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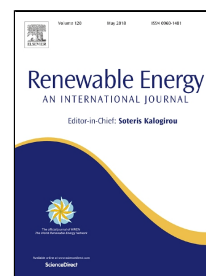
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Real-time monitoring of removal of trace compounds with PTR-MS: Biochar experimental investigation.

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1 Abstract

2 The removal of trace compounds contained in a biogas from the dry anaerobic digestion of organic
3 waste was accomplished. The resulting data were monitored online with a direct injection mass
4 spectrometry technique. Biochar from the pyrolysis of recovered wood waste was used as sorbent
5 material. This material was selected to demonstrate the usefulness of recovered waste for the energy
6 production purposes. Biochar withstands the removal of 2-butanone (158.8 mg/g), toluene (140.1
7 mg/g) and limonene (64 mg/g) better compared to sulfur (H_2S 1.05 mg/g) and siloxane (D3, 1.28
8 mg/g) compounds. Hydrogen sulfide was the most abundant sulfur compound with the average
9 concentration about 24 ppm(v). The tested sorbent material was able to withstand the H_2S and
10 siloxane concentration for almost 30 h with the biogas pilot plant conditions before to achieve the
11 limit value for SOFC applications, 1 ppm(v) and 150 ppb(v) respectively. The performance
12 achieved with this material are comparable to some commercial carbons, even if some more
13 optimized and selective materials show better results especially for the removal of sulfur
14 compounds.

15

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

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24 **Nomenclature**

25 Cads. Adsorption capacity mg/m³;

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.

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46 **1. Introduction**

47 The management of solid waste is a global issue due to population growth and problems related to
48 environment and energy. Organic waste is a feedstock for energy production and could have an
49 added value with advantages related to energy production and the reduction of pollutant emissions
50 into air, soil and water. Biogas produced from this waste can be utilized in several energy
51 generators, usually using a mechanical or an electrochemical approach to generate clean energy.
52 Carnot cycle is the key limitation of this approach regarding efficiency and exploitability. Among
53 electrochemical systems, solid oxide fuel cells (SOFC) currently receive much attention [1–11].
54 SOFCs present several advantages compared to mechanical competitors for electricity production
55 (ICE, mTurbine, Rankine cycles, etc). Benefits of these systems are mainly their high efficiency,
56 low noise levels, low pollutant emissions, the availability of a wide range of suitable fuels, and the
57 possibility to be scaled up with practically no variation in the efficiency value. [12]. However, the
58 main drawback is the low resistance to trace compounds [6,7,13–18]. Literature studies focus
59 mainly on gas cleaning or SOFC material tolerability against these trace compounds [3,19–21].

60 The removal of trace compounds with sorbent materials was investigated considering the effect of
61 temperature, relative humidity and contemporary removal of several compounds to simulate real
62 conditions [19,20,22]. In our previous work it was showed the temperature dependency on the
63 removal performance of commercial carbons [21]. Another parameter that affects removal
64 performance is the relative humidity content [21,23]. In fact, the water humidity content could have
65 a positive or negative impact depending on the presence of basic active sites. Barelli et al., (2017)
66 demonstrated that, for carbons activated with KOH and KI, the formation of water film around
67 carbon pores favors H₂S molecules dissociation [23]. Conversely, humidity could be a problem for
68 carbons activated with metals, such as Cu or Fe. Here, the interaction between H₂S and metals
69 loaded on carbon surface results in metal sulfide (MeS) and water production. The water contained
70 in the gas matrix downsides the sulfur removal. As reported in the literature, a relative humidity
71 value above 50% lead the adsorption capacity to zero mg/g [21]. Finally, the multiple removals of

72 trace compounds has to be considered. This condition is crucial for the industrialization of the direct
73 biogas to energy production systems with SOFCs. Preliminary laboratory results highlighted the
74 strong decrease of removal performance with the simultaneous presence of more than one
75 compound, i.e. H₂S [24]. All of these factors can be present at the same time in a real plant. An
76 experimental pilot plant for gas cleaning with ashes was investigated as a more realistic case [25].
77 Results showed the higher efficiency of ashes in removing H₂S, alcohols and some terpenes, while
78 the removal of thiols, siloxanes, and carbonyl compounds was less successful. Results of the
79 experiment demonstrated that ashes are not economically and technically exploitable to work with
80 SOFC energy generators. This is due to the stringent gas concentration requirements. The low cost
81 of activated carbons and the low sulfur capacity of ashes are also involved in this process. In this
82 work, considering the philosophy of circular economy, we want to investigate utilization of biochar
83 for the gas cleaning for SOFC applications. Biochar from the wood pyrolysis chain was selected for
84 the removal of trace compounds. Biochar has a relative structure carbon matrix with a high specific
85 surface area and high degree of porosity able to act as a surface sorbent. These features are similar
86 to optimized commercial activated carbons. Char material was tested elsewhere for the removal of
87 only sulfur compounds [26,27]. The adsorption characteristics of biochar are a function of the raw
88 material, the production process, and the temperature. Ahmad et al., (2012) showed the importance
89 of temperature of the char production to increase its surface area and porosity [28]. Both, surface
90 area and porosity are linked to the adsorption capacity of trace compounds [27]. To the best of our
91 knowledge, this paper is the first attempt to monitor the removal of biogas trace compounds, using a
92 recoverable waste as a sorbent material with PTR-MS instrument.

93 **2. Experimental and methods**

94 **2.1. Anaerobic digestion pilot plant**

95 The organic fraction of municipal solid waste was selected as substrate biomass for biogas
96 production. These wastes were treated in a pilot plant placed at Foundation Edmund Mach - S.

97 Michele a/A, Italy (TN). Bio-wastes were pretreated in a cylindrical sieve to avoid undesired
 98 components, such as stones, papers, plastics and glasses. The rectangular digester was made by
 99 concrete (16 m³) and it was sealed with resin. Before the waste loading, OFMSW was mixed with
 100 chipped wood, collected from the local municipality (San Michele a/A, TN Italy), at a volume ratio
 101 of 0.6 – 0.7 (wood to biomass) to achieve suitable biomass porosity. For a rapid start of the methane
 102 production the biomass was subjected to a four day preoxidation process, no air was sparged in the
 103 waste. Consequently, the initial lag phase was reduced, from an average of ten days to five days.
 104 The temperature increased up to 35 °C due to the aerobic digestion process, and a significant release
 105 of carbon dioxide and other VOCs was recorded. After the aerobic phase, the digester was sealed
 106 for the transition from aerobic to anaerobic condition. The biomass temperature was
 107 thermostatically controlled by fixed floor, wall coils and by leachate sprinkling as needed. Under
 108 these conditions, the anaerobic digestion was accomplished in approximately 30 days. The biomass
 109 was subjected to a composting treatment for 20 days before final use as fertilizer. Table 1
 110 summarizes the composition and physicochemical characteristics of the OFSMW batch used in this
 111 study.

112 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]

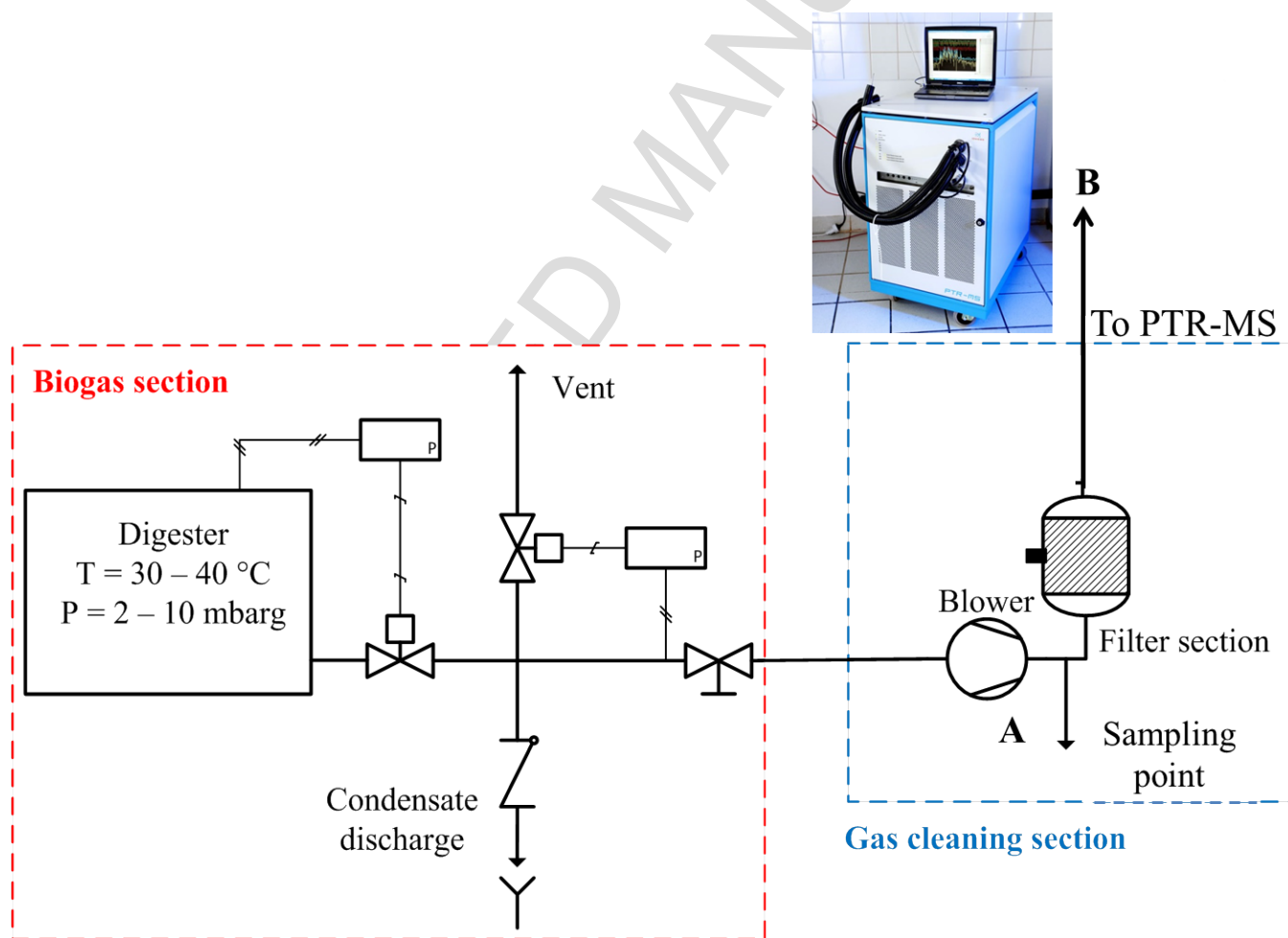
113 Where:

- 114 • pH in: pH measured at the beginning of loading into the digester
- 115 • pH out: pH at end of digestion process
- 116 • Mix: total biomass loaded into the digester
- 117 • Square brackets indicate the standard deviation of measurements
- 118 • * Mix was left at ambient temperature for 4 days prior to loading into the digester, thereby probably changing the
- 119 pH e.g. via CO₂ escaping into the atmosphere.

120 **2.2. Sorbent material characterization and experimental settings**

121 Biochar from the pyrolysis of wood, from local municipality (Civitella in Val di Chiana (Ar)) was
 122 produced by Gruppo RM Impianti srl. (Italy), in a 200 kW_e reactor at low temperature (150 °C) for
 123 24 h. This sorbent sample was tested in a glass reactor filter of 340 ml. The experimental set-up is
 124 described in Figure 1. The blower coupled with the digester flushes an average flow rate of 0.3
 125 Nm³/h with a gas hourly space velocity (GHSV) of 882 h⁻¹, at ambient temperature and pressure
 126 around 80 mbar. The value chosen for the GHSV parameter is compatible with space velocities
 127 expected for 1 kW_e SOFC micro-CHP application [29].

128



129

130 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

156 tube of the instrument via a heated PEEK line (110 °C). Table 2 lists a selection of the mass peaks
 157 which are the subject of this paper. Each compound is characterized by its nominal mass (m/z),
 158 protonated chemical formula, and tentative identification based on the previous studies.

159 Table 2 – Mass peaks which were used in this study along with their experimental and expected m/z values, their
 160 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]

161

162 **3. Results and discussion**163 **3.1. Biochar characterization**

164 These measurements were able to characterize the sample in terms of specific surface area. Samples
 165 were outgassed at 423 K overnight prior to the adsorption measurements. The equipment allows
 166 measurement of relative pressure of 10^{-6} bar. Specific surface areas have been calculated by
 167 Langmuir model. Langmuir surface area resulted to be $75 \text{ m}^2/\text{g}$ (average value of 3 samples). This
 168 value, although lower than activated carbons (typically $1500 \text{ m}^2/\text{g}$), is significantly higher than
 169 ashes ($\sim 1 \text{ m}^2/\text{g}$) [25]. The porosity was evaluated indirectly considering the mass of sample, the
 170 micro, meso and total pore volume of the filter. The porosity was about 4%. **Error! Reference**
 171 **source not found.** shows the FESEM images for the biochar sample.

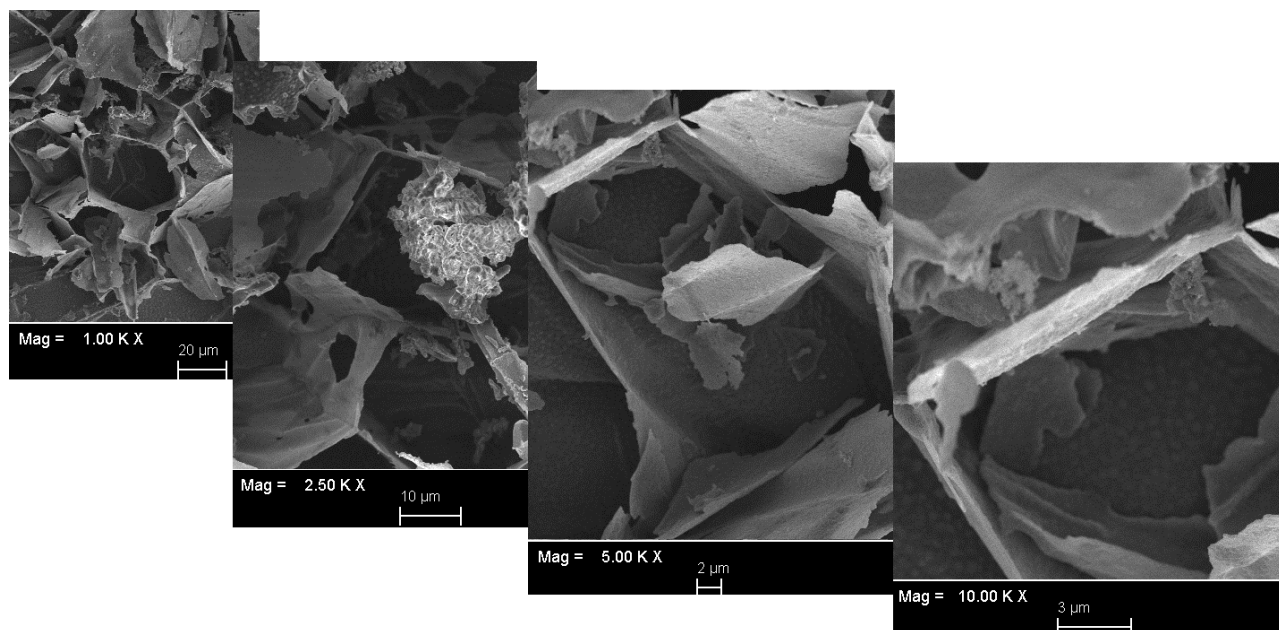


Figure 2 – FESEM biochar characterization

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

185 shows some lacks due to the instability of some compounds. This instability was studied and results
186 suggest to improve the collecting system, as reported elsewhere [56,57]. To the best of our
187 knowledge, this research was the first attempt to build a direct connection from the biogas anaerobic
188 digester, to the monitoring system. Rapid and reliable results were achieved in real time, as
189 demonstrated from the comparison between the monitored and tentative identification compounds
190 reported in literature (Table 2). The effectiveness of an OFMSW anaerobic digestion process for
191 large-scale application depends to a great extent on the quantity and quality of the produced biogas.
192 In all the experimental tests, the initial lag phase when carbon dioxide production predominated was
193 reduced using aerobic and alkaline pre-treatments. The anaerobic digestion process lasted about
194 three weeks after the first stage of loading. For the first week, the process produced mainly carbon
195 dioxide (max 70% with an average flow rate of 3 m³/h) with a low fraction of methane (min 5-6%
196 with an average flow rate 0.01 m³/h), as reported in our previous studies [1,38]. The amount of
197 CO₂-rich biogas produced in the first phase is not useful for the energy purposes. After this period
198 of time, the methane production phase starts and it lasted for the remaining two weeks with an
199 average concentration of CH₄ around 60-65 %vol. with an average flow rate value of 0.5 m³/h. The
200 average value and the standard deviation of trace compounds monitored along the digestion process
201 are reported in Table 4. The variability between replicates is rather small and varies in the range
202 from +/- 11%.

203 It is possible to group the trace compounds into the following families: terpene, siloxane,
204 hydrocarbon, sulfur, carbonyl, carboxyl and aromatic compounds. Taking in consideration the
205 average value, the biogas composition can be divided as follows: siloxanes 1%, sulfur compounds
206 6%, higher hydrocarbons 9%, terpenes 13%, carbonyl-carboxyl and aromatic compounds 35% and
207 37%, respectively. The most important compounds detected for the biogas use in SOFCs, are
208 mainly sulfurs and siloxanes. Sulfur compounds are important due to their concentration level and
209 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 H₂S depend on the aerobic to anaerobic transition phase
220 [38]. H₂S 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 CO₂
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	

250

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

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	

251

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
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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	
	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	

253

254

255 3.3. Adsorption capacity evaluation

256 The adsorption capacity is inversely correlated to the breakthrough capacity for a given sorbent
257 material. The adsorption capacity estimation is often the major determinant of service lifetime for
258 an adsorbent. The adsorption capacity was evaluated considering the following equation, [66]:

$$259 \quad C_{ads} = \frac{\dot{Q} \cdot MW \cdot (C_{in} \cdot t_1 - (t_1 - t_0) \cdot 0.5)}{Vm \cdot m \cdot 10^3} \quad (1)$$

260 Where:

261 Q, total gas flow rate (NI/h);

262 MW, molecular weight (H₂S 34 g/mol);

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

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

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

266 Vm, molar volume (24.414 NI/mol);

267 m, mass of adsorbent material (g).

268

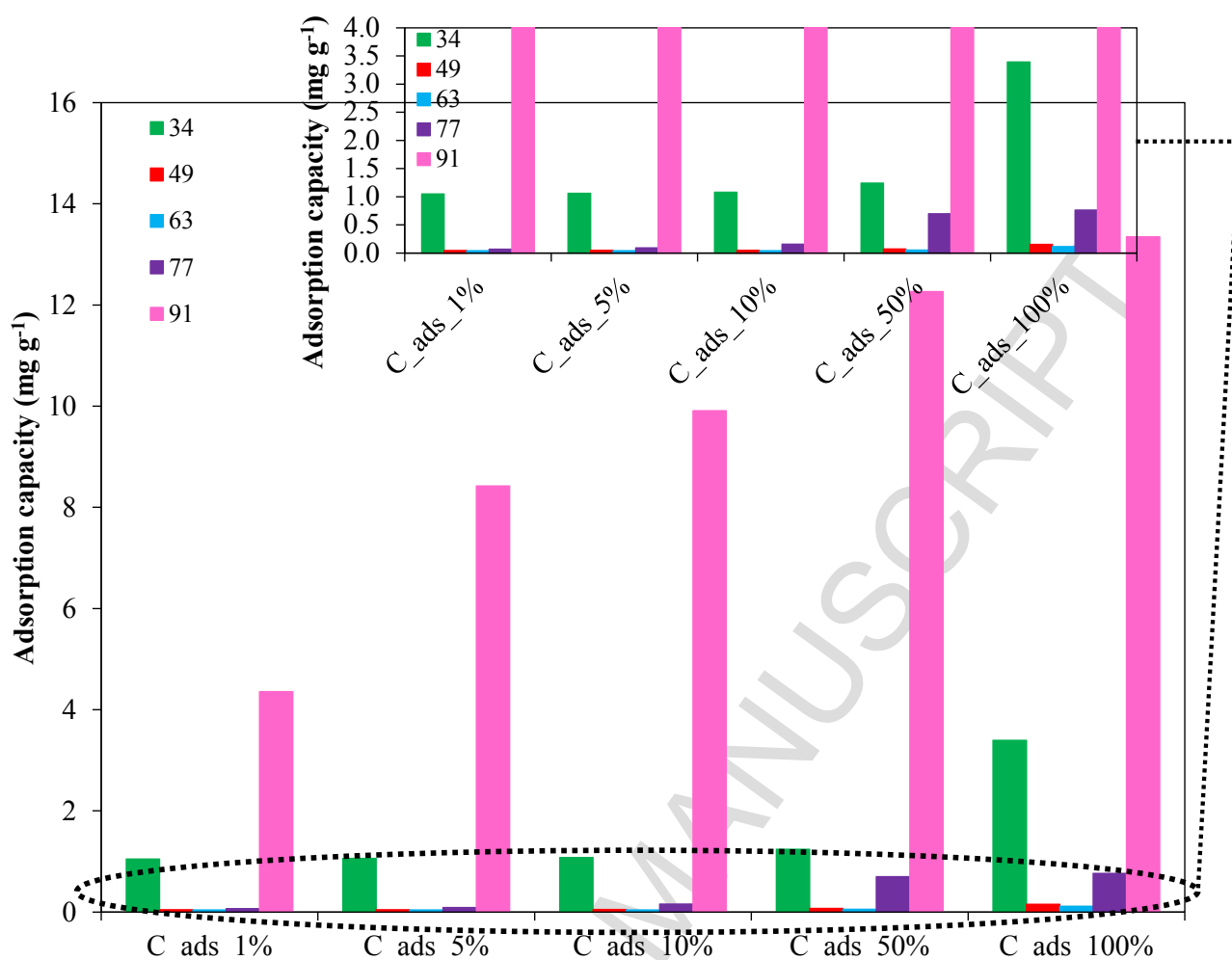


Figure 3 – Adsorption capacity for sulfur compounds

269
 270
 271 The adsorption capacity for sulfur compounds evaluated with equation 1, is reported in Table 5 and
 272 in Figure 3. The initial breakthrough time for the SOFC feeding system and to plan a maintenance
 273 operation process for the sorbent replacement is crucial. In fact, as reported in literature, the
 274 tolerable levels of trace compounds contained in the biogas fuel are low [2,3,60,67]. The adsorption
 275 capacity achieved to remove H₂S was about 1.05 mg/g when it was achieved 1% of the starting H₂S
 276 concentration (limit fixed for the initial breakthrough value for SOFC requirements). This
 277 adsorption capacity value increased to 3.39 mg/g when the saturation of filter is reached. As
 278 reported in Papurello et al., (2016) simulated biogas with only H₂S, using two different commercial
 279 activated carbons showed an adsorption capacity that ranged from 3 – 6 mg/g. In this study biochar
 280 was selected as sorbent material in a real biogas pilot plant. Results achieved are comparable with

281 literature results for H₂S removal. The second sulfur compound in terms of abundance was
282 butanethiol. Biochar showed an adsorption capacity value around 4.4 mg/g at the initial
283 breakthrough up to 13.3 mg/g at the saturation of the filter. Considering the other sulfur
284 compounds, due to their lower concentration showed an adsorption capacity relatively low. Values
285 achieved ranged from 0.04 mg/g to 0.76 mg/g, from initial breakthrough to saturation. As reported
286 elsewhere, [21] adsorption capacity increases with the pollutant concentration. This is due to the
287 increase of driving force up to achieve a limit value above which the adsorption capacity remains
288 constant. The effectiveness of the adsorption treatment is determined also by the type of substance
289 to be removed. Substances with a high molecular weight and low water solubility are better
290 adsorbed with activated sorbent materials. In fact, H₂S showed a lower adsorption capacity than
291 butanethiol even with higher concentration values.

292 Commercial activated carbons, properly prepared for siloxanes removal have an adsorption capacity
293 that ranged around 100-200 mg/g in the single removal test (laboratory conditions). At the
294 beginning biochar showed an adsorption capacity of 1.28 mg/g at 1% of the starting D3
295 concentration. With time it increased up to achieve, at 50% of the initial concentration, 12.28 mg/g
296 and at the saturation of the filter, remains quite stable with 13.15 mg/g.

297 The adsorption capacity for the removal of terpenes is reported in Table 5 and in Figure 4. The most
298 abundant terpene compound was p-cymene, followed by limonene. For these compounds the
299 adsorption capacity started from 35 mg/g and 64 mg/g, respectively. The trend for p-cymene
300 showed a significant increase from 1% to 5% of initial concentration of more than 50% up to
301 achieve, at the saturation condition 97.6 mg/g. The adsorption capacity increased significantly up to
302 102 mg/g at saturation conditions for limonene. Cumene and isoprene showed a lower adsorption
303 capacity due to pollutant concentration contained in the biogas.

304 Among aromatic compounds: benzene, toluene, styrene and xylene were detected. The most
305 abundant aromatic compound is toluene with an average value around 21 ppm(v), while benzene,

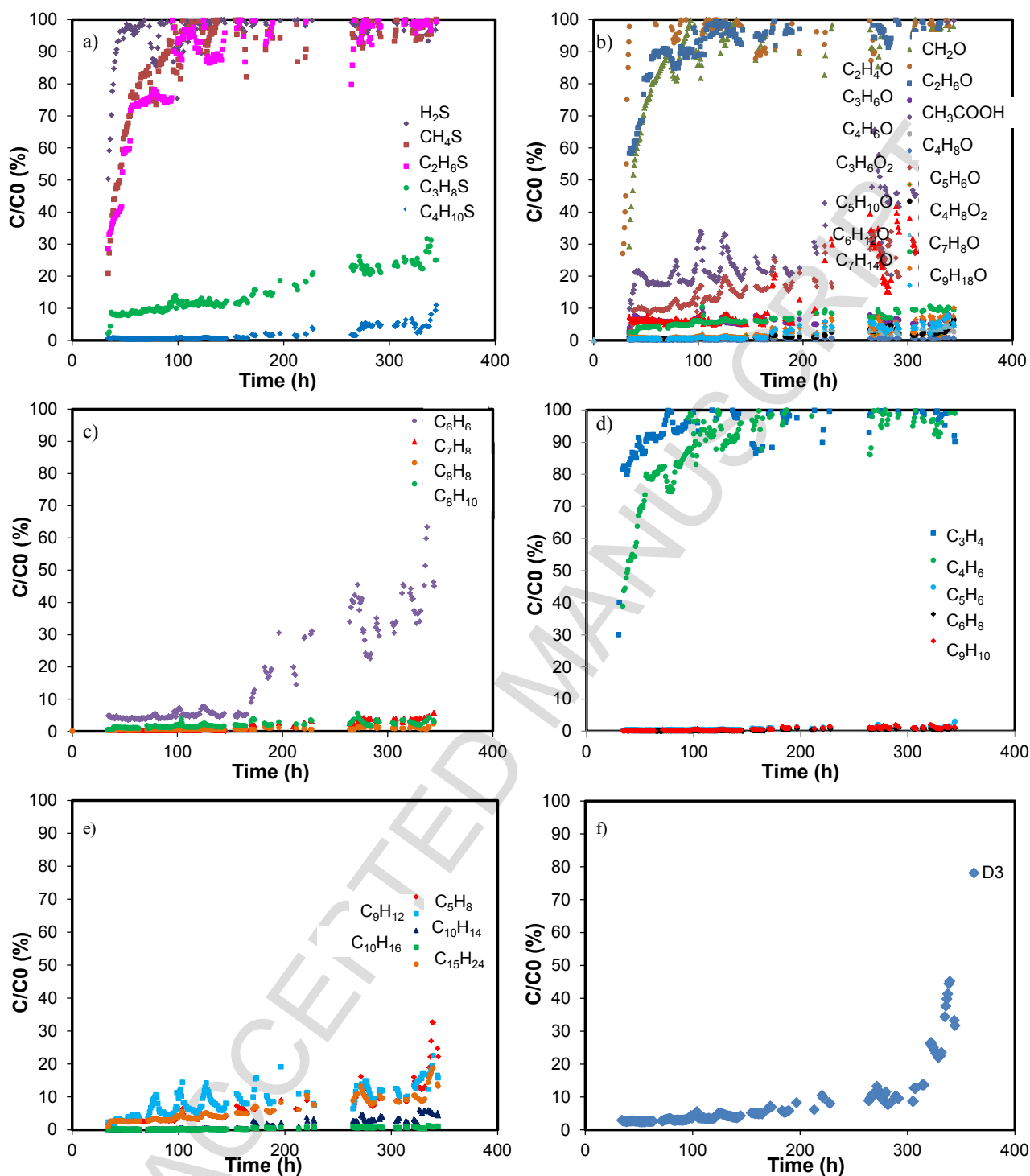
306 styrene and xylene showed a concentration below 10 ppb(v). The adsorption capacity of toluene, at
307 the starting condition showed a value above 140 mg/g up to achieve, rapidly the maximum capacity
308 at the saturation conditions (40% by weight of the carbon), see Figure 4 and Table 5.

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

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

322 form of H₂S, C₇H₈, C₄H₈O, C₁₀H₁₆ and C₁₀H₁₄. These compounds belong to the family of sulfur,
 323 aromatic, carbonyl and terpene compounds.

324 Hydrogen sulfide was the most abundant sulfur compound with the average concentration about 24
 325 ppm(v). The tested sorbent material was able to withstand the H₂S concentration for almost 30 h
 326 with the biogas pilot plant conditions before achieving the limit value for SOFC applications, 1
 327 ppm(v) [3]. This concentration is the tolerable limit for SOFC applications able to guarantee a
 328 reversible behavior rather than a dramatic and irreversible loss of performance [6]. Considering the
 329 other detected sulfur compounds and due to their lower concentration inside the biogas matrix, H₂S
 330 is the compound that fixes the replacement time for the filter. Siloxanes are the other important
 331 trace compounds that strongly affect the SOFC performance. The average concentration detected
 332 for D3 was about 3.9 ppm(v). As reported elsewhere, this concentration irreversibly affects the
 333 SOFC performance in few hours [6,8]. The limit for D3 for SOFC applications is 1% of the average
 334 concentration detected in the real biogas pilot plant. The time required to achieve this limit is
 335 around 30 h, which confirms the time limit set by H₂S.

336 Table 6 – Time required to achieve the adsorption capacity percentage

Compounds			Time (h)				
			1%	5%	10%	50%	100%
31	CH ₂ O	formaldehyde	14.6	16.0	17.8	36.2	93.1
34	H ₂ S	hydrogen sulfide	28.3	28.6	29.1	33.6	92.8
41	C ₃ H ₄	propyne	24.0	24.4	25.0	30.7	90.8
45	C ₂ H ₄ O	acetaldehyde	24.5	24.8	25.2	29.5	35.7
47	C ₂ H ₆ O	ethanol	6.7	8.1	9.9	28.4	126.0
49	CH ₄ S	methanethiol	21.0	22.4	24.3	43.2	119.2
55	C ₄ H ₆	butadiene	13.5	15.0	17.0	37.5	215.4
59	C ₃ H ₆ O	acetone	13.5	37.0	367.9	428.8	458.7
61	CH ₃ COOH	acetic acid	22.6	26.5	32.4	314.9	352.0
63	C ₂ H ₆ S	dimethylsulfide	21.1	22.6	24.7	46.2	163.5
67	C ₅ H 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

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.

343 CHO compounds are less problematic for SOFC applications in terms of concentration in the biogas
344 fuel mixture. To achieve 1% of the starting concentration for the main CHO compounds, the
345 following times are necessary: ethanol with 6.7 h, acetone with 13.5 h, methylfuran with 153.6 h
346 and 2-butanone with 366.9 h. Even if lower than H₂S and D3, these compounds are less detrimental
347 for SOFC applications.

348 The time required for terpenes to achieve 1% of the starting concentration are showed below. These
349 values are sorted in ascending order: cumene with 34.5 h, isoprene with 35.4 h, p-cymene with
350 164.7 h and limonene with 347 h. When the time required to achieve the desired outlet
351 concentration is shorter, the resulting adsorption capacity is lower.

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

356 **4. Conclusions**

357 It was decided to investigate on the removal performance of a sorbent material that comes from the
358 waste chain treatment: biochar. This adsorbent material was tested in a real pilot plant and the outlet
359 of the filter was monitored online with a PTR-MS instrument, for the first time. The performance
360 achieved with this material are almost comparable with those achieved by reference commercial
361 carbons, even if some most optimized and selective materials show better results. Biochar
362 withstands the removal of 2-butanone, toluene and limonene better compared to sulfur and siloxane
363 compounds. For these reasons to guarantee the long term operation of SOFC systems, biochar
364 sorbents should be placed in a lead and lag configurations systems of reactors.

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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.