c) aromatic compounds, d) hydrocarbon compounds, e) terpenes, f) siloxanes

4. Discussion

The contemporary presence of trace compounds in the fuel mixture for SOFC applications were monitored online with a DIMS technique. The main compounds monitored were the protonated form of H_2S, C_7H_8, C_4H_8O, $C_{10}H_{16}$ and $C_{10}H_{14}$. These compounds belong to the family of sulfur, aromatic, carbonyl and terpene compounds.

Hydrogen sulfide was the main sulfur compound detected. The average concentration was about 24 ppm(v). The tested sorbent material was able to withstand the H_2S concentration for almost 30 h with the biogas pilot plant conditions before achieving the limit value for SOFC applications, 1 ppm(v) (Davide Papurello et al., 2014a). This concentration is the tolerable limit for SOFC applications able to guarantee a reversible behavior rather than a dramatic and irreversible loss of performance (Davide Papurello et al., 2016a). Considering the other detected sulfur compounds and due to their lower concentration inside the biogas matrix, H_2S is the compound that fixes the replacement time for the filter. The other important trace compounds that strongly affect the SOFC performance are siloxanes. The average concentration detected for D3 was about 3.9 ppm(v). As reported elsewhere, this concentration irreversibly affects the SOFC performance in few hours (Madi et al., 2015; Davide Papurello et al., 2016a). The limit for D3 for SOFC applications is 1% of the average concentration detected in the real biogas pilot plant. The time required to achieve this limit is around 30 h, which confirms the time limit set by H_2S.

Table 6 – Time required to achieve the adsorption capacity percentage

Compounds			**Time (h)**				
			1%	**5%**	**10%**	**50%**	**100%**
31	**CH_2O**	**formaldehyde**	14.6	16.0	17.8	36.2	93.1
34	**H_2S**	**hydrogen sulfide**	28.3	28.6	29.1	33.6	92.8
41	**C_3H_4**	**propyne**	24.0	24.4	25.0	30.7	90.8
45	**C_2H_4O**	**acetaldehyde**	24.5	24.8	25.2	29.5	35.7
47	**C_2H_6O**	**ethanol**	6.7	8.1	9.9	28.4	126.0
49	**CH_4S**	**methanethiol**	21.0	22.4	24.3	43.2	119.2
55	**C_4H_6**	**butadiene**	13.5	15.0	17.0	37.5	215.4
59	**C_3H_6O**	**acetone**	13.5	37.0	367.9	428.8	458.7
61	**CH_3COOH**	**acetic acid**	22.6	26.5	32.4	314.9	352.0
63	**C_2H_6S**	**dimethylsulfide**	21.1	22.6	24.7	46.2	163.5

67	**C_5H_6**	**ciclobutadiene**	193.8	377.4	402.1	473.6	512.8
69	**C_5H_8**	**isoprene**	35.4	150.8	305.5	367.3	392.5
71	**C_4H_6O**	**crotonaldehyde**	175.5	369.4	398.4	474.4	514.6
73	**C_4H_8O**	**2-butanone**	366.9	442.2	476.6	575.6	629.4
75	**$C_3H_6O_2$**	**propionic acid**	12.6	28.1	61.3	397.2	450.4
77	**C_3H_8S**	**propanethiol**	20.6	33.4	73.5	396.1	435.2
79	**C_6H_6**	**benzene**	34.8	50.1	164.4	337.0	369.6
81	**C_6H_8**	**ciclohexadiene**	242.8	437.1	468.4	559.4	609.1
83	**C_5H_6O**	**methylfuran**	153.6	366.1	395.3	457.6	492.2
87	**$C_5H_{10}O$**	**2pentanone**	164.1	360.9	387.4	451.3	484.8
89	**$C_4H_8O_2$**	**butyric acid**	13.7	31.3	173.1	349.1	394.4
91	**$C_4H_{10}S$**	**butanethiol**	159.5	320.2	379.2	472.2	515.0
93	**C_7H_8**	**toluene**	161.4	349.2	386.1	462.4	500.5
101	**$C_6H_{12}O$**	**2-hexanone**	123.2	348.0	380.1	451.0	487.4
105	**C_8H_8**	**styrene**	223.8	420.8	455.7	552.0	603.5
107	**C_8H_{10}**	**xylene**	46.6	368.2	396.8	466.9	503.8
109	**C_7H_8O**	**benzilic acid**	20.2	79.0	339.3	491.5	543.0
115	**$C_7H_{14}O$**	**2-heptanone**	129.6	304.7	348.2	408.0	437.9
119	**C_9H_{10}**	**methylstyrene**	210.4	414.1	444.3	529.2	575.2
121	**C_9H_{12}**	**cumene**	34.6	62.9	176.1	382.5	425.1
135	**$C_{10}H_{14}$**	**p-cymene**	164.7	345.8	366.9	431.5	464.6
137	**$C_{10}H_{16}$**	**limonene**	347.1	404.2	431.2	510.4	554.0
143	**$C_9H_{18}O$**	**2-nonanone**	143.1	328.4	357.2	414.6	443.9
205	**$C_{15}H_{24}$**	**sesquiterpene**	32.1	153.8	316.7	391.2	419.3
223	**$C_6H_{18}O_3Si_3$**	**hexamethylcyclotrisiloxane**	32.5	150.4	287.1	350.5	375.5

Considering the selected time limit (30 h), the saturation of the filter to toluene was 0.2%, 2-butanone 0.1%, p-cymene 0.1% and limonene 0.04%.

The time required to achieve 1% of the starting concentration is reported in Table 6. For aromatic compounds these times are the following: benzene with 34.8 h, xylene with 46.6 h, toluene with 161.4 h and styrene with 223.8 h.

CHO compounds are less problematic for SOFC applications in terms of concentration in the biogas fuel mixture. To achieve 1% of the starting concentration for the main CHO compounds, the following times are necessary: ethanol with 6.7 h, acetone with 13.5 h, methylfuran with 153.6 h and 2-butanone with 366.9 h. Even if lower than H_2S and D3, these compounds are less detrimental for SOFC applications.

The time required for terpenes to achieve 1% of the starting concentration are showed below. These values are sorted in ascending order: cumene with 34.5 h, isoprene with 35.4 h, p-cymene with 164.7 h and limonene with 347 h. When the time required to achieve the desired outlet concentration is shorter, the resulting adsorption capacity is lower.

Biochar withstands the removal of 2-butanone, toluene and limonene better compared to the other compounds. Hydrogen sulfide and D3 are crucial in terms of trace compounds removal due to their strong and irreversible impact on SOFC performance. More attention should be payed to these compounds in view of the long-term operation of SOFC co-generators.

5. Preliminary economic analysis

Despite biochar shows lower performance compared with commercial sorbent materials, a preliminary economic evaluation can improve the choice of sorbent material. A similar evaluation was accomplished with ashes as sorbent material and negative results were analyzed (Davide Papurello et al., 2016d).

A schematic view of the pilot plant is reported, see Figure 5. As reported elsewhere, the pilot plant must be optimized in terms of SOFC coupling with reformer and in terms of anaerobic digester in order to increase the total electrical efficiency (Papurello et al., 2015a).

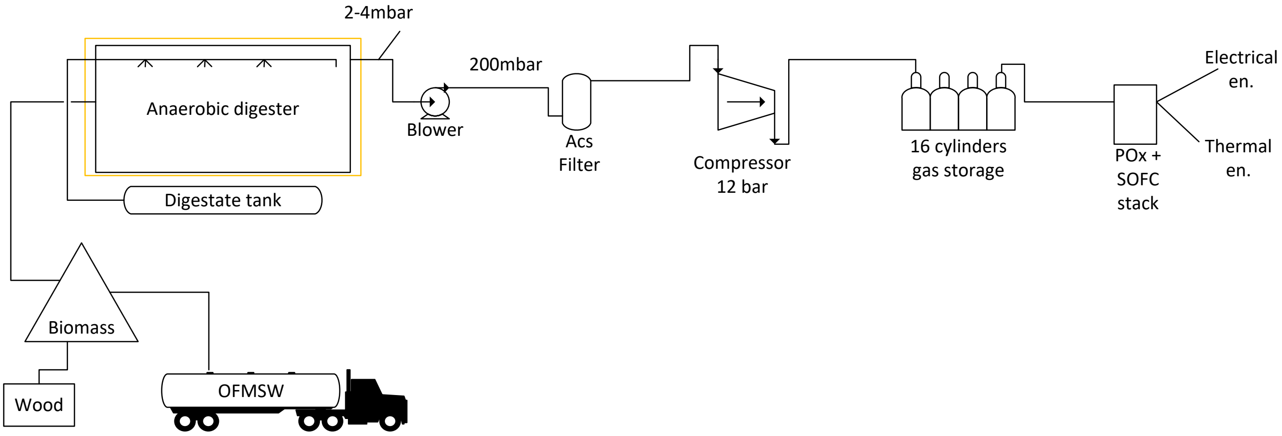

Figure 5 – Schematic view of the pilot plant – waste to energy concept

The goal of this section is essentially to clarify the role of the biochar as sorbent material in comparison to the other commercial adsorbents. The total costs of the sorbent material were divided in four different contributions. These costs are related to: the material purchase, the electricity for the plant operation, the replacement of spent material and the disposal costs as special waste (CER code 190904). The regeneration of spent sorbents has not been considered due to energy and additional material requirements. For the preliminary economic evaluations were considered the following points:

- Working time of the plant, 252 days;
- Reactor volume, 0.34 l;
- Average biogas flow, 300 Nl/h;
- Cost of electricity, 0.12 €/kWh;
- H_2S density, 1.36 kg/m^3;
- Blower size, 250 W;
- H_2S concentration, 15 ppm(v);
- The disposal costs for carbons, 1.2 €/kg (APAT 2010);
- Costs for maintenance, 20 €/h;

- The bulk density ranged from 450 g/l to 550 g/l (carbons), biochar 615 g/l, ZnO 1090 g/l and ash 1035 g/l.

Two different breakthrough levels were selected in order to evaluate the adsorption capacity at 1% and at the saturation condition. The materials considered were: commercial carbons (RST3, Carbox, CKC, CKI and R8G), metallic oxide (ZnO) and waste materials (ashes and biochar).

Table 7 – Adsorption capacity and time to change for the gas cleaning filter

	RST3	**Carbox**	**ZnO**	**CKC**	**CKI**	**R8G**	**Biochar**	**Ash**
Cads (mg/g)-1%	0.94	1.1	2.4	2.5	2.3	18.7	1.1	0.0
Time to change (h)-1%	24.5	27.9	61.7	65.1	59.1	486.4	27.4	0.1
Cads (mg/g)-100 %	7.7	3.2	12.5	3.7	3.1	22.1	3.4	0.1
Time to change (h)	200.6	84.1	325.4	97.4	81.8	575.2	88.3	1.6

The biochar adsorption capacity at 1% is comparable with commercial activated carbon samples, RST3 and Carbox. Better results are achieved considering new commercial activated carbons such as CKC and CKI. This is due to different impregnating elements, such as metal oxides, alkali and alkaline hearth metals, such as CaO and FeO. The best performance are achieved considering the R8G sample. This is due to the impregnating agents but also it is due to the structure optimization made from the producer company (Sulfatrap, TDA USA). According to the adsorption capacity the time to change ratio of filter is directly linked to this parameter. In fact, sorbents with similar adsorption capacity show similar time to change ratio: biochar and Carbox with similar adsorption capacity (1.1 mg/g) show a 27.4 h and 27.9 h time to change ratio, respectively.

Table 8 – Costs sharing to achieve the breakthrough at 1%

1%	**RST3**	**Carbox**	**ZnO**	**CKC**	**CKI**	**R8G**	**Biochar**	**Ash**
p% material (%)	20.68	20.6	77.4	7.2	12.9	6.5	4.9	8.1
p% operating (%)	41.57	38.9	5.6	27.5	27.6	5.1	47.0	91.8
p% electricity (%)	33.9	36.4	11.9	62.2	56.4	87.9	43.2	0.2
p% disposal (%)	3.8	4.1	5.2	3.1	3.1	0.5	4.9	0.0

Table 9 – Costs sharing to achieve the breakthrough at 100%

sat	RST3	Carbox	ZnO	CKC	CKI	R8G	Biochar	Ash
p% material (%)	5.7	11.6	50.9	5.5	10.6	5.6	2.4	7.7
p% operating (%)	11.5	21.9	3.7	20.9	22.6	4.4	23.3	87.4
p% electricity (%)	81.6	64.2	42.1	71.3	64.3	89.6	71.8	4.9
p% disposal (%)	1.1	2.3	3.4	2.3	2.5	0.4	2.4	0.0

The main item that weighs on the economic evaluation of the commercial sorbent material to achieve the removal of H_2S is the electricity. The other term that contributes to the economic evaluation is the operating costs required for the material replacement. The costs sharing of biochar is divided into electricity (71.8%) and operating costs (23.3%), the remaining percentage is due to the material purchase and the disposal cost. The main contribution to the ashes is due to the operating work required for the sorbent replacement, due to the several changes needed. This solution, as reported elsewhere (Davide Papurello et al., 2016d) is not feasible. Biochar is comparable to some commercial carbons, such as RST3 and Carbox. R8G shows the lowest total costs, considering all the four contributions reported above. The other materials that follow R8G are reported in the following order: CKC, CKI, biochar and the other activated commercial carbons. Even if the performance of ZnO are considerable, the purchase cost of the material heavily weighs on the total cost that favors the choice of other materials.

Future works will be focused on the regeneration and activation studies of biochar, reducing the disposal and total cost.

6. Conclusions

The effectiveness of the adsorption process is mainly determined by the type of substance to be removed, even if in a real pilot plant this approach is almost prohibitive. It was decided to investigate on the removal performance of a sorbent material that comes from the waste chain treatment: biochar. This adsorbent material was tested in a real pilot plant and the outlet of the filter was monitored online with a PTR-MS instrument, for the first time. The performance achieved with this material are comparable with those achieved by reference commercial carbons, even if some most optimized and selective materials show better results.

The main economic terms that weighs on the biochar service life time is the electricity consumption followed by the costs required for the material replacement.

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