

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

Original

Real-time monitoring of removal of trace compounds with PTR-MS: Biochar experimental investigation / Papurello, Davide; Boschetti, Andrea; Silvestri, Silvia; Khomenko, Iuliia; Biasioli, Franco. - In: RENEWABLE ENERGY. - ISSN 0960-1481. - ELETTRONICO. - 125:(2018), pp. 344-355. [10.1016/j.renene.2018.02.122]

Availability:

This version is available at: 11583/2728435 since: 2019-03-15T08:42:26Z

Publisher:

Elsevier Ltd

Published

DOI:10.1016/j.renene.2018.02.122

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

Elsevier postprint/Author's Accepted Manuscript

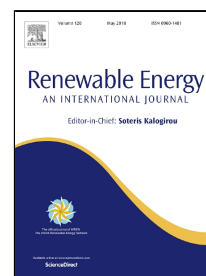
© 2018. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>. The final authenticated version is available online at:
<http://dx.doi.org/10.1016/j.renene.2018.02.122>

(Article begins on next page)

Accepted Manuscript

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

Davide Papurello, Andrea Boschetti, Silvia Silvestri, Iuliia Khomenko, Franco Biasioli



PII: S0960-1481(18)30274-X
DOI: 10.1016/j.renene.2018.02.122
Reference: RENE 9853
To appear in: *Renewable Energy*
Received Date: 24 July 2017
Revised Date: 25 January 2018
Accepted Date: 27 February 2018

Please cite this article as: Davide Papurello, Andrea Boschetti, Silvia Silvestri, Iuliia Khomenko, Franco Biasioli, Real-time monitoring of removal of trace compounds with PTR-MS: Biochar experimental investigation., *Renewable Energy* (2018), doi: 10.1016/j.renene.2018.02.122

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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

Davide Papurello^{a,b}, Andrea Boschetti^c, Silvia Silvestri^b, Iuliia Khomenko^{d,e}, 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 IMEM -Institute of Materials for Electronic and Magnetism - Italian National Research Council, Fondazione Bruno Kessler, via alla Cascata 56/C, Povo - 38123 Trento (TN).

^d Sensory quality unit, Department of Food quality and nutrition, Fondazione Edmund Mach, Via E. Mach, 1, 38010, San Michele a/A, Italy.

^e Institute for Ion Physics and Applied Physics, University of Innsbruck, Technikerstr. 25, Innsbruck, Austria.

*Corresponding author. Tel.: +393402351692. Email address: davide.papurello@polito.it

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 used as sorbent material. This material was selected to demonstrate the usefulness of recovered waste for the energy production purposes. Biochar withstands the removal of 2-butanone (158.8 mg/g), toluene (140.1 mg/g) and limonene (64 mg/g) better compared to sulfur (H_2S 1.05 mg/g) and siloxane (D3, 1.28 mg/g) compounds. Hydrogen sulfide was the most abundant sulfur compound with the average concentration about 24 ppm(v). The tested sorbent material was able to withstand the H_2S and siloxane concentration for almost 30 h with the biogas pilot plant conditions before to achieve the limit value for SOFC applications, 1 ppm(v) and 150 ppb(v) respectively. The performance achieved with this material are comparable to some commercial carbons, even if some more optimized and selective materials show better results especially for the removal of sulfur compounds.

Keywords: Adsorption, Volatile organic compounds removal, Biogas, Solid Oxide Fuel Cell , Carbon, Proton Transfer Reaction Mass Spectrometry.

24 **Nomenclature**

25 Cads. Adsorption capacity mg/m^3 ;

26 CHO, carbonyl and carboxyl compounds;

27 D3, hexamethylcyclotrisiloxane;

28 D4, octamethylcyclotetrasiloxane;

29 D5, decamethylcyclopentasiloxane;

30 EDS, Energy Dispersive X-ray Spectroscopy;

31 GHSV, Gas Hourly Space Velocity;

32 ICE, Internal Combustion Engine;

33 L2 MM, hexamethyldisiloxane;

34 MIEC, Mixed Ionic Electronic Conducting ceramic material;

35 MSW, Municipal Solid Waste;

36 OFMSW, Organic Fraction of Municipal Solid Waste;

37 OW, Organic Waste;

38 PTR-MS, Proton Transfer Reaction Mass Spectrometer;

39 PTR-Q-MS, Proton Transfer Reaction Quadrupole Mass Spectrometer;

40 SEM, Scanning Electron Microscopy;

41 SOFC, Solid Oxide Fuel Cell;

42 VOCs, Volatile Organic Compounds.

43

44

45

46 **1. Introduction**

The management of solid waste is a global issue due to population growth and problems related to environment and energy. Organic waste is a feedstock for energy production and could have an added value with advantages related to energy production and the reduction of pollutant emissions into air, soil and water. Biogas produced from this waste can be utilized 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 regarding efficiency and exploitability. Among electrochemical systems, solid oxide fuel cells (SOFC) currently receive much attention [1–11]. SOFCs present several advantages compared to mechanical competitors for electricity production (ICE, mTurbine, Rankine cycles, etc). Benefits 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. [12]. However, the main drawback is the low resistance to trace compounds [6,7,13–18]. Literature studies focus mainly on gas cleaning or SOFC material tolerability against these trace compounds [3,19–21].

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 [19,20,22]. In our previous work it was showed the temperature dependency on the removal performance of commercial carbons [21]. Another parameter that affects removal performance is the relative humidity content [21,23]. In fact, the water humidity content could have a positive or negative impact depending on the presence of basic active sites. Barelli et al., (2017) demonstrated that, for carbons activated with KOH and KI, the formation of water film around carbon pores favors H_2S molecules dissociation [23]. 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 downsides the sulfur removal. As reported in the literature, a relative humidity value above 50% lead the adsorption capacity to zero mg/g [21]. Finally, the multiple removals 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 laboratory results highlighted the strong decrease of removal performance with the simultaneous presence of more than one compound, i.e. H_2S [24]. All of these factors can be present at the same time in a real plant. An experimental pilot plant for gas cleaning with ashes was investigated as a more realistic case [25]. 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 successful. Results of the experiment 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 investigate utilization of biochar 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 [26,27]. The adsorption characteristics of biochar are a function of the raw material, the production process, and the temperature. Ahmad et al., (2012) showed the importance of temperature of the char production to increase its surface area and porosity [28]. Both, surface area and porosity are linked to the adsorption capacity of trace compounds [27]. To the best of our knowledge, this paper is the first attempt to monitor 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 biomass for biogas production. These wastes were 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 was made by concrete (16 m³) and it was sealed with resin. Before the waste loading, OFMSW was mixed with chipped wood, collected from the local municipality (San Michele a/A, TN Italy), at a volume ratio of 0.6 – 0.7 (wood to biomass) to achieve suitable biomass porosity. For a rapid start of the methane production the biomass was subjected to a four day preoxidation process, no air was sparged in the waste. Consequently, the initial lag phase was reduced, from an average of ten days to five days. The temperature increased up to 35 °C due to the aerobic digestion process, 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 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 CO₂ escaping into the atmosphere.

2.2. Sorbent material characterization and experimental settings

Biochar from the pyrolysis of wood, from local municipality (Civitella in Val di Chiana (Ar)) was produced by Gruppo RM Impianti srl. (Italy), in a 200 kW_e reactor at low temperature (150 °C) for 24 h. 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 Nm³/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 kW_e SOFC micro-CHP application [29].

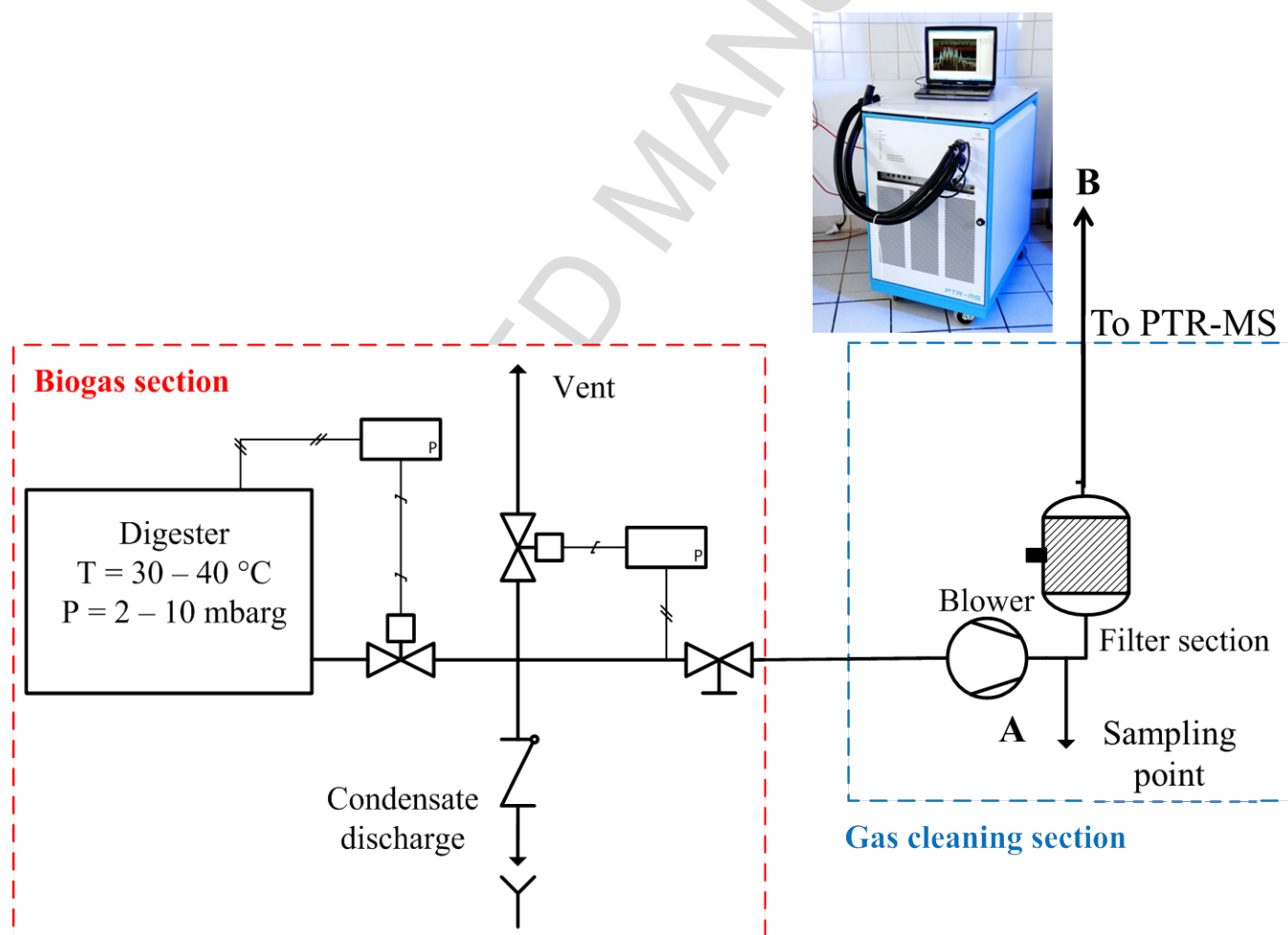


Figure 1 – Biogas to gas cleaning section – experimental set up for biochar testing

131 Adsorption isotherms for N₂ at 77 K were determined using a Quantachrome Autosorb 1 (Boynton
132 Beach, Florida, USA).

133 Elemental composition measurements were performed by scanning electron microscopy (SEM)
134 (FEI Inspect, Philips 525 M) coupled with EDS (SW9100 EDAX) analysis.

135 **2.3. Online monitoring technique – PTR-MS**

136 Trace compounds were monitored using a PTR-QMS 500 instrument (Ionicon Analytik GmbH,
137 Innsbruck, Austria) connected directly to the gas cleaning section (Figure 1). Biogas was sampled in
138 two points: before the filter (point (A)) and after the filter (point (B)). All the lines were made in
139 Teflon. This has been done to guarantee the trace compounds stability along the lines. Several
140 studies have investigated the suitability of different materials for VOC gas sample storage [30].
141 Pet'ka et al., (2000) found that tedlar and saran bags were two inappropriate material for storage
142 applications due to high levels of contaminant compounds emanating from the bag materials [31].
143 For Teflon material it was reported a compound losses over time, function of the trace compound
144 type [31]. Van Harreveld (2003) investigated nalophan bags and found that samples remained
145 relatively stable between 4 and 12 h after sampling. Concentration decreases after 30 h of storage to
146 about half of their initial levels. This was attributed to diffusion effects [32]. In our case, contrarily
147 to the common literature studies, VOCs analysis was performed in real time (B). Here, the
148 information losses related to the concentration diffusion are limited to the minimum. The
149 concentration from point (A) was monitored once a day, for at least one hour, to find the
150 breakthrough of clean gas. The clean biogas, point (B) was monitored continuously 23 h per day.
151 The concentrated sample (A) was diluted with nitrogen at a ratio of 1:10. This procedure is required
152 to maintain the instrument linearity, between 300 pptv and 10 ppm(v). PTR-QMS 500 is able to
153 detect compounds from 1 – 300 amu, with a resolution close to 1 amu, a response time of 100 ms
154 and a linearity range of 300 ppt(v) – 10 ppm(v) (Ionicon datasheet). Detail investigation on the
155 instrument settings was reported elsewhere [1,33]. The sample was directly injected into the drift

tube of the instrument via a heated PEEK line (110 °C). Table 2 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 2 – 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 ₃ O ⁺	Formaldehyde	[34]	[35,36]
34	H ₃ S ⁺	Hydrogen sulfide	[37,38]	[35,36,39]
41	C ₃ H ₅ ⁺	Alkyl fragment	[40,41]	[42]
45	C ₂ H ₅ O ⁺	Acetaldehyde	[34,43]	[35,44–46]
47	CH ₃ O ₂ ⁺	Formic acid	[43]	[42]
49	CH ₅ S ⁺	Methanethiol	[38]	[35,39,45]
55	C ₄ H ₇ ⁺	Butadiene	[40]	[42]
59	C ₃ H ₇ O ⁺	Acetone	[34]	[35,44,45]
61	C ₂ H ₅ O ₂ ⁺	Acetic acid	[34,47]	[35,44,45]
63	C ₂ H ₇ S ⁺	Dimethylsulfide (DMS)	[48]	[35,39]
67	C ₅ H ₇ ⁺	Cyclopentadiene	[49]	[50]
69	C ₄ H ₅ O ⁺	Isoprene	[48]	[35]
71	C ₅ H ₁₁ ⁺	Cyclopentane	[51]	[38]
73	C ₃ H ₅ O ₂ ⁺	Acrylic acid	[49]	[50]
75	C ₃ H ₇ O ₂ ⁺	Propionic acid/propanoates	[34,47]	[35,44,45]
77	C ₃ H ₉ S ⁺	Propanethiol	[38]	[52]
79	C ₆ H ₇ ⁺	Benzene	[48]	[35,44,45]
81	C ₆ H ₉ ⁺	Cyclohexadiene		[42]
83	C ₅ H ₇ O ⁺	Cyclopentenone		[50]
87	C ₅ H ₁₁ O ⁺	2-Pentanone/Pentanal	[34]	[35,44,45]
89	C ₄ H ₉ O ₂ ⁺	Butyric acid/butyrate	[34,47]	[35]
91	C ₄ H ₁₁ S ⁺	Butanethiol	[38]	[52]
93	C ₇ H ₉ ⁺	Toluene	[43,48]	[35,53]
101	C ₆ H ₁₃ O ⁺	2-Hexanone/hexanal	[34]	[44]
105	C ₈ H ₉ ⁺	Styrene	[48]	[35,44,45]
107	C ₈ H ₁₁ ⁺	Xylene	[48]	[35,44,45]
109	C ₇ H ₉ O ⁺	Benzyl alcohol	[49]	[50]

115	$C_7H_{15}O^+$	2-Heptanone/heptanal	[34]	[44]
119	$C_9H_{11}^+$	Methylstyrene	[51]	[50]
121	$C_9H_{13}^+$	Cumene	[43]	[36,44]
135	$C_{10}H_{15}^+$	p-Cymene	[48]	[35,36,44,45]
137	$C_{10}H_{17}^+$	Monoterpenes	[48]	[35,36,44,45]
143	$C_9H_{19}O^+$	2-Nonanone/nonanal	[34]	[36,44]
205	$C_{15}H_{25}^+$	Sesquiterpenes	[43,48]	[36,50]
223	$C_6H_{18}O_3Si_3H^+$	D3, hexamethylcyclotrisiloxane	[37]	[42]

3. Results and discussion

3.1. Biochar characterization

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 $75 \text{ m}^2/\text{g}$ (average value of 3 samples). This value, although lower than activated carbons (typically $1500 \text{ m}^2/\text{g}$), is significantly higher than ashes ($\sim 1 \text{ m}^2/\text{g}$) [25]. 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%. **Error! Reference source not found.** shows the FESEM images for the biochar sample.

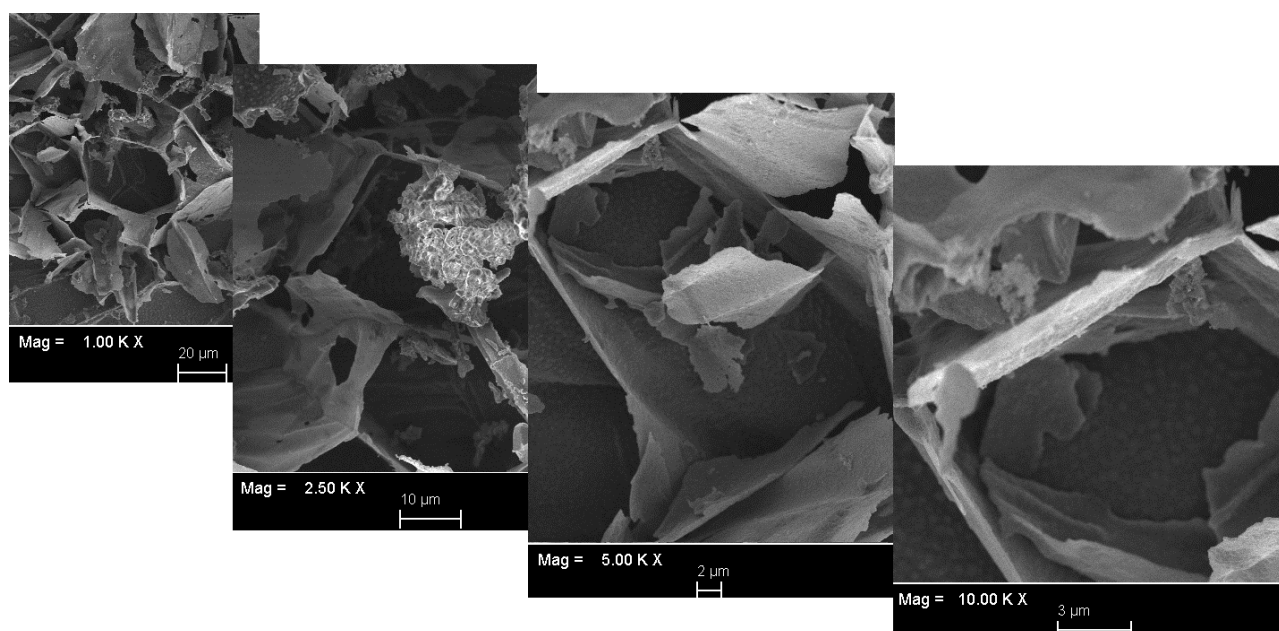


Figure 2 – FESEM biochar characterization

EDS results are reported in the following table:

Table 3 – 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) [54,55]. 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.

3.2. Biogas composition of trace compounds

Commonly, the biogas composition of trace compounds was monitored using a bag collection system, as reported from literature [3,19,20,22,24,25,38]. 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 [56,57]. 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 2). 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 when 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% with an average flow rate of 3 m³/h) with a low fraction of methane (min 5-6% with an average flow rate 0.01 m³/h), as reported in our previous studies [1,38]. The amount of CO₂-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 an average concentration of CH₄ around 60-65 %vol. with an average flow rate value of 0.5 m³/h. The average value and the standard deviation of trace compounds monitored along the digestion process are reported in Table 4. The variability between replicates is rather small and varies in the 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. The most important compounds detected for the biogas use in SOFCs, are mainly sulfurs and siloxanes. Sulfur compounds are important due to their concentration level and their deactivation power over the catalyst, while for siloxanes their importance is due to their

210 production of silica that obstructs anode active pores. As reported elsewhere, few ppb(v) of
211 siloxanes can irreversibly affect SOFC performance [58–62].

212 Siloxanes can be found in a non-perfect separate collection because they are included in many
213 industrial processes and consumer products [57] [63], such as soaps and cosmetics. Siloxanes were
214 tentatively identified in Papurello et al., (2016) in a biogas produced from dry anaerobic digestion
215 of OFMWS [25]. The release of organosilicon compounds from the biomass to the biogas, in
216 general, depends on the temperature, pressure and digestion process. At present, there is no standard
217 method for the analysis of volatile siloxanes in a gaseous mixture. In this batch the only siloxanes
218 detected is D3 (m/z 223).

219 Sulfur compounds, presented mainly by H_2S depend on the aerobic to anaerobic transition phase
220 [38]. H_2S represents 76% of the total sulfur compounds detected. The remaining contribution
221 derives from butanethiol (m/z 91) (21%), dimethylsulfide (m/z 63) (2%) and metanethiol (m/z 49)
222 (1%). These thiols are mainly produced at the end of the digestion process. As reported in other
223 testing campaigns the production of sulfur compounds occur mainly at the beginning and at the end
224 of the digestion process [1,3,38].

225 Terpenes originate from the inherited organic matter, fruits and vegetables contained in the
226 OFMSW and they are released into the gas matrix. The main terpene compound detected is p-
227 cymene (m/z 135) with 48%, followed by limonene (m/z 137) with 41%. The remaining
228 contribution derives from sesquiterpene (m/z 205) (6%) and isoprene (m/z 69) (5%). The high
229 levels of p-cymene in the biogas suggests the occurrence of d-limonene transformation by the
230 anaerobic bacteria, as reported by [45].

231 Aromatic compounds can be detected in organic material decomposition and from a non-biogenic
232 origin [45]. In fact, Eitzer (1995), reported during unsorted MSW-composting, the high presence of
233 terpenes, but also the high presence of aromatic hydrocarbons [64]. In another study, Komilis et al.,

234 (2004) indicated that aromatic hydrocarbons were emitted even if only food waste were composted
235 [65]. In the present study aromatic hydrocarbons detected were toluene (m/z 93) (80%),
236 cyclohexadiene (m/z 81) (14%) followed by cyclopentane (m/z 71) and propyne (m/z 41).

237 Carbonyl and carboxyl compounds can be detected in the biogas due to the decomposition of
238 OFMSW. Two different mechanistic approaches could be adopted in order to explain the release of
239 carbonyl compounds: (a) direct oxidation of alcohols in the presence of oxygen – formation of 2-
240 ketones during the acetogenesis and (b) formation of 2-ketones through methanogens induced
241 oxidative reactions under alkaline conditions [38,44]. Formic (m/z 47), acetic (m/z 61), propionic
242 (m/z 75), and butyric (m/z 89) acid are detected along the anaerobic digestion process. The
243 emissions of carboxylic acids are strongly dependent on pH. At the beginning of the digestion pH is
244 neutral to basic, and at the end of digestion pH is alkaline. This is confirmed by the increase of CO_2
245 production. Carboxylic acids formation is generally related to the inherited organic matter. In fact, it
246 derives from the lipids breakdown and also from acidogenic bacteria action on the carbohydrate
247 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 CH ₂ O		34 H ₂ S		41 C ₃ H ₄		45 C ₂ H ₄ O		47 C ₂ H ₆ O		49 CH ₄ S		55 C ₄ H 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 C ₃ H ₆ O		61 CH ₃ COOH		63 C ₂ H ₆ S		67 C ₅ H ₆		69 C ₅ H ₈		71 C ₅ H ₁₀		73 C ₄ H ₈ O	
	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 C ₃ H ₆ O ₂		77 C ₃ H ₈ S		79 C ₆ H ₆		81 C ₆ H ₈		83 C ₅ H ₆ O		87 C ₅ H ₁₀ O		89 C ₄ H ₈ O 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

251

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 C ₄ H ₁₀ S		93 C ₇ H ₈		101 C ₆ H ₁₂ O		105 C ₈ H ₈		107 C ₈ H ₁₀		109 C ₇ H ₈ O		115 C ₇ H 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	

252

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

Time (h)	119 C ₉ H ₁₀		121 C ₉ H ₁₂		135 C ₁₀ H ₁₄		137 C ₁₀ H ₁₆		143 C ₉ H ₁₈ O		205 C ₁₅ H ₂₄		223 C ₆ H ₁₈ O ₃ Si ₃	
	methylstyren e	std.dev.	cumen e	std.dev.	p- cymen e	std.dev.	limonen e	std.dev.	2- nonanon e	std.dev.	sesquiterpen e	std.dev.	hexamethyle clotrisiloxane	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	

253

254

3.3. 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 lifetime for an adsorbent. The adsorption capacity was evaluated considering the following equation, [66]:

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

Where:

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

MW, molecular weight (H₂S 34 g/mol);

C_{in}, inlet H₂S concentration (ppm(v));

t₁, breakthrough time when the outlet H₂S concentration is 1 ppm(v) (h);

t₀, breakthrough time at the last detection of 0 ppm(v) (h);

V_m, molar volume (24.414 NL/mol);

m, mass of adsorbent material (g).

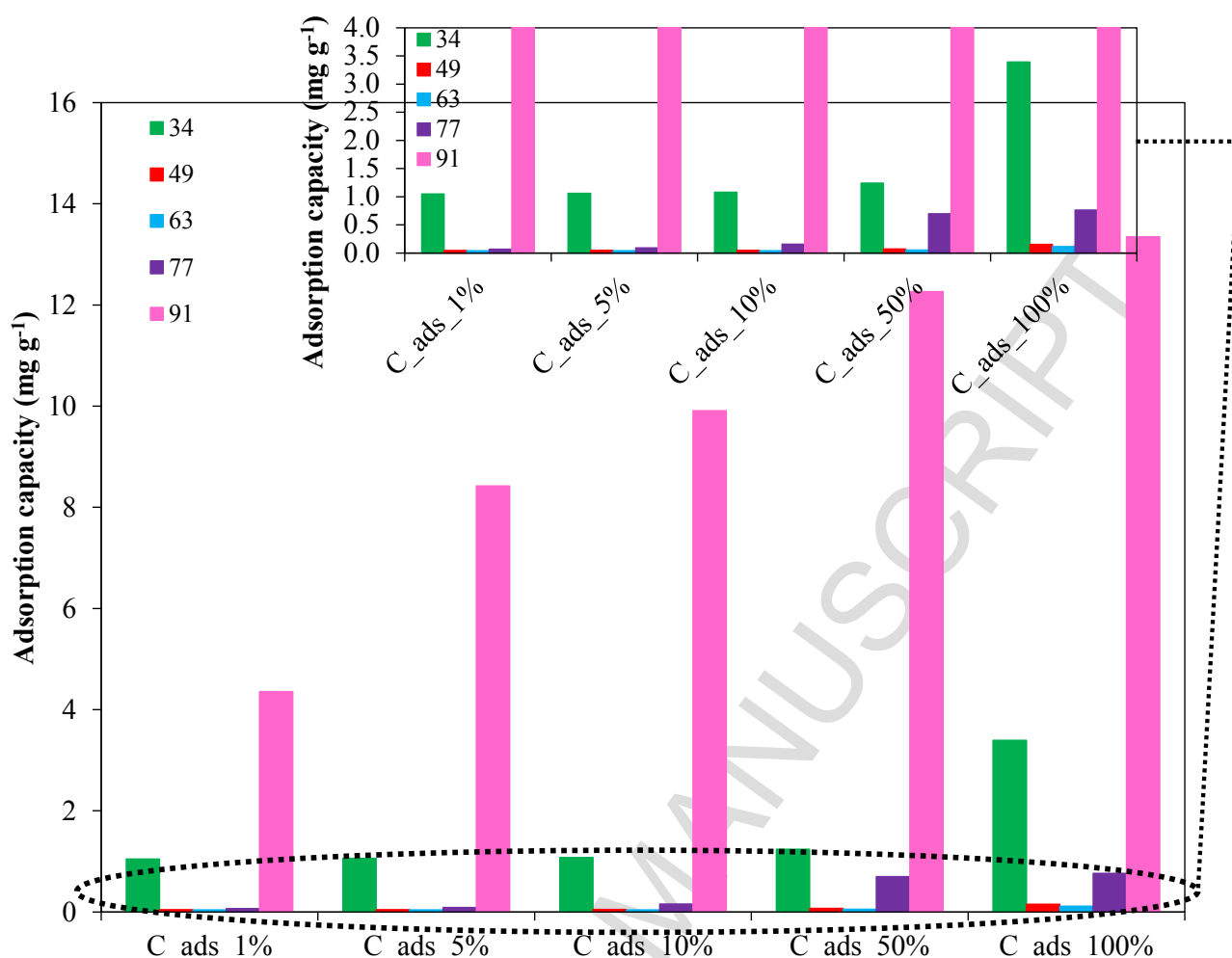


Figure 3 – Adsorption capacity for sulfur compounds

The adsorption capacity for sulfur compounds evaluated with equation 1, is reported in Table 5 and in Figure 3. The initial breakthrough time for the SOFC feeding system and to plan a maintenance operation process for the sorbent replacement is crucial. In fact, as reported in literature, the tolerable levels of trace compounds contained in the biogas fuel are low [2,3,60,67]. The adsorption capacity achieved to remove H₂S was about 1.05 mg/g when it was achieved 1% of the starting H₂S 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 H₂S, 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 H₂S removal. The second sulfur compound in terms of abundance was butanethiol. Biochar showed an adsorption capacity value around 4.4 mg/g at the initial breakthrough up to 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, [21] adsorption capacity increases with the pollutant concentration. This is due to the increase of driving force 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 activated sorbent materials. In fact, H₂S 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). At the beginning biochar showed an adsorption capacity of 1.28 mg/g at 1% of the starting D3 concentration. With time it 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,

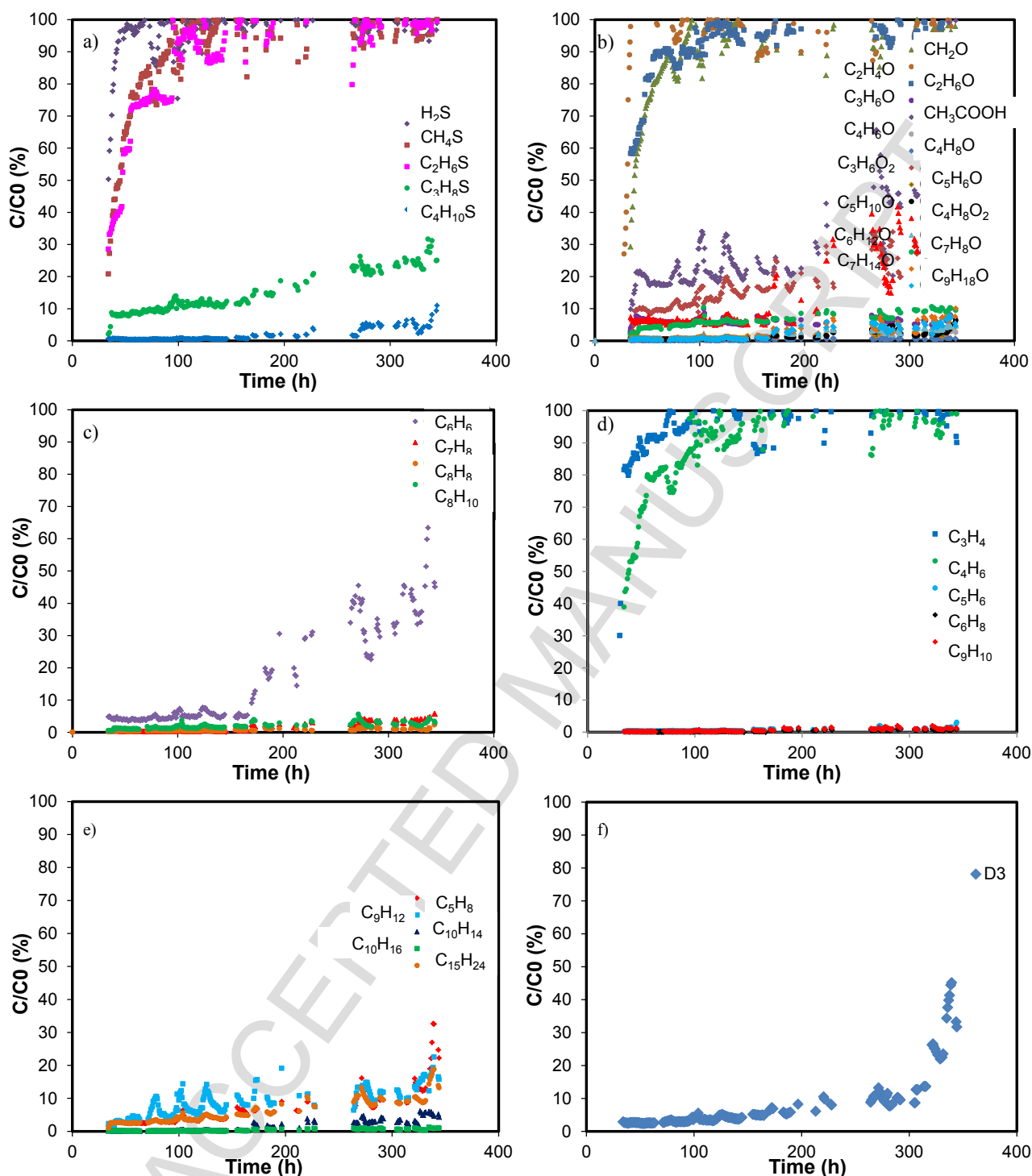
306 styrene and xylene showed a concentration below 10 ppb(v). The adsorption capacity of toluene, at
307 the starting condition showed a value above 140 mg/g up to achieve, rapidly the maximum capacity
308 at the saturation conditions (40% by weight of the carbon), see Figure 4 and Table 5.

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

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

	31	34	41	45	47	49	55	59	61	63	67	
Cads (mg/g)	CH₂O formalde hyde	H₂S hydrogen sulfide	C₃H₄ propyne	C₂H₄O acetaldehyde	C₂H₆O ethanol	CH₄S methanet hiol	C₄H₆ butadiene	C₃H₆O acetone	CH₃COOH acetic acid	C₂H₆S dimethylsu lfide	C₅H₆ 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	
	69	71	73	75	77	79	81	83	87	89	91	93
Cads (mg/g)	C₅H₈ isoprene	C₄H₆O crotonalde hyde	C₄H₈O 2- butanone	C₃H₆O₂ propionic acid	C₃H₈S propanethiol	C₆H₆ benzene	C₆H₈ ciclohexad iene	C₅H₆O methylfu ran	C₅H₁₀O 2pentanone	C₄H₈O₂ butyric acid	C₄H₁₀S butanethiol	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
	101	105	107	109	115	119	121	135	137	143	205	223
Cads (mg/g)	C₆H₁₂O 2- hexanone	C₈H₈ styrene	C₈H₁₀ xylene	C₇H₈O benzilic acid	C₇H₁₄O 2-heptanone	C₉H₁₀ methylsty rene	C₉H₁₂ cumene	C₁₀H₁₄ p- cymene	C₁₀H₁₆ limonene	C₉H₁₈O 2- nonanone	C₁₅H₂₄ sesquiterpene	C₆H₁₈O₃Si 3 hexamethy lcyclotrisil oxane
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

316



317

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

320 The contemporary presence of trace compounds in the fuel mixture for SOFC applications were
 321 monitored online with a DIMS technique. The main monitored compounds 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 most abundant sulfur compound with the average concentration 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) [3]. This concentration is the tolerable limit for SOFC applications able to guarantee a reversible behavior rather than a dramatic and irreversible loss of performance [6]. 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. Siloxanes are the other important trace compounds that strongly affect the SOFC performance. 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 [6,8]. 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	cyclohexadiene	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	$C_5H_{10}O$	2-pentanone	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	benzoic 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

337

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

340 The time required to achieve 1% of the starting concentration is reported in Table 6. For aromatic
341 compounds these times are the following: benzene with 34.8 h, xylene with 46.6 h, toluene with
342 161.4 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 H₂S 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 sulfur and siloxane 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 paid to these compounds in view of the long-term operation of SOFC co-generators.

4. Conclusions

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 almost comparable with those achieved by reference commercial carbons, even if some most optimized and selective materials show better results. Biochar withstands the removal of 2-butanone, toluene and limonene better compared to sulfur and siloxane compounds. For these reasons to guarantee the long term operation of SOFC systems, biochar sorbents should be placed in a lead and lag configurations systems of reactors.

Acknowledgments

This research is part of the BWS project (Biowaste for SOFCs) carried out with Fondazione Edmund Mach and SOLIDpower SpA. The project is funded by the contribution of Fondazione Caritro (TN). This research is also part of the DEMOSOFC project (European project Grant agreement no: 671470).

387 References

- 388 [1] D. Papurello, A. Lanzini, L. Tognana, S. Silvestri, M. Santarelli, Waste to energy:
389 Exploitation of biogas from organic waste in a 500 W solid oxide fuel cell (SOFC) stack,
390 Energy. 85 (2015) 145–158. doi:10.1016/j.energy.2015.03.093.
- 391 [2] D. Papurello, R. Borchellini, P. Bareschino, V. Chiodo, S. Freni, A. Lanzini, F. Pepe, G.A.
392 Ortigoza, M. Santarelli, Performance of a Solid Oxide Fuel Cell short-stack with biogas
393 feeding, Appl. Energy. 125 (2014) 254–263.
- 394 [3] D. Papurello, A. Lanzini, P. Leone, M. Santarelli, S. Silvestri, Biogas from the organic
395 fraction of municipal solid waste: Dealing with contaminants for a solid oxide fuel cell
396 energy generator, Waste Manag. 34 (2014) 2047–2056.
- 397 [4] Y. Shiratori, T. Ijichi, T. Oshima, K. Sasaki, Internal reforming SOFC running on biogas, Int.
398 J. Hydrogen Energy. 35 (2010) 7905–7912. doi:10.1016/j.ijhydene.2010.05.064.
- 399 [5] J. Van Herle, Y. Membrez, O. Bucheli, Biogas as a fuel source for SOFC co-generators, J.
400 Power Sources. 127 (2004) 300–312. doi:10.1016/j.jpowsour.2003.09.027.
- 401 [6] D. Papurello, A. Lanzini, D. Drago, P. Leone, M. Santarelli, Limiting factors for planar solid
402 oxide fuel cells under different trace compound concentrations, Energy. 95 (2016) 67–78.
403 doi:10.1016/j.energy.2015.11.070.
- 404 [7] D. Papurello, A. Lanzini, S. Fiorilli, F. Smeacetto, R. Singh, M. Santarelli, Sulfur poisoning
405 in Ni-anode solid oxide fuel cells (SOFCs): Deactivation in single cells and a stack, Chem.
406 Eng. J. 283 (2016) 1224–1233. doi:10.1016/j.cej.2015.08.091.
- 407 [8] H. Madi, A. Lanzini, S. Diethelm, D. Papurello, J. Van herle, M. Lualdi, J. Gutzon Larsen,
408 M. Santarelli, Solid oxide fuel cell anode degradation by the effect of siloxanes, J. Power
409 Sources. 279 (2015) 460–471. doi:10.1016/j.jpowsour.2015.01.053.

- 410 [9] V. Chiodo, A. Galvagno, A. Lanzini, D. Papurello, F. Urbani, M. Santarelli, S. Freni, Biogas
411 reforming process investigation for SOFC application, *Energy Convers. Manag.* 98 (2015)
412 252–258. doi:10.1016/j.enconman.2015.03.113.
- 413 [10] D. Papurello, D. Menichini, A. Lanzini, Distributed relaxation times technique for the
414 determination of fuel cell losses with an equivalent circuit model to identify physicochemical
415 processes, *Electrochim. Acta.* 258 (2017) 98–109. doi:10.1016/j.electacta.2017.10.052.
- 416 [11] D. Papurello, S. Silvestri, L. Tomasi, I. Belcari, F. Biasioli, M. Santarelli, Biowaste for
417 SOFCs, *Energy Procedia.* 101 (2016) 424–431. doi:10.1016/j.egypro.2016.11.054.
- 418 [12] M.M. Maghanki, B. Ghobadian, G. Najafi, R.J. Galogah, Micro combined heat and power
419 (MCHP) technologies and applications, *Renew. Sustain. Energy Rev.* 28 (2013) 510–524.
420 doi:10.1016/j.rser.2013.07.053.
- 421 [13] M. Turco, A. Ausiello, L. Micoli, The Effect of Biogas Impurities on SOFC, in: *Treat.*
422 *Biogas Feed. High Temp. Fuel Cells Remov. Harmful Compd. by Adsorpt. Process.*,
423 Springer International Publishing, Cham, 2016: pp. 137–149. doi:10.1007/978-3-319-03215-
424 3_6.
- 425 [14] A.L. Facci, V. Cigolotti, E. Jannelli, S. Ubertini, Technical and economic assessment of a
426 SOFC-based energy system for combined cooling, heating and power, *Appl. Energy.* (2016).
427 doi:10.1016/j.apenergy.2016.06.105.
- 428 [15] R. Torii, Y. Tachikawa, K. Sasaki, K. Ito, Anode gas recirculation for improving the
429 performance and cost of a 5-kW solid oxide fuel cell system, *J. Power Sources.* 325 (2016)
430 229–237. doi:10.1016/j.jpowsour.2016.06.045.
- 431 [16] L. Blum, L.G.J. de Haart, J. Malzbender, N. Margaritis, N.H. Menzler, Anode-Supported
432 Solid Oxide Fuel Cell Achieves 70 000 Hours of Continuous Operation, *Energy Technol.* 4

- 433 (2016) 939–942. doi:10.1002/ente.201600114.
- 434 [17] D. Papurello, A. Lanzini, P. Leone, M. Santarelli, The effect of heavy tars (toluene and
435 naphthalene) on the electrochemical performance of an anode-supported SOFC running on
436 bio-syngas, *Renew. Energy*. 99 (2016) 747–753. doi:10.1016/j.renene.2016.07.029.
- 437 [18] H. Madi, A. Lanzini, D. Papurello, S. Diethelm, C. Ludwig, M. Santarelli, J. Van herle, Solid
438 oxide fuel cell anode degradation by the effect of hydrogen chloride in stack and single cell
439 environments, *J. Power Sources*. 326 (2016) 349–356. doi:10.1016/j.jpowsour.2016.07.003.
- 440 [19] D. Papurello, L. Tognana, A. Lanzini, F. Smeacetto, M. Santarelli, I. Belcari, S. Silvestri, F.
441 Biasioli, Proton transfer reaction mass spectrometry technique for the monitoring of volatile
442 sulfur compounds in a fuel cell quality clean-up system, *Fuel Process. Technol.* 130 (2015)
443 136–146. doi:10.1016/j.fuproc.2014.09.041.
- 444 [20] D. Papurello, E. Schuhfried, A. Lanzini, A. Romano, L. Cappellin, T.D. Märk, S. Silvestri,
445 M. Santarelli, F. Biasioli, Proton transfer reaction-mass spectrometry as a rapid inline tool for
446 filter efficiency of activated charcoal in support of the development of Solid Oxide Fuel Cells
447 fueled with biogas, *Fuel Process. Technol.* 130 (2015) 78–86.
448 doi:10.1016/j.fuproc.2014.09.042.
- 449 [21] D. Papurello, L. Tomasi, S. Silvestri, M. Santarelli, Evaluation of the Wheeler-Jonas
450 parameters for biogas trace compounds removal with activated carbons, *Fuel Process.*
451 *Technol.* 152 (2016) 93–101. doi:10.1016/j.fuproc.2016.06.006.
- 452 [22] D. Papurello, A. Lanzini, E. Schufried, M. Santarelli, S. Silvestri, Proton Transfer Reaction-
453 Mass Spectrometry (PTR-MS) as a rapid online tool for biogas VOCs monitoring in support
454 of the development of Solid Oxide Fuel Cells (SOFCs), 6th Int. PTR-MS Conf. 130 (2013)
455 144–150. doi:10.1016/j.fuproc.2014.09.042.

- [23] L. Barelli, G. Bidini, N. De Arespacochaga, P. Laura, E. Sisani, Biogas use in high temperature fuel cells : Enhancement of KOH-KI activated carbon performance toward H₂S removal, 2 (2017). doi:10.1016/j.ijhydene.2017.02.021.
- [24] D. Papurello, E. Schuhfried, A. Lanzini, A. Romano, L. Cappellin, T.D. Märk, S. Silvestri, F. Biasioli, Influence of co-vapors on biogas filtration for fuel cells monitored with PTR-MS (Proton Transfer Reaction-Mass Spectrometry), Fuel Process. Technol. 118 (2014) 133–140. doi:10.1016/j.fuproc.2013.08.011.
- [25] D. Papurello, L. Tomasi, S. Silvestri, I. Belcari, M. Santarelli, F. Smeacetto, F. Biasioli, Biogas trace compound removal with ashes using proton transfer reaction time-of-flight mass spectrometry as innovative detection tool, Fuel Process. Technol. 145 (2016) 62–75. doi:10.1016/j.fuproc.2016.01.028.
- [26] G. Shang, G. Shen, L. Liu, Q. Chen, Z. Xu, Bioresource Technology Kinetics and mechanisms of hydrogen sulfide adsorption by biochars, Bioresour. Technol. 133 (2013) 495–499. doi:10.1016/j.biortech.2013.01.114.
- [27] G. Shang, Q. Li, L. Liu, P. Chen, X. Huang, Adsorption of hydrogen sulfide by biochars derived from pyrolysis of different agricultural / forestry wastes, J. Air Waste Manage. Assoc. 66 (2016) 8–16. doi:10.1080/10962247.2015.1094429.
- [28] M. Ahmad, S. Soo, X. Dou, D. Mohan, J. Sung, J.E. Yang, Y. Sik, Bioresource Technology Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water, Bioresour. Technol. 118 (2012) 536–544. doi:10.1016/j.biortech.2012.05.042.
- [29] L. Barelli, G. Bidini, U. Desideri, G. Discepoli, E. Sisani, Dimethyl sul fi de adsorption from natural gas for solid oxide fuel cell applications, Fuel Process. Technol. 140 (2015) 21–31. doi:10.1016/j.fuproc.2015.08.012.

- 480 [30] J. Beauchamp, J. Herbig, R. Gutmann, A. Hansel, On the use of Tedlar® bags for breath-gas
481 sampling and analysis., *J. Breath Res.* 2 (2008) 46001. doi:10.1088/1752-7155/2/4/046001.
- 482 [31] J. Pet'ka, P. Étievant, G. Callement, Suitability of different plastic materials for head or nose
483 spaces short term storage, *Analisis.* 28 (2000) 330–335. doi:10.1051/analisis:2000123.
- 484 [32] A.P. van Harreveld, Odor concentration decay and stability in gas sampling bags., *J. Air*
485 *Waste Manag. Assoc.* 53 (2003) 51–60.
- 486 [33] A. Boschetti, F. Biasioli, M. Van Opbergen, C. Warneke, A. Jordan, R. Holzinger, P.
487 Prazeller, T. Karl, A. Hansel, W. Lindinger, S. Iannotta, PTR-MS real time monitoring of the
488 emission of volatile organic compounds during postharvest aging of berryfruit, *Postharvest*
489 *Biol. Technol.* 17 (1999) 143–151. doi:10.1016/S0925-5214(99)00052-6.
- 490 [34] K. Buhr, S. Van Ruth, C. Delahunty, Analysis of volatile flavour compounds by Proton
491 Transfer Reaction-Mass Spectrometry: Fragmentation patterns and discrimination between
492 isobaric and isomeric compounds, *Int. J. Mass Spectrom.* 221 (2002) 1–7.
493 doi:10.1016/S1387-3806(02)00896-5.
- 494 [35] X. Font, A. Artola, A. Sánchez, Detection, composition and treatment of volatile organic
495 compounds from waste treatment plants, *Sensors.* 11 (2011) 4043–4059.
496 doi:10.3390/s110404043.
- 497 [36] J. Mata-Alvarez, S. Macé, P. Llabrés, Anaerobic digestion of organic solid wastes. An
498 overview of research achievements and perspectives, *Bioresour. Technol.* 74 (2000).
- 499 [37] W. Singer, J. Herbig, R. Gutmann, K. Winkler, I. Kohl, A. Hansel, Applications of PTR-MS
500 in Medicine and Biotechnology, *Life Sci. Solut. Am. Lab.* (2011) 2–5.
- 501 [38] D. Papurello, C. Soukoulis, E. Schuhfried, L. Cappellin, F. Gasperi, S. Silvestri, M.
502 Santarelli, F. Biasioli, Monitoring of volatile compound emissions during dry anaerobic

digestion of the Organic Fraction of Municipal Solid Waste by Proton Transfer Reaction
Time-of-Flight Mass Spectrometry, in: *Bioresour. Technol.*, 2012: pp. 254–265.

[39] B.P. Lomans, C. Van Der Drift, A. Pol, H.J.M. Op Den Camp, Cellular and Molecular Life
Sciences Microbial cycling of volatile organic sulfur compounds, *Cell. Mol. Life Sci.* 59
(2002) 575–588.

[40] W.B. Knighton, S.C. Herndon, J.F. Franklin, E.C. Wood, J. Wormhoudt, W. Brooks, E.C.
Fortner, D.T. Allen, Direct measurement of volatile organic compound emissions from
industrial flares using real-time online techniques: Proton transfer reaction mass spectrometry
and tunable infrared laser differential absorption spectroscopy, *Ind. Eng. Chem. Res.* 51
(2012) 12674–12684. doi:10.1021/ie202695v.

[41] K. Morozova, A. Romano, F. Lonardi, R. Ferrarini, F. Biasioli, M. Scampicchio,
Microcalorimetric monitoring of grape withering, *Thermochim. Acta.* 630 (2016) 31–36.
doi:10.1016/j.tca.2016.01.011.

[42] D.D. Papadimas, S. Ahmed, R. Kumar, Fuel quality issues with biogas energy - An economic
analysis for a stationary fuel cell system, *Energy.* 44 (2012) 257–277.
doi:10.1016/j.energy.2012.06.031.

[43] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky,
P. Sulzer, T.D. Märk, A high resolution and high sensitivity proton-transfer-reaction time-of-
flight mass spectrometer (PTR-TOF-MS), *Int. J. Mass Spectrom.* 286 (2009) 122–128.
doi:10.1016/j.ijms.2009.07.005.

[44] B. Scaglia, V. Orzi, a. Artola, X. Font, E. Davoli, a. Sanchez, F. Adani, Odours and volatile
organic compounds emitted from municipal solid waste at different stage of decomposition
and relationship with biological stability, *Bioresour. Technol.* 102 (2011) 4638–4645.
doi:10.1016/j.biortech.2011.01.016.

- [45] V. Orzi, E. Cadena, G.D. Imporzano, A. Artola, E. Davoli, M. Crivelli, F. Adani, Bioresource Technology Potential odour emission measurement in organic fraction of municipal solid waste during anaerobic digestion : Relationship with process and biological stability parameters, *Bioresour. Technol.* 101 (2010) 7330–7337. doi:10.1016/j.biortech.2010.04.098.
- [46] X. Wang, T. Wu, Release of isoprene and monoterpenes during the aerobic decomposition of orange wastes from laboratory incubation experiments., *Environ. Sci. Technol.* 42 (2008) 3265–3270.
- [47] E. Aprea, F. Biasioli, T.D. Märk, F. Gasperi, PTR-MS study of esters in water and water/ethanol solutions: Fragmentation patterns and partition coefficients, *Int. J. Mass Spectrom.* 262 (2007) 114–121. doi:10.1016/j.ijms.2006.10.016.
- [48] F. Biasioli, C. Yeretizian, T.D. Märk, J. Dewulf, H. Van Langenhove, Direct-injection mass spectrometry adds the time dimension to (B)VOC analysis, *TrAC - Trends Anal. Chem.* 30 (2011) 1003–1017. doi:10.1016/j.trac.2011.04.005.
- [49] F. Brilli, B. Gioli, P. Ciccioli, D. Zona, F. Loreto, I. a Janssens, R. Ceulemans, Proton Transfer Reaction Time-of-Flight Mass Spectrometric (PTR-TOF- MS) determination of volatile organic compounds (VOCs) emitted from a biomass fi re developed under stable nocturnal conditions, *Atmos. Environ.* 97 (2014) 54–67. doi:10.1016/j.atmosenv.2014.08.007.
- [50] A. Demirbas, Products from Lignocellulosic Materials via Degradation Processes, *Energy Sources, Part A Recover. Util. Environ. Eff.* 30 (2007) 27–37. doi:10.1080/00908310600626705.
- [51] B. Yuan, W.W. Hu, M. Shao, M. Wang, W.T. Chen, S.H. Lu, L.M. Zeng, M. Hu, VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China,

- 551 Atmos. Chem. Phys. 13 (2013) 8815–8832. doi:10.5194/acp-13-8815-2013.
- 552 [52] A. Vairavamurthy, K. Mopper, Geochemical formation of organosulphur compounds (thiols)
553 by addition of H₂S to sedimentary organic matter, Nature. 329 (1987) 623–625.
554 <http://dx.doi.org/10.1038/329623a0>.
- 555 [53] B.F. Staley, F. Xu, S.J. Cowie, M.A. Barlaz, G.R. Hater, Release of trace organic compounds
556 during the decomposition of municipal solid waste components, Environ. Sci. Technol. 40
557 (2006) 5984–5991. doi:10.1021/es060786m.
- 558 [54] F. Tepper, Alkali metal, Chemical element, Encycl. Br. Online. (n.d.).
559 <http://www.britannica.com/science/alkali-metal> (accessed September 7, 2017).
- 560 [55] S.C. Richardson J., Bjorheden R., Hakkala P., Lowe AT., Bioenergy from sustainable
561 forestry - guiding principles and practice, Kluwer academic publisher, New York, Boston,
562 Dordrecht, London, Moscow, 2002.
- 563 [56] S. Beghi, J.-M. Guillot, Use of poly(ethylene terephthalate) film bag to sample and remove
564 humidity from atmosphere containing volatile organic compounds., J. Chromatogr. A. 1183
565 (2008) 1–5. doi:10.1016/j.chroma.2007.12.051.
- 566 [57] M. Arnold, Reduction and monitoring of biogas trace compounds, 2009.
- 567 [58] K. Haga, S. Adachi, Y. Shiratori, K. Itoh, K. Sasaki, Poisoning of SOFC anodes by various
568 fuel impurities, Solid State Ionics. 179 (2008) 1427–1431. doi:10.1016/j.ssi.2008.02.062.
- 569 [59] D. Papurello, C. Iafrate, A. Lanzini, M. Santarelli, Trace compounds impact on SOFC
570 performance : Experimental and modelling approach, Appl. Energy. (2017) 0–1.
571 doi:10.1016/j.apenergy.2017.09.090.
- 572 [60] K. Sasaki, K. Haga, T. Yoshizumi, D. Minematsu, E. Yuki, R. Liu, C. Uryu, T. Oshima, T.
573 Ogura, Y. Shiratori, K. Ito, M. Koyama, K. Yokomoto, Chemical durability of Solid Oxide

- 574 Fuel Cells: Influence of impurities on long-term performance, *J. Power Sources*. 196 (2011)
575 9130–9140. doi:10.1016/j.jpowsour.2010.09.122.
- 576 [61] N. de Arespacochaga, C. Valderrama, C. Mesa, L. Bouchy, J.L. Cortina, Biogas deep clean-
577 up based on adsorption technologies for Solid Oxide Fuel Cell applications, *Chem. Eng. J.*
578 255 (2014) 593–603. doi:10.1016/j.cej.2014.06.072.
- 579 [62] D. Papurello, A. Lanzini, SOFC single cells fed by biogas : Experimental tests with trace
580 contaminants, *Waste Manag.* (2017). doi:10.1016/j.wasman.2017.11.030.
- 581 [63] S. Rasi, J. Läntelä, J. Rintala, Trace compounds affecting biogas energy utilisation - A
582 review, *Energy Convers. Manag.* 52 (2011) 3369–3375.
583 doi:10.1016/j.enconman.2011.07.005.
- 584 [64] B.D. Eitzer, Emissions of volatile organic chemicals from municipal solid waste composting
585 facilities., *Environ. Sci. Technol.* 29 (1995) 896–902.
- 586 [65] D.P. Komilis, R.K. Ham, J.K. Park, Emission of volatile organic compounds during
587 composting of municipal solid wastes., *Water Res.* 38 (2004) 1707–1714.
588 doi:10.1016/j.watres.2003.12.039.
- 589 [66] E. Sisani, G. Cinti, G. Discepoli, D. PENCHINI, U. Desideri, F. Marmottini, Adsorptive
590 removal of H₂S in biogas conditions for high temperature fuel cell systems, *Int. J. Hydrogen*
591 *Energy*. 39 (2014) 21753–21766. doi:10.1016/j.ijhydene.2014.07.173.
- 592 [67] A. Hagen, J.F.B. Rasmussen, K. Thydén, Durability of solid oxide fuel cells using sulfur
593 containing fuels, *J. Power Sources*. 196 (2011) 7271–7276.
594 doi:10.1016/j.jpowsour.2011.02.053.

595

Highlights

- VOCs were monitored online with PTR-Q-MS and H₂S and D₃ identified.
- Biochar withstand the H₂S and siloxane concentration for almost 30 h.
- Biochar performance are comparable to some commercial carbons.