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Biogas trace compounds removal with ashes using Proton Transfer Reaction Time-of-Flight Mass Spectrometry as innovative detection tool

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Abstract

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

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

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

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Nomenclature:

- a1, 15th day of digestion process with an ash dry filter;

- a2, 16th day of digestion process with an ash wet filter;

- AD, Anaerobic Digestion;

- BET, Brunauer–Emmett–Teller;

- C/C_0, pass through ratio of an organic compound; final/initial concentrations

- C_0, concentration detected before the filter;

- FEM, Fondazione Edmund Mach Research and Innovation Center;

- GHSV, gaseous hourly space velocity, h^{-1};

- OFMSW, Organic Fraction of Municipal Solid Waste;

- m/z, mass to charge of ionic compound;

- ppb(v), parts per billion volume;

- ppm(v), parts per million volume;

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

- SEM, Scanning Electrode Microscopy;

- SOFC, Solid Oxide Fuel Cell;

- VOC, Volatile Organic Compound;

- VOSC, Volatile Organic Sulfur Compound;

- WWTP, Waste Water Treatment Plant;

- % v/v, volume concentration in percent.

1. **Introduction**

In recent years, anaerobic digestion has emerged as one of the technologies of high interest because of its potential usefulness as an alternative to fossil fuel energy. Anaerobic digestion is a biological process in which biodegradable matter, e.g. OFMSW is degraded or decomposed by the activity of

specific microorganisms in the absence of oxygen. The resulting biogas (mainly methane and carbon dioxide) can be used for electricity generation [1]. Organic Fraction of Municipal Solid Waste (OFMSW) offers the possibility to obtain a valuable bio-fuel from a waste that otherwise would be disposed in landfill. Typically, the biogas produced by anaerobic digestion of OFMSW is comprised of 50-70 % v/v methane, 30-50 % v/v carbon dioxide and trace volatile compounds [2–4]. Aside from the main components, methane and carbon dioxide, biogas from the organic sources can contain a large number of other trace compounds, e.g., sulfurs, terpenes, aromatics and hydrocarbons, carbonyls and carboxyls, siloxanes and alcohols [2,5,6]. In addition, these trace gas can include other odorous compounds such as hydrogen sulphide and ammonia [7]. Biogas from anaerobic digestion of OFMSW could be adopted as renewable fuel for several energy generators, e.g. internal combustion engines, fuel cells, micro-turbines, etc. Among these technologies Solid Oxide Fuel Cells (SOFCs) is the most promising in terms of overall efficiency. SOFC have an advantage over the fuel cell technologies with its carbon dioxide tolerance [8–10]. The direct use of biogas containing trace contaminants may lead to cell anode damage after few hours of operation due to the carbon deposition and catalyst deactivation [9,10]. These contaminants need to be removed by the proper choice of a reforming agent and a gas cleaning method [8–11]. Sulfur and siloxanes compounds are probably the trace constituents of most concern that strongly affect SOFC anode activity [12,13][9,10]. In particular, exposure to more than 1-2 ppm(v) of H_2S SOFC performance decrease strongly and irreversibly. The decrease caused by surface adsorption of sulfur to produce nickel sulfides, reduce the catalyst activity [9,10,13]. The presence of siloxanes can cause deposition-type degradation. A study by Haga et al., (2008) reveals a strong cell voltage decrease. Hydrogen with 10 ppm(v) of decamethylcyclopentasiloxane (D5), contained in a biogas from waste water treatment plant (WWTP), induces cell voltage decrease and fatal degradation after 50 h of test at 800 °C due to the formation of $SiO_2(s)$ [14]. Madi et al., (2015) investigated the siloxanes impact on SOFC single cells. High degradation rates are observed already at ppb(v) level of contaminant in the fuel stream [11].

To be technically viable methods are required to reduce the impurity concentrations to tolerable levels, if not to eliminate the impurities entirely. These methods represent the cleaning section for fuel cells applications. Contaminant removal increases the complexity of the system, raising the capital and operating costs [15]. Potential technologies for removal of the trace compounds in biogases include various adsorbents [16], absorbents [17] and biofilters [18]. Generally, activated carbons are used as sorbent materials, when impregnated with metals, such as iron, copper or chromium [19,20]. For reasons related to technical, environmental and economic aspects we decided to investigate the VOCs removal with ashes obtained from a wood boiler. Considering the low cost, and the possible recycling of environmental pollutants, wood ash is an attractive choice for VOCs capture. The fly ash from biomass or from municipal solid waste incineration are investigated to remove organic compounds from biogas stream [21–23]. Previously Kastner et al., (2003) [24] investigated sulfur compounds removal using wood and coal fly ash. Wood fly ash demonstrated a lower removal capacity for H_2S and CH_4S compared to activated carbon. However, no literature studies were found with wood ash used to remove VOCs from biogas. In general, there is a need for sensitive and robust methods of real-time analysis of the volatile trace compounds to protect public health and welfare and to allow optimal process control. In this context, one alternative for contaminant analysis is direct injection mass spectrometry (DIMS). DIMS offers advantages in terms of rapidity and sensitivity without need for pretreatments [2,19,20,25]. In particular, the recent introduction of time of flight (ToF) mass analyzers coupled with proton transfer reaction mass spectrometry (PTR-ToF-MS, [26]) indicates the possibility of maintaining high sensitivity with improved time resolution (0.1 s), mass range (virtually not limited) and mass resolution (better than 4000). This improved mass resolution allows the separation of isobaric compounds and the identification of the chemical formula of the spectrometric peaks. Of concern for the use of PTR-ToF are problems in data analysis (handling of large data sets (gigabyte/hour), spectra alignment, peak extraction). Recent literature describes how these problems can be overcome to make PTR-ToF-MS a routine technique for monitoring of VOCs [27,28].

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

2. Materials and methods

2.1 Anaerobic digestion plant

OFMSW was adopted as organic source to produce biogas with an anaerobic digester pilot plant, located at Foundation Edmund Mach (S. Michele a/A, Italy) (FEM). Biowaste was obtained from selected sources to avoid undesired components (such as stones, paper, plastic, glass) in the organic fraction. The biomass comes from the local organic waste (San Michele a/A (TN), Italy). The plant is based on a barrel shape design with a working volume of 16 m^3 with frontal loading. The digester is composed of resin sealed rectangular reinforced concrete modules. Before digester loading, OFMSW at a volume ratio from 0.6 to 0.7 was mixed with chipped wood to achieve a suitable biomass porosity. Before the anaerobic digestion phase, biomass was subjected to a four day of pre-oxidation process. The temperature increased 35 °C and released significant amounts of carbon dioxide and other VOCs. After the aerobic phase, the digester was isolated to transition from aerobic to anaerobic conditions. The biomass temperature was thermostatically controlled by fixed floor and wall coils and by leachate sprinkling as needed. Under these conditions the anaerobic digestion was accomplished in approximately 30 days. The biomass was subjected to a further aerobic composting treatment for 20 days before final use as fertilizer. Table 1 summarizes the composition and physicochemical characteristics of the OFSMW batch used in this study.

	Volume (m³)	Mass (t)	Water content (%)	Volatile Solids (%)	pH in	pH out
Digestate from previous batch	7.33 [±0.43]	6.67 [±0.52]	61.6 [±1.02]	55.3 [±3.1]	8.7 [±0.2]	

OFSMW + Wood	9.29 [±0.51]	5.34 [±0.53]	59.5 [±0.75]	82 [±3.2]	5.8 [±0.2]	
Mix	14.95 [±0.52]	12.01 [±0.46]	58.8 [±1.19]	59.8 [±3.3]	7.8 [±0.2]	8.3 [±0.2]

**Table 1 - Starting values of digestion cycle – Initial biomass parameters.**

Where:

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

* Mix was left at ambient temperature for 4 days prior to loading into the digester, thereby probably changing the pH e.g. via CO_2 escaping into the atmosphere.

2.2 Experimental Sorbent characterization and VOCs removal section

Ashes from a forestry wood-chips boiler (3.3 MW, Viessman, Allendorf Germany) were tested in a glass reactor filter of 340 ml. Two different VOCs removal tests were performed with ashes; the first in dry conditions and the second one with ashes wetted with a demineralized water nebulizer. The experimental set-up is described in the following figure. The blower coupled with the digester can flush an average flow of about 0.3 Nm^3/h with a gas hourly space velocity (GHSV) of 882 h^{-1}, ambient temperature and pressure around 1.8 bar.
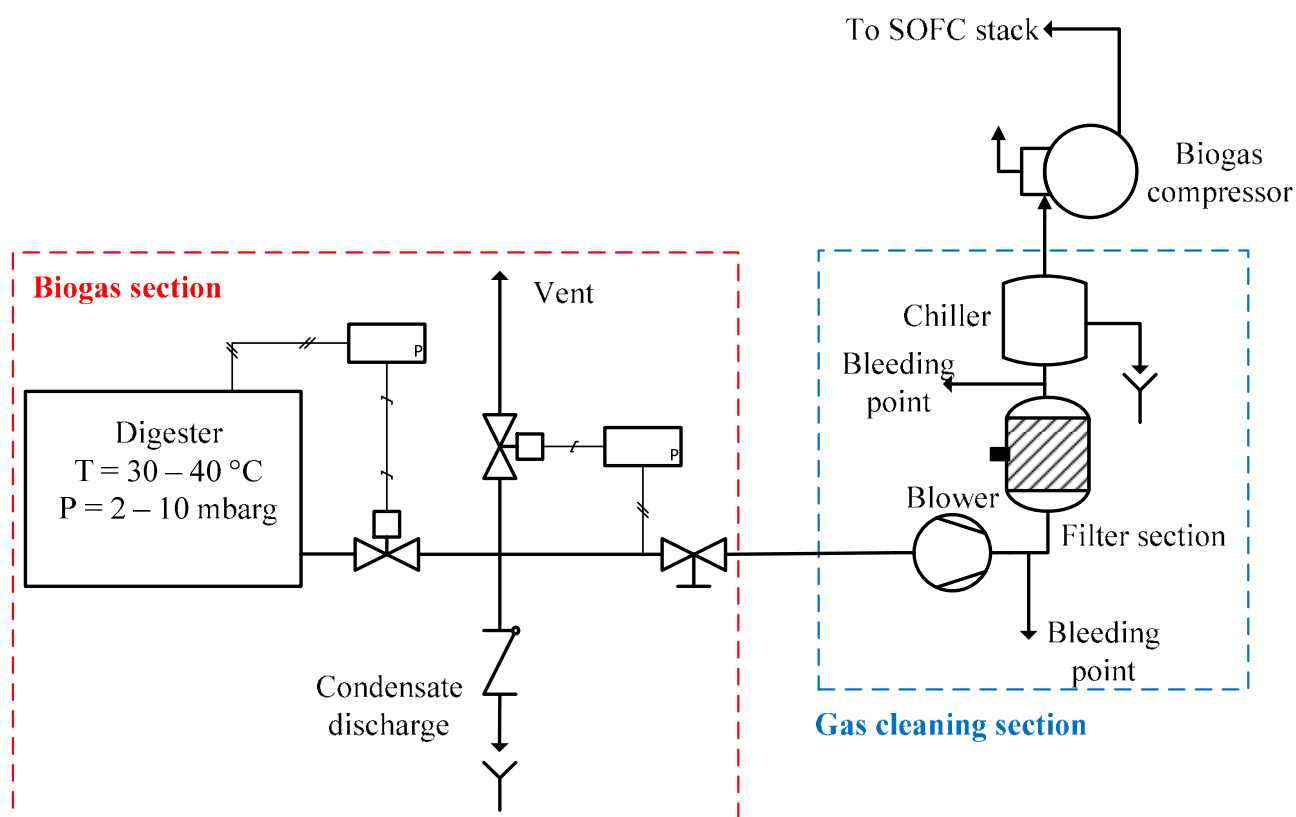
Figure 1 – Biogas to gas cleaning section – experimental set up.

The sorbent material was analyzed to measure the specific surface area. Adsorption isotherms for N_2 at 77 K were determined using a Quantachrome Autosorb 1 (Boynton Beach, Florida, USA). 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 B.E.T. (Brunauer–Emmett–Teller) model in the relative pressure range 0.04–0.1 bar. The specific surface area (<1 m^2/g) is much lower than activated carbon (typically 1500 m^2/g), this means that ashes are mostly extremely dense oxides, as seen in figure 2. Figure 2A shows the SEM image for the ash sample. Ash has much lower porosity compared to figure 2B, where a commercial activated carbon is shown.
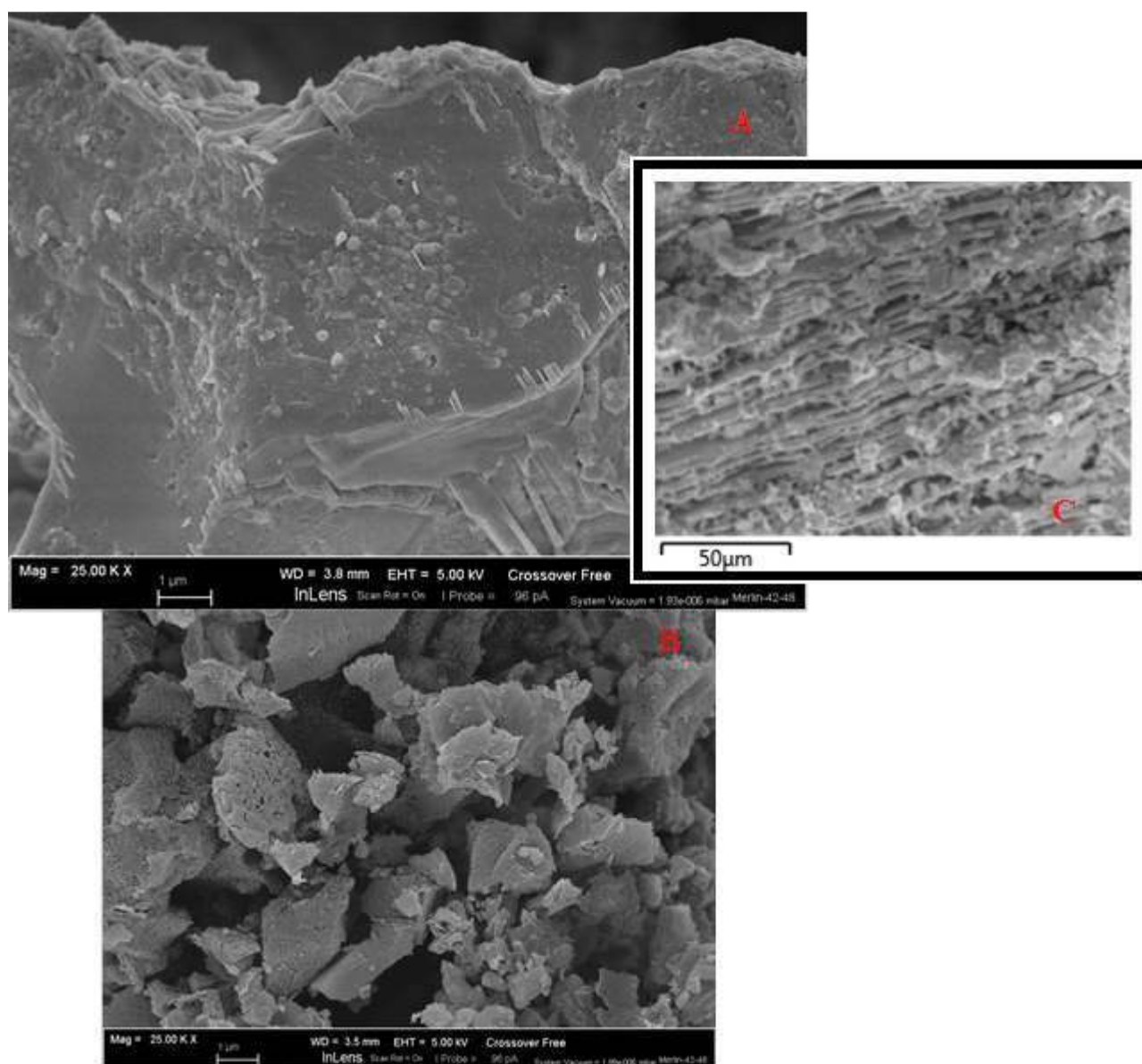
Figure 2 – A SEM image of the ash sample tested, B SEM image of the activated carbon sample, C SEM image of the virgin ash sample.

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

Element	Atomic % virgin	Atomic % tested
C	7.73	17.65
O	39.99	54.18

Mg	2.74	0.56
Al	4.07	0.50
Si	9.09	19.46
Cl	-	0.15
K	10.82	6.65
Ca	10.87	0.86
Fe	11.68	-
Ti	0.85	-
Na	0.68	-
Mn	0.73	-
Total:	100.00	100.00

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

The most abundant compound is oxygen followed by silicon, carbon, potassium, calcium, magnesium and aluminum. The concentrations of K and Ca are important for removal of sulfur compounds, as reported by Tepper and Richardson et al., (2002) [29,30]. It is difficult to correlate the elements identified with the EDS analysis before and after the experimental test. A decreasing of magnesium, aluminum, potassium, calcium and iron could be related to the reactions that could take place between metals, alkaline earth metals and alkaline metals and trace compounds that have to be removed.

2.3 VOC sampling and PTR-MS measurements

Biogas samples (0.3 L) were collected in 3L Nalophan bags and sealed with Teflon stoppers [31]. Nalophan bags were selected as preferable to Tedlar bags because they gave a cleaner background, as shown by Beghi and Guillot (2008) [32]. It is noted that for some compounds, such as H_2S, Tedlar bags permit better compound recovery as shown by Hansen et al., (2011) [33]. Samples are collected upstream (C_0) and downstream (C) of the gas cleaning section, in order to measure the pass through ratio for a trace contaminant compound. Time between sampling and analyses was kept short to minimize concentration losses. Analysis was performed at maximum 30 min after

sample collection prior to the PTR-ToF-MS analyses, the biogas samples were diluted with nitrogen gas at a ratio of 1:10 and incubated at 35 °C for 30 min using a thermostatic bath (Techne Ltd, Cambridge, UK). Methane and carbon dioxide were detected in situ by an infrared detector (EC 322, Eco Control Milan, Italy) while oxygen was measured by an electrochemical cell (EC 322, Eco Control Milan, Italy). VOCs analysis was conducted using a PTR-ToF-MS 8000 instrument in its V-mode configuration (Ionicon Analytik GmbH, Innsbruck, Austria). The sample was directly injected into the drift tube of the instrument via a heated (110 °C) PEEK inlet tube. The sampling time per channel of the ToF was 0.1 ns amounting to about 350,000 channels for a mass spectrum up to m/z 400 under drift tube conditions of 600 V, 2.25 mbar and 110 °C achieving a E/N ratio of about 155 Td (Td = Townsend, $1Td = 10^{-17}Vcm^2mol^{-1}$). An average of 30 spectra were acquired for every sample corresponding to a measurement time of 30 s. Analysis of the spectral data was carried out using the procedure developed by Cappellin et al., (2012) [28]. This allowed the quantification of more than 600 peaks and the identification of the chemical formulas. This number includes isotopologues and fragments which corresponds to a smaller number of independent signals. Table 3 lists a selection of the spectrometric peaks which are the subject of this paper. Each compound has its experimental and expected m/z values, its chemical formula and tentative identification. PTR-ToF-MS provides only the chemical formula of the spectrographic peaks.

Measured m/z	Theoretical m/z	Protonated chemical formula	Tentative identification	References for PTR-MS spectra	References for biogas from waste management
18.033	18.0338	NH_4^+	Ammonia	[26]	[3,34,35]
31.018	31.018	CH_3O^+	Formaldehyde	[36]	[3,35]
34.995	34.995	H_3S^+	Hydrogen sulfide	[2,37]	[3,35,38]
41.038	41.039	$C_3H_5^+$	Propyne	[39]	[15]
45.033	45.033	$C_2H_5O^+$	Acetaldehyde	[26,36]	[34,35,40,41]
47.013	47.013	$CH_3O_2^+$	Formic acid	[26]	[15]
47.049	47.049	$C_2H_7O^+$	Ethanol	[36]	[34,35,40]
49.01	49.011	CH_5S^+	Methanethiol	[2]	[35,38,40]
55.054	55.054	$C_4H_7^+$	Butadiene	[39]	[15]
57.07	57.07	$C_4H_9^+$	Butene	[39]	[15]
59.049	59.049	$C_3H_7O^+$	Acetone	[36]	[34,35,40]

61.028	61.0284	$C_2H_5O_2^+$	Acetic acid	[36,42]	[34,35,40]
63.022	63.0284	$C_2H_7S^+$	Dimethylsulfide (DMS)	[25]	[35,38]
67.054	67.054	$C_5H_7^+$	Cyclopentadiene	[43]	[44]
69.035	69.0335	$C_4H_5O^+$	Furan	[25]	[35]
69.069	69.07	$C_5H_9^+$	Isoprene	[25]	[6]
71.086	71.086	$C_5H_{11}^+$	Cyclopentane	[45]	[2]
73.028	73.028	$C_3H_5O_2^+$	Acrylic acid	[43]	[44]
73.065	73.065	$C_4H_9O^+$	2-butanone/butanal	[36]	[34,35,40]
75.044	75.044	$C_3H_7O_2^+$	Propionic acid/propanoates	[36,42]	[34,35,40]
77.041	77.042	$C_3H_9S^+$	Propanethiol	[2]	[46]
79.054	79.054	$C_6H_7^+$	Benzene	[25]	[34,35,40]
81.068	81.07	$C_6H_9^+$	Cyclohexadiene		[15]
83.049	83.049	$C_5H_7O^+$	Cyclopentenone		[44]
83.085	83.086	$C_6H_{11}^+$	Cyclohexene	[43,45]	[15]
87.081	87.080	$C_5H_{11}O^+$	2-Pentanone/Pentanal	[36]	[34,35,40]
89.059	89.059	$C_4H_9O_2^+$	Butyric acid/butyrates	[36,42]	[35]
91.057	91.057	$C_4H_{11}S^+$	Butanethiol	[2]	[46]
93.07	93.07	$C_7H_9^+$	Toluene	[25,26]	[6,35]
95.086	95.085	$C_7H_{11}^+$	2,5-Dihydrotoluene	[45]	[44]
101.096	101.096	$C_6H_{13}O^+$	2-Hexanone/hexanal	[36]	[34]
105.07	105.07	$C_8H_9^+$	Styrene	[25]	[34,35,40]
107.086	107.086	$C_8H_{11}^+$	Xylene	[25]	[34,35,40]
109.065	109.065	$C_7H_9O^+$	Benzyl alcohol	[43]	[44]
115.113	115.112	$C_7H_{15}O^+$	2-Heptanone/heptanal	[36]	[34]
119.086	119.085	$C_9H_{11}^+$	Methylstyrene	[45]	[44]
121.101	121.101	$C_9H_{13}^+$	Cumene	[26]	[3,34]
135.117	135.117	$C_{10}H_{15}^+$	p-Cymene	[25]	[3,34,35,40]
137.126	137.132	$C_{10}H_{17}^+$	Monoterpenes	[25]	[3,34,35,40]
143.143	143.143	$C_9H_{19}O^+$	2-Nonanone/nonanal	[36]	[3,34]
205.195	205.195	$C_{15}H_{25}^+$	Sesquiterpenes	[25,26]	[3,44]
223.061	223.064	$C_6H_{18}O_3Si_3H^+$	D3	[37]	[15]
297.075	297.082	$C_8H_{24}O_4Si_4H^+$	D4	[37]	[15]
311.162	311.135	$C_{10}H_{30}O_3Si_4H^+$	L4	[37]	[15]
371.092	371.101	$C_{10}H_{30}O_5Si_5H^+$	D5	[37]	[15]

[2] = Papurello et al., (2012); [3] = Mata-Alvarez et al., (2000); [6] = Staley et al., (2008); [15] = Papadias et al., (2012); [25] = Biasioli et al., (2011); [26] = Jordan et al., (2009); [34] = Scaglia et al (2011); [35] = Font et al., (2011); [36] = Buhr et al., 2002; [37] = Singer et al., (2011); [38] = Lomans et al., (2002); [39] = Knighton et al., (2012); [40] = Orzi et al., (2010); [41]

= Wang and Wu (2008); [42] = Aprea et al., 2007; [43] = Brilli et al., (2014); [44] = Demirbas et al., (2007); [45] = Yuan et al., (2013); [46] = Vairavamurthy and Mopper (1987).
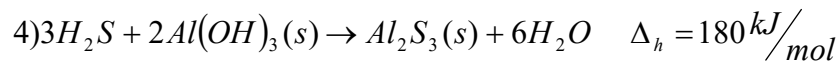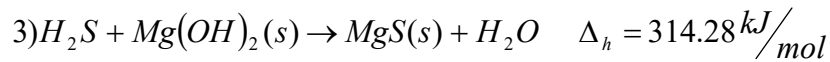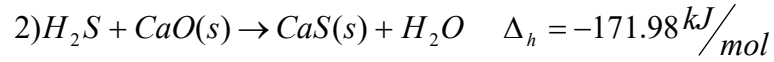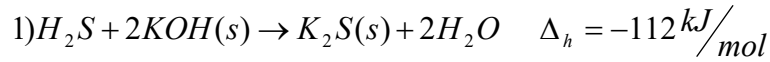
Table 3 - Spectrometric peaks which has been used in this paper along with their experimental and expected m/z values, their chemical formula and tentative identification supported also by available literature.

3   Results and discussion

Monitoring of Volatile Organic Compounds removal by ashes

Volatile organic molecules interact with sorbent surfaces with forces originating either from the "physical" (physisorption) Van der Waals interaction, or from the "chemical" (chemisorption) hybridization of their orbitals with atoms of the ash. Ashes are predicted to work by a physisorption mechanism, while for example ZnO works through a chemisorption mechanism, as reported also in literature to remove sulfur compounds, especially H_2S [1].

As an example of H_2S removal from the biogas stream possible reactions that can occur are equations 1-4:

$$1) H_2S + 2KOH(s) \rightarrow K_2S(s) + 2H_2O \quad \Delta_h = -112 \frac{kJ}{mol}$$

$$2) H_2S + CaO(s) \rightarrow CaS(s) + H_2O \quad \Delta_h = -171.98 \frac{kJ}{mol}$$

$$3) H_2S + Mg(OH)_2(s) \rightarrow MgS(s) + H_2O \quad \Delta_h = 314.28 \frac{kJ}{mol}$$

$$4) 3H_2S + 2Al(OH)_3(s) \rightarrow Al_2S_3(s) + 6H_2O \quad \Delta_h = 180 \frac{kJ}{mol}$$

Equations 3 and 4 are endothermic, requiring heat to produce the final products. These two reactions are not spontaneous. Equations 1 and 2 show a negative enthalpy of formation, these reactions are spontaneous. Potassium and calcium, see table 2, are the most abundant components of the ash enabling removal of sulfur compounds contained in the biogas stream. Calcium and potassium are alkaline earth metal and alkali metal which are able to react to form stable compounds with sulfur [29][30]. The following sections describe the pass through ratio of the

primary VOCs in biogas by wood ash. To permit the comparison between the different compounds and between the two removal tests, dry or wet sorbent conditions, results are plotted in terms of final to initial concentrations, C/C_0 or a "pass through" ratio.
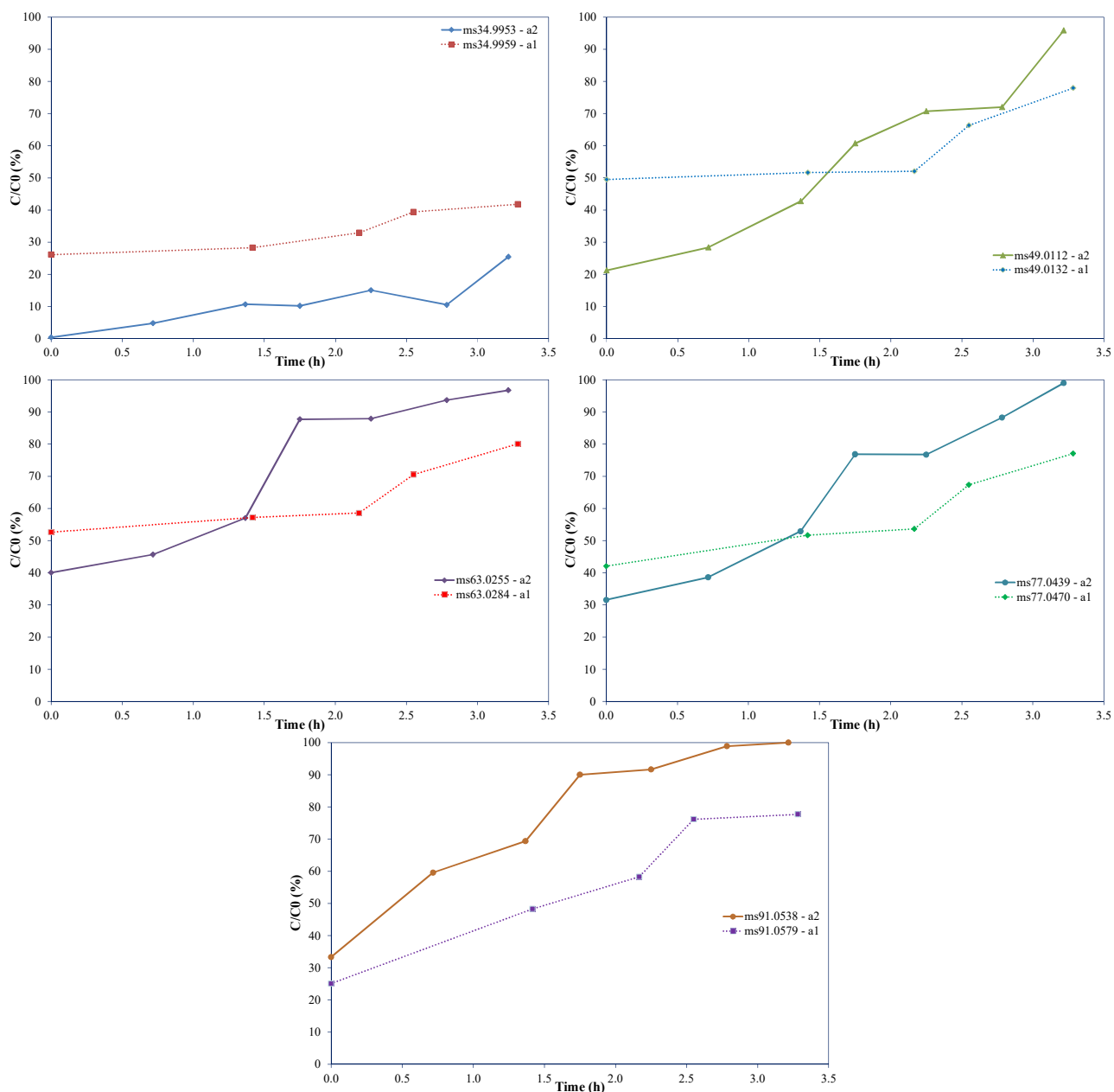
3.1 Sulfur compounds

As reported in our previous study, the organic waste digestion which produces trace sulfur compounds (mainly H_2S and thiols) is dependent on the transition between aerobic to anaerobic digestion [2]. H_2S burst peaks occur at the beginning and at the end of the digestion process. The most abundant thiols, propanethiol and butanethiol are mainly produced at the end of the digestion process. This means that in the middle of the digestion process, the time period of interest, sulfur compounds are produced more slowly. This period of sulfur production corresponds to the best fuel quality and quantity of methane and carbon dioxide levels for SOFC applications. The maximum concentration of sulfur compounds detected during the ash fuel cleaning experiment, in the biogas from the digester is reported in table 4.

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
H_3S^+	Hydrogen sulfide	1673	1730	482000
CH_5S^+	Methanethiol	778	19.4	29180
$C_2H_7S^+$	Dimethylsulfide (DMS)	13.4	15.3	22490
$C_3H_9S^+$	Propanethiol	64	2066	3780
$C_4H_{11}S^+$	Butanethiol	1685	-	1855

Table 4 – Spectrometric sulfur peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

The maximum concentration detected for sulfur compounds during the anaerobic digestion batch is H_2S (1.6 ppm(v)) and $C_4H_{10}S$ (1.7 ppm(v)). The H_2S, CH_4S and C_2H_6S concentrations show a comparable behavior with a previous batch digested at FEM.

Figure 3 – 34.995 H_2SH^+, 49.01 CH_4SH^+, 63.02 $C_2H_6SH^+$, 77.041 $C_3H_8SH^+$, 91.057 $C_4H_{10}SH^+$, VOCs pass through ratio for sulfur compounds.

Fig. 3 depicts the pass through ratio of sulfur compounds of the ash sorbent gas cleaning section during a period of time in the digestion process. The identifier "a1" is for data on the 15th day of digestion with a dry ash cleaning section while "a2" identifies the 16th day of digestion with a wet ash filter. Comparing the dry condition to the wet condition, at the start of test, sulfur compounds show a C/C_0 between 30 and 50%. This is expected due to the low specific surface area and porosity, as pictured in fig. 2. This means that materials are mostly oxidized and extremely dense.

After 3 h of removal test only H_2S shows a pass through ratio still below 50% while the other sulfur compounds have a pass through ratio above 80% (dry condition). Considering the wet ash condition, H_2S is the only compound that shows a notable improvement. This is probably due to the higher solubility in water of H_2S on the liquid film that covers the Ca and K oxide particles in the ash sample, as reported in table 4. Compared to the other sulfur compounds, H_2S shows an improvement of 40% in the pass through ratio. This behavior was also reported by Kastner et al., (2003) [24]. In contrast, CH_4S, C_2H_6S, C_3H_8S and $C_4H_{10}S$ instead show a reduction of removal performance that ranges from 17 to 23% compared to the dry ash condition. This behavior is caused by the plugging of sorbent pores by water. The water acts as inert for higher molecular weight components. The total sulfur removed by dry ash is 61.8 mg$_S$/kg$_{ash}$ while in wet ash is 15 mg$_S$/kg$_{ash}$. One of the few compounds that shows better performance of removal in wet conditions is H_2S. The method adopted to evaluate the sulfur capacity, as well as the other adsorption capacities, follows this formula:

$$5)\, Ac = \sum_i \frac{x_i(ppb(v)) \cdot MW}{24.45 \cdot 1000} \cdot \dot{G_i} \cdot t_i \cdot \left(1 - \frac{C_i}{C_0}\right) \cdot \frac{1}{S_m}$$

Where:

- Ac, adsorption capacity (mg/g),
- x_i, ppb(v) concentration detected from the PTRMS instrument during i-time,
- MW, molecular weight (g/mol),
- G_i, fuel flow rate during i-time (l/min),
- t_i, testing time (min),
- S_m, sorbent material tested (g),
- C_i/C_0, pass through ratio between concentration detected in i-time and C_0 maximum concentration detected.

3.2 Ammonia

15

Kayhanian (1999) shows how ammonia production is related to the biological decomposition of proteins contained in the OFMWS batch [48]. The ammonia emission profiles, as reported in our previous work (Papurello et al., (2012)) shows a burst peak during the methanogenesis area [49]. Table 5 lists the ammonia peak concentration. The maximum concentration detected at 15th day of AD process of OFMSW, is comparable with a previous batch (2012), in a similar digestion phase. These two OFMSW batches were conducted according to the same procedure to produce biogas.

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))
NH_4^+	Ammonia	2613.4	2781

Table 5 – Spectrometric ammonia peak: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Figure 4 shows the ammonia pass through ratio for the two ash conditions: dry or wet. After 3.3 h breakthrough was complete when the ammonia passed completely through the cleaning section with no further reduction. Compared to sulfur, NH_3 at start of test shows a C/C_0 value around 80% for both dry and wet ash conditions. Considering this result, ashes are not suitable to remove ammonia from a biogas stream. As reported by Fuerte et al., (2009), ammonia does not represents a problem for SOFC applications, but rather for the balance of plant of the system [50]. Following equation 5 the adsorption capacity of ammonia ranges from 4 and 2 mg/kg, respectively in dry and wet conditions.
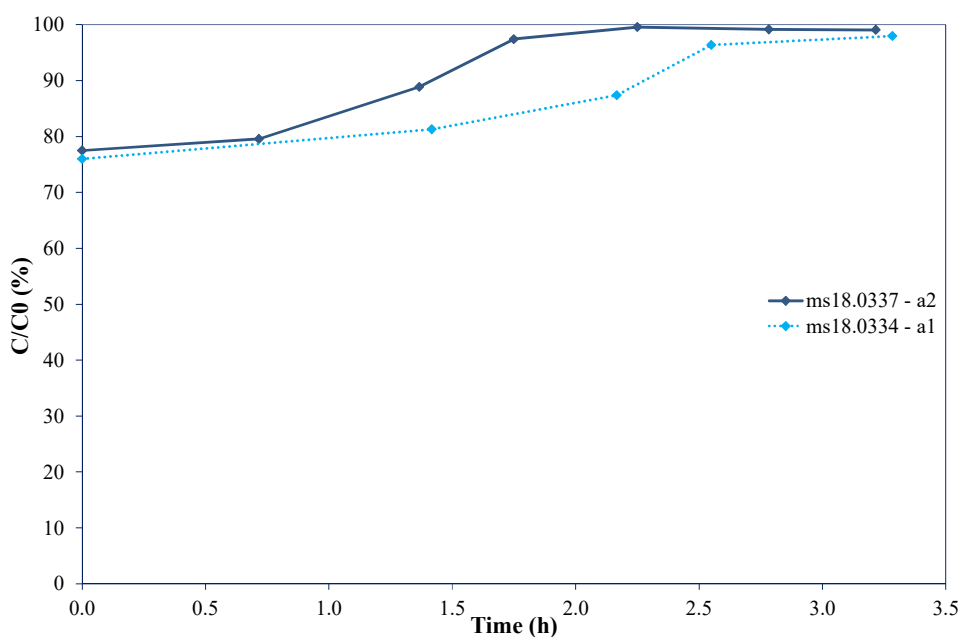
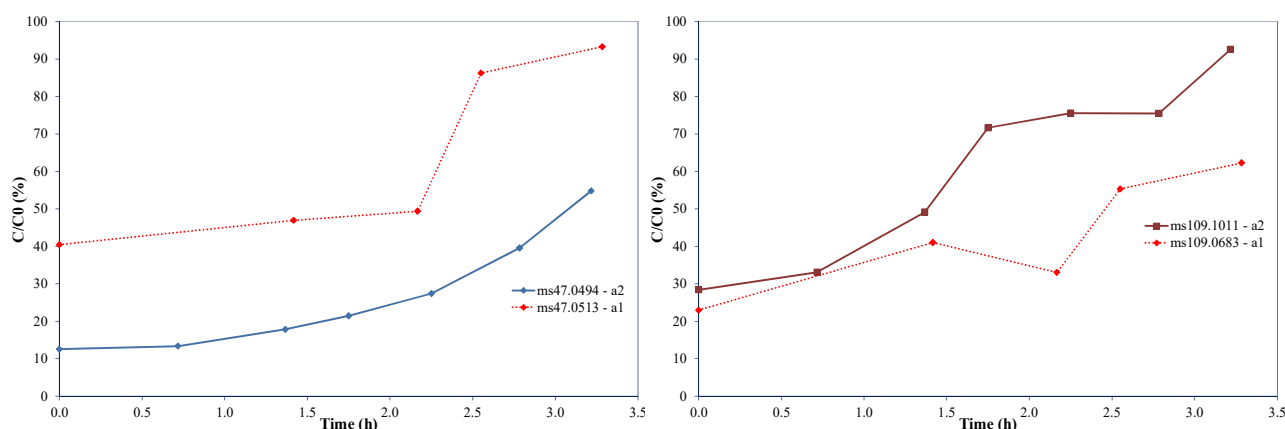**Figure 4 – 18.033 NH_3H^+, VOCs pass through ratio for ammonia.**

3.3 Alcohols

Due to the similarity of the fragmentation pattern several alcohols cannot be tentatively identified with the PTR-ToF-MS [42]. The alcohols which were identified are mainly ethanol and benzyl alcohol. They were strongly released during the first days of the digestion process and a contoinuing reduction of production during the remaining days of process [49]. This behavior, as reported by Staley et al., (2006) is due to the fermentative biopolymers decomposition during the hydrolysis stage in an acidic environment [6]. Table 6 compares the ethanol and benzyl alcohol concentrations detected in two different batches at similar times during digestion. The concentrations are the same order of magnitude. The highest alcohol concentration was ethanol at 1.7 ppm(v).

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_2H_7O^+$	Ethanol	1691.5	1006	792100
$C_7H_9O^+$	Benzyl alcohol	7.3	17.5	9246

Table 6 – Spectrometric alcohol peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

The higher water solubility of ethanol compared to benzyl alcohol accounts for its pass through ratio improvement in wet conditions. This is due to the formation of a liquid film around the ash particle. For the entire test removal of ethanol by wet ash, is always better than the performance in dry ash. This improvement is not observed for benzyl alcohol. Here the pass through ratio starts to be around 20-30 % at the beginning of test and rises to 60 and 90% in dry and wet conditions. See figure 5.

Figure 5 – 47.049 $C_7H_8OH^+$, 109.06 $C_2H_6OH^+$, VOCs pass through ratio for alcohol compounds.

Removal of benzyl alcohol the pass through ratio was better with dry ash due to water plugging of the sorbent pores and acting inert to the component. Following equation 5 the adsorption capacity of alcohols ranges from 15 and 3 mg/kg, respectively in dry and wet conditions.

3.4 Carbonyl and carboxyl compounds

In general, low molecular weight aldehydes, formaldehyde and acetaldehyde are well identified by PTR-ToF-MS despite being isobaric aldehydes. Carbonyl compounds derive from the oxidation of alcohols and can be formed under both aerobic and anaerobic conditions. PTR-ToF-MS detected essentially two production peaks: the first during the aerobic stage and the other during the methanogenesis stage [49]. Throughout the entire digestion process high carbonyl levels were detected, as also reported in Orzi et al., (2010) [40]. In Papurello et al., (2012) two different mechanistic approaches were proposed and investigated [49]. Table 7 shows the chemical formula,

tentative identification and maximum concentrations detected during the entire AD process of two different batches. Batch T2 was used for comparison for removal of carbonyl and carboxyl compounds by ashes. The most abundant compound is 2-butanone (m/z 73.06) at 24.7 ppm(v), followed by acetone (m/z 59.05) at 2.5 ppm(v), acetaldehyde (m/z 31.02) at 0.8 ppm(v) and 2-pentanone (m/z 89.06) at 0.7 ppm(v). The formation of carboxylic compounds is generally due to the lipids breakdown or action of acidogenic bacteria on carbohydrates [36,42]. The concentration of carboxyl compounds is lower than carbonyl compounds. The most abundant compound is formic acid (m/z 47.01) at 370.4 ppb(v), acetic acid (m/z 61.03) at 226 ppb(v), propionic acid (m/z 75.04) at 20.6 ppb(v) and butyric acid (m/z 89.06) at 15.3 ppb(v). The formation of these compounds is predominant at the first stages of digestion under acidic conditions. The concentrations measured are generally in agreement with data measured in a previous batch on a similar day of digestion, see table 7 [49].

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
CH_3O^+	Formaldehyde	190	183.4	57020
$C_2H_5O^+$	Acetaldehyde	819	728	256800
$CH_3O_2^+$	Formic acid	370.4	53.8	955200
$C_3H_7O^+$	Acetone	2542.7	1691	219900
$C_2H_5O_2^+$	Acetic acid	226	571.4	475900
$C_4H_9O^+$	2-butanone/butanal	24728.6	25666	76100
$C_3H_7O_2^+$	Propionic acid/propanoates	20.6	141.4	173600
$C_5H_7O^+$	Cyclopentenone	187.9	148	32190
$C_5H_{11}O^+$	2-Pentanone/Pentanal	689.4	287.3	21230
$C_4H_9O_2^+$	Butyric acid/butyrates	15.3	15	66060
$C_6H_{13}O^+$	2-Hexanone/hexanal	272.3	86	7745
$C_7H_{15}O^+$	2-Heptanone/heptanal	116	175	2145

Table 7 – Spectrometric carbonyl and carboxyl peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.
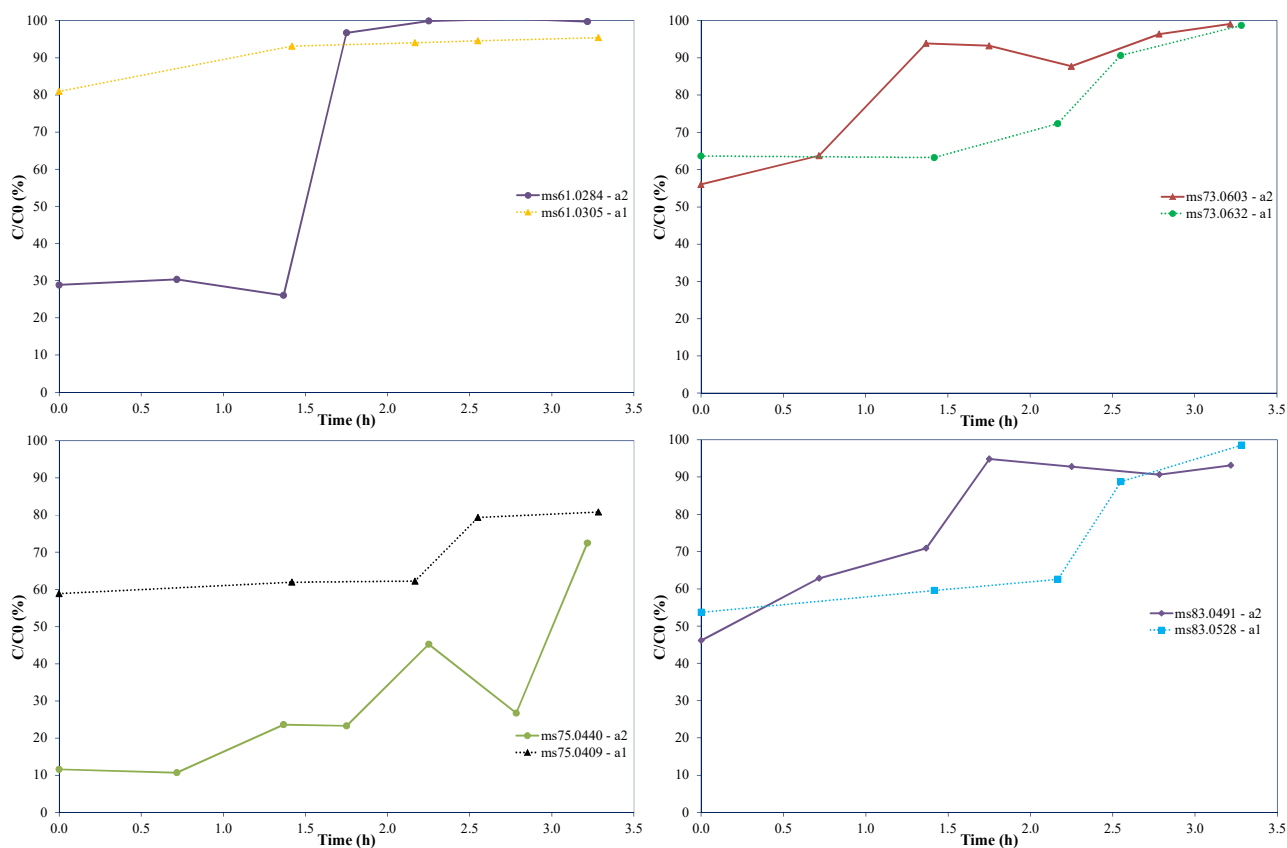
Fig. 6 depicts the pass through ratio for m/z 31, m/z 45, m/z 47 and m/z 59 in dry and wet ash conditions. After 3.3 h of test the pass through ratio is almost 100%. After this time the carbonyl and carboxyl compounds can pass into a SOFC energy generator where they serve as fuel. The removal trend is similar for the various compounds. The liquid water film accounts for their removal in the early hours of testing, see figs. 6, 7 and 8.
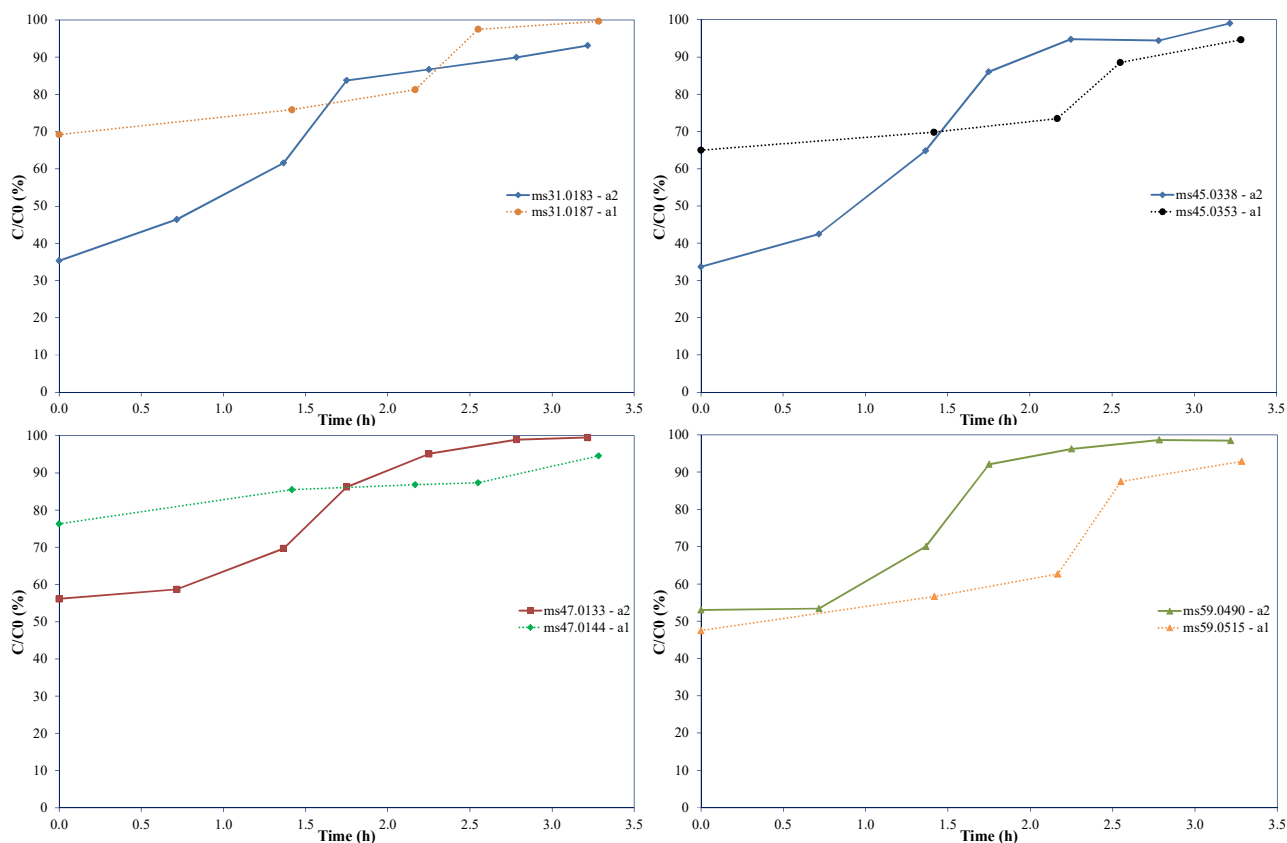
Figure 6 – 31.017 CH_2OH^+, 45.033 $C_2H_4OH^+$, 47.013 $CH_2O_2H^+$, 59.049 $C_3H_6OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

Fig. 7 depicts the pass through ratio for m/z 61, m/z 73, m/z 75 and m/z 83 in dry and wet ash conditions. Except for m/z 75, the sorbent is saturated after 3.3 h of test and no more removal occurs. At the beginning of test m/z 73 is reduced to half the initial concentration. However this could be a problem for a SOFC energy generator if the starting concentration value is high (≈ 25 ppm(v)). The liquid water film improves the removal performance especially at the beginning of test. Due to their higher water solubility m/z 61 and m/z 75 shows better removal performance by

wet ash. For the compounds with low solubility water plugs the few pores, causing a decrease of the removal performance. At the end of test the low solubility compounds continue to pass through the wet ash.

Figure 7 – 61.028 $C_2H_4O_2H^+$, 73.065 $C_4H_8OH^+$, 75.044 $C_3H_6O_2H^+$, 83.049 $C_5H_6OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

Fig. 8 depicts the pass through ratio for m/z 87, m/z 89, m/z 101 and m/z 115. The C/C_0 profiles in different conditions (wet or dry) are similar except for 2-heptanone. Here, the wet ash does not remove the 2-heptanone as strongly. This could be related to its poor water solubility. Following equation 5 the adsorption capacity of carbonyls ranges from 291 and 132 mg/kg, respectively in dry and wet conditions; while for carboxyls the adsorption capacity remains fixed at 3 mg/kg in both conditions.
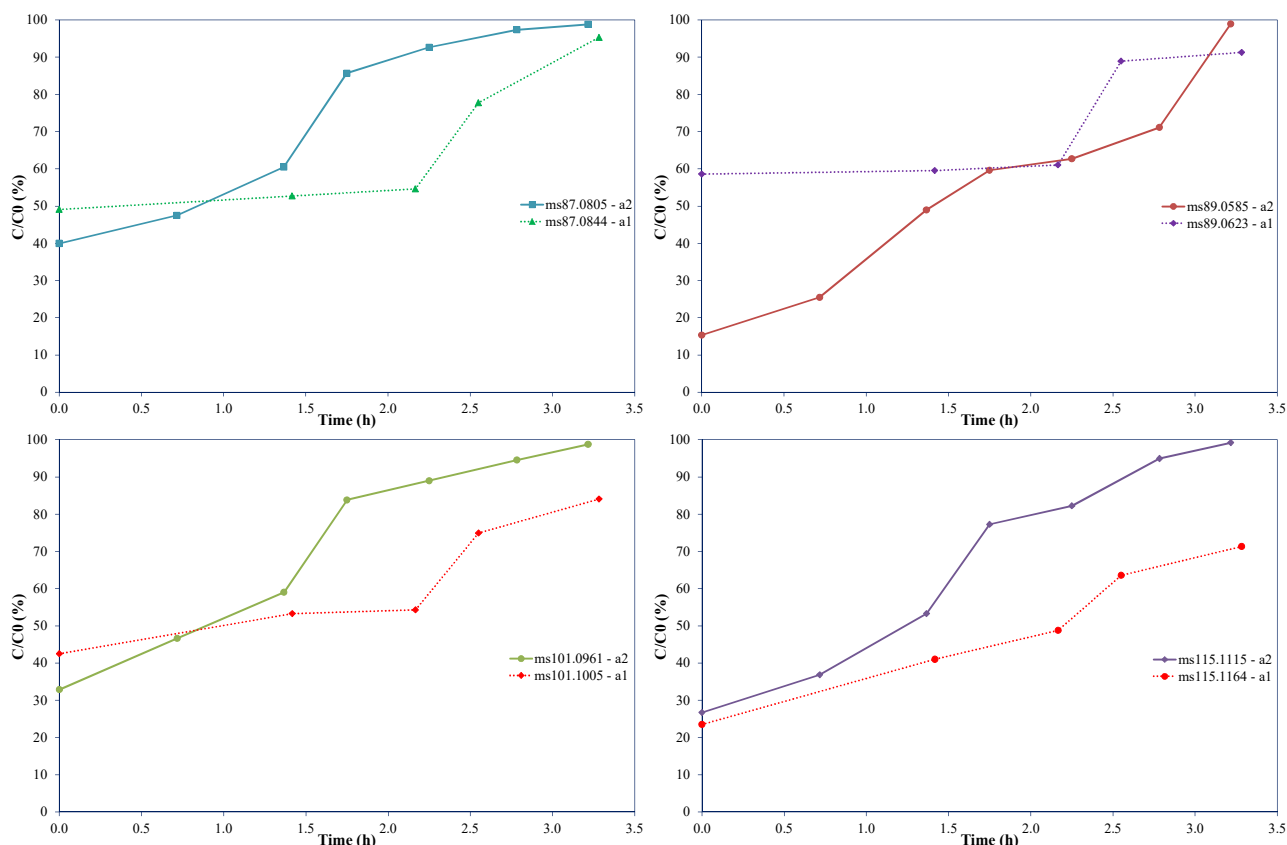
Figure 8 – 87.08 $C_5H_{10}OH^+$, 89.059 $C_4H_8O_2H^+$, 101.096 $C_6H_{12}OH^+$, 115.11 $C_7H_{14}OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

3.5 Terpenes

Terpenes measured by PTR-ToF-MS spectra are: m/z 69.07 (isoprene), m/z 135.11 (p-cymene), m/z 137.13 (monoterpenes), and m/z 205.01 (sesquiterpenes). These compounds, come from the high content of fruit and vegetables in OFMSW as reported in literature [40,51]. As we previously reported, at the beginning of the digestion process both isoprene and monoterpenes have high concentrations. At the end of digestion process, production of monoterpenes rapidly increase and finally stabilize at higher concentration [49]. Table 8 reports the terpenes concentration measured during the AD process in the 15th day of process in addition to the measurements from another batch, 13th day. Both batches had the same starting conditions. The most abundant compound detected is monoterpene (m/z 137.13) (postulated to actually be limonene) at 7.7 ppm(v), followed by p-cymene (m/z 135.11) at 6.6 ppm(v) and isoprene (m/z 69.07) at 0.6 ppm(v). The high levels of p-cymene in the biogas indicate the occurrence of d-limonene transformation by the anaerobic

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bacteria, as reported by Orzi et al., (2010) [40]. Terpenes concentrations are in agreement with similar day of digestion from another OFMSW batch processed with same starting conditions [49].

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_5H_9^+$	Isoprene	618	873.4	338.6
$C_9H_{13}^+$	Cumene	77.3	222.4	75.3
$C_{10}H_{15}^+$	p-Cymene	6574	13400.5	28
$C_{10}H_{17}^+$	Monoterpenes	7728	20017	4.6
$C_9H_{19}O^+$	2-Nonanone/nonanal	29	49	170.6
$C_{15}H_{25}^+$	Sesquiterpenes	12.7	26.7	0.1

Table 8 – Spectrometric terpene peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Fig. 9 and 10 depicts the pass through ratio for terpenes. Wood ash is a better sorbent for m/z 135.11, m/z 143.14 and m/z 205.19. Dry ash was a better sorbent for m/z 135.11 during the early hours of test. For m/z 143.14 and m/z 205.19 the removal at the end of test did not reach total breakthrough. A C/C_0 value of 60% is the pass through ratio achieved for m/z 143.11 and 40% for m/z 205.19 at the end of test in dry ash. For the remaining compounds the C/C_0 value range from 80 to 90% in dry conditions. Results plotted in figures 9 and 10, show generally dry ash is better for removal of terpenes compared to wet ash. This is related to the poor water solubility of terpenes. Following equation 5 the adsorption capacity of terpenes ranges from 487 and 126 mg/kg, respectively in dry and wet conditions.
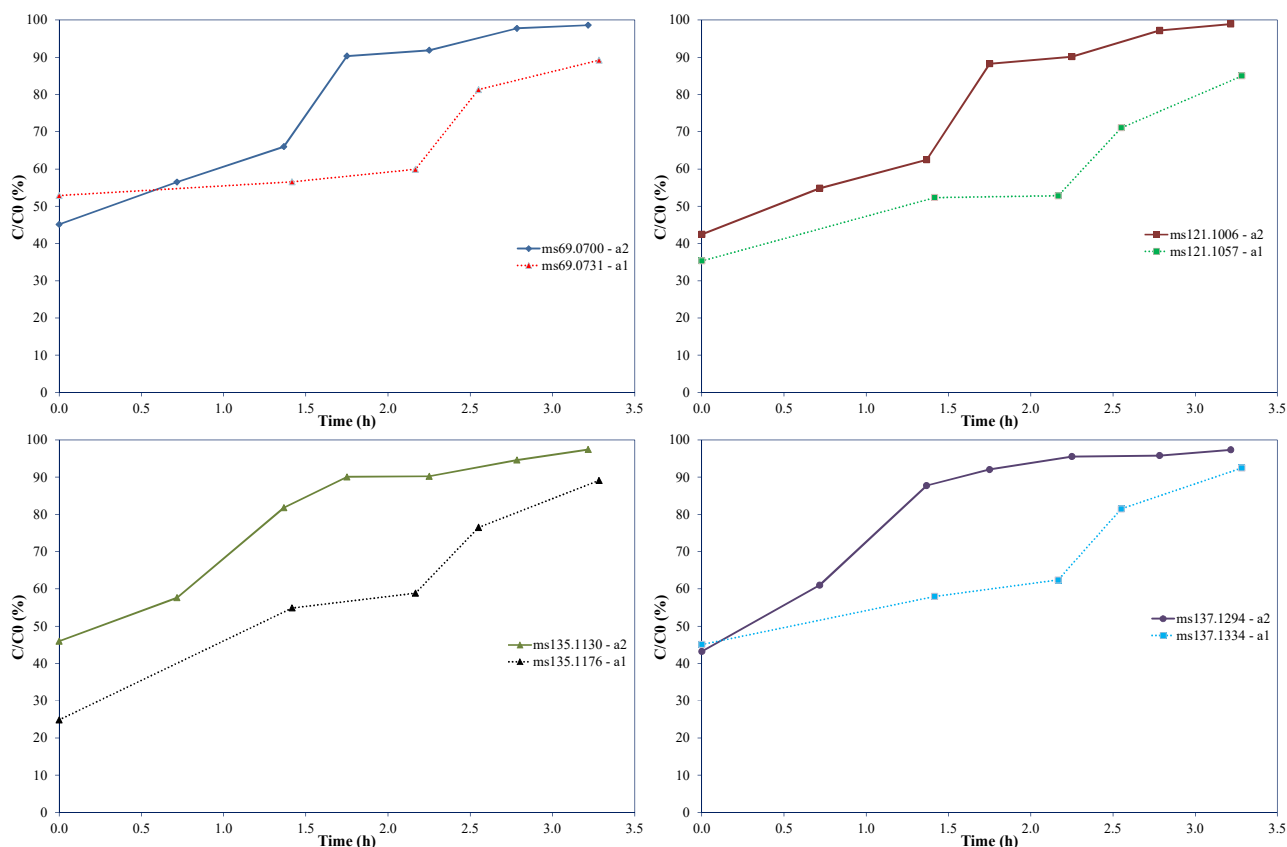
Figure 9 – 69.07 $C_5H_8H^+$, 121.101 $C_9H_{12}H^+$, 135.12 $C_{10}H_{14}H^+$, 137.13 $C_{10}H_{16}H^+$, VOCs pass through ratio for terpene compounds.
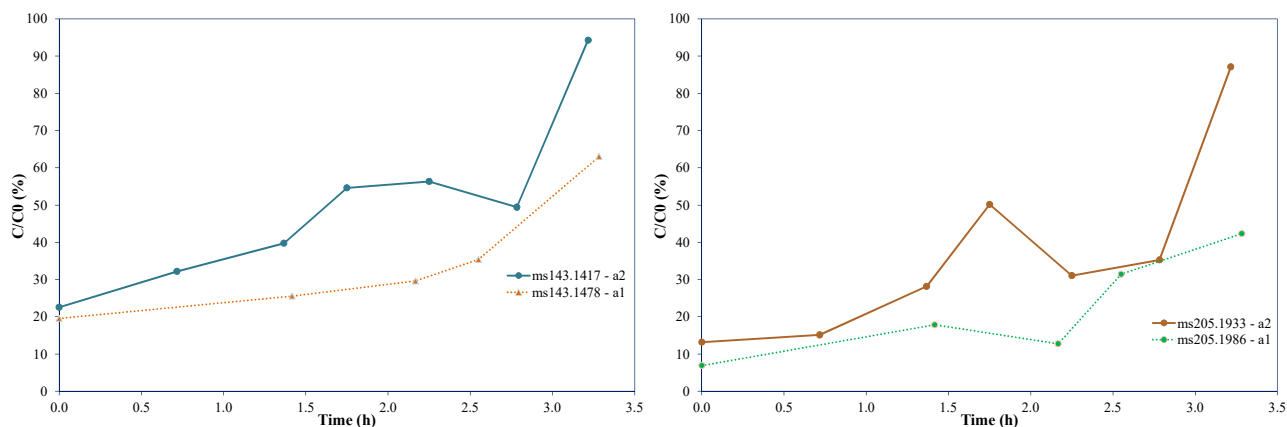
Figure 10 – 143.14 $C_9H_{18}OH^+$, 205.19 $C_{15}H_{24}H^+$, VOCs pass through ratio for terpene compounds.

3.6 Siloxanes

Organosilicon compounds are included in many industrial processes and consumer products, such as hygiene products, cosmetic and biopharmaceuticals, fuel additives, car waxes, detergents and antifoams [52]. Siloxanes contained in the biogas from OFMSW stream are mainly released from

the digestion of biological matter. They come from silicon released from the mass treated inside the digester [53]. The release of organosilicon compounds from the biomass to the biogas, in general, is dependent on the T, p and digestion process. Kazuyuki et al., (2007) estimated that 20–50 % of D5, defined in table 9, in wastewater and activated sludge outgases to the biogas and the rest remains in the digestion residue [54]. At present, there is no standard method for the analysis of volatile siloxanes in a gaseous mixture. Several different methods are studied in literature. See Huppmann et al., (1996) [55], Grümping et al., (1998) [56], Narros et al., (2009) [57], Schweigkofler and Niessner [58], (1999) and Rasi, (2009) [59]. Singer et al., (2011) measured the D5 concentration with a PTR-ToF-MS instrument [37]. The measured isotopic abundance of the compound allowed unambiguous identification of D5 at m/z 371. Singer evidenced how siloxanes in biogas will subsequently deposit in the form of a white powder on hot section components of combustion engine or gas turbine [37].

Table 9 shows the siloxanes concentrations measured in two different OFMSW batches and from a WWTP located in Turin. The most abundant siloxanes compound detected is D5 at 255 ppb(v), followed by D3 at 63.5 ppb(v), D4 at 47.1 ppb(v) and L4 at 26.7 ppb(v). These concentrations are consistent with measurements from a previous AD batch processed at FEM on similar days of the digestion process. A comparison between OFMSW siloxanes and WWTP siloxanes is reported in table 9. For WWTP the most abundant compound is D5 at 482 ppb(v), followed by L4 at 415 ppb(v), D3 at 187 ppb(v) and D4 at 129 ppb(v). As easily seen in table 9, generally the siloxanes concentration in WWTPs is higher compared to OFMSW plants. This has been reported also by others [59–61].

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Smat digester (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_6H_{18}O_3Si_3H^+$	D3	63.5	187	67	1.6
$C_8H_{24}O_4Si_4H^+$	D4	47	129	39.8	0.1
$C_{10}H_{30}O_3Si_4H^+$	L4	26.7	415		0.0

| $C_{10}H_{30}O_5Si_5H^+$ | D5 | 255 | 482 | 310 | 0.0 |

Table 9 – Spectrometric siloxanes peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with SMAT digester and another AD batch.

Fig. 11 depicts the pass through ratio for siloxanes (D3, D4, L4 and D5). At the beginning of the removal test D3, D4 and L4 show a C/C_0 ratio in dry conditions above 50%. D5 shows a C/C_0 below 30% at the beginning of removal test. Wet ash at the beginning of test improves the removal performance except for D5. Here the C/C_0 is $\approx$ 40%. This behavior is related to the higher molecular weight and low water solubility of siloxanes. In fact, increasing the removal time improves dry ash filter performance. During the wet test the reduction of free pores by water plugging inhibits the sorbent material by reducing the available surface area. Following equation 5 the adsorption capacity of siloxanes ranges from 0.21 and 0.14 mg/kg, respectively in dry and wet conditions.
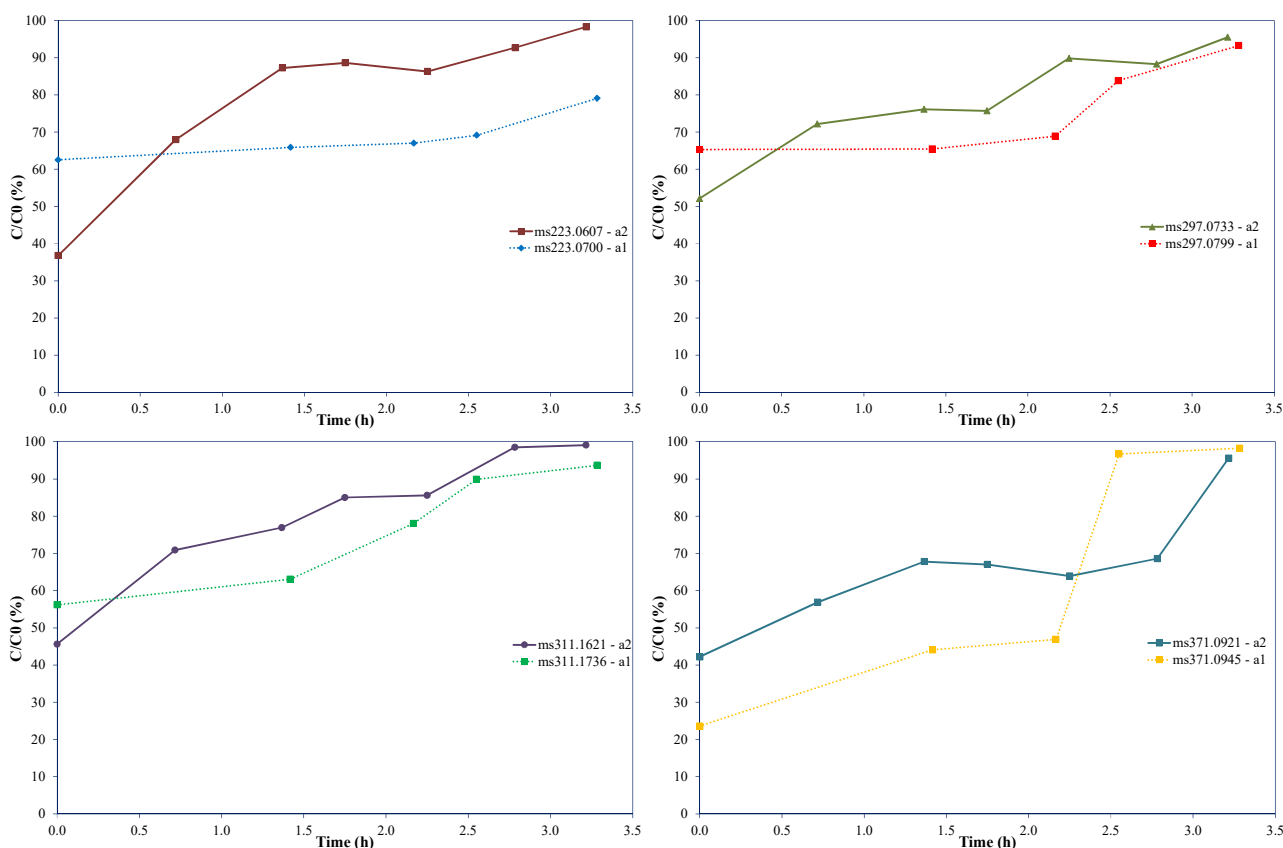
Figure 11 – 223.064 $C_6H_{18}O_3Si_3H^+$, 297.082 $C_8H_{24}O_4Si_4H^+$, 311.13 $C_{10}H_{30}O_3Si_4H^+$, 371.1 $C_{10}H_{30}O_5Si_5H^+$, VOCs pass through ratio for siloxane compounds.

3.7 Preliminary costs evaluation

A preliminary economic study to clean a biogas fuel is conducted comparing two different materials: ashes from a boiler fed by forestry wood-chips and a commercial activated carbon sample. In order to compare these materials we have to consider the purchase cost and the disposal cost avoided or performed. Norit RTS3 was adopted as the commercial activated carbon with a purchased cost of 6.5 €/kg, while was 0 €/kg for ashes. This because they are by-products coming from the local boiler plant of Fondazione Edmund Mach. The size of the boiler considered was 30 kW fed by forestry wood-chips coming from the local area. In Italy, if ashes from woodchips are not treated with solvents, are considered as fertilizers and compostable materials, with a CER code 100103. Here, we can consider the disposal costs of ashes avoided or costs reduced for the soil enrichment. This is true if we can re-use the material as fertilizer inside the agricultural cycle of the Institute. The adoptable amount as fertilizer ranges from 200-3100 kg/ha/y. Otherwise, the disposal costs in landfills can range from 0.1 to 0.25 €/kg (Regione Piemonte). Considering the activated carbon disposal costs an average value can be fixed around at 0.81 €/kg (APAT, 2010), with a CER code 190110. For the economic evaluation, was considered a production of biogas around 1 m^3/h for 30 days from the anaerobic digestion of OFMSW. 30 days is the typical cycle for the anaerobic digestion process to exploit OFMSW to produce biogas. H_2S, is the main compound detected from the biogas and it is the most detrimental compound for the SOFC performance. For the concentrations detected and for the SOFC effects, H_2S is crucial compared to the other compounds that could affect the energy generator. An average value was fixed around 80 ppm(v) of concentration and it was kept constant during the process. The sulfur capacity found for the activated commercial sample is around 207 mgS/g. This data was found experimentally (data not shown in this paper), while ashes from wood-chips show a sulfur capacity around 0.66 mgS/g. Both of results were achieved considering a biogas with water content around 30%. For 30 days of biogas production to feed a 500 We SOFC energy generator, 389 g of activated carbon and 122.2 kg of ashes are required. To obtain the amount of desired ashes, considering a process of combustion with forestry wood-chips with 1% of ashes, the boiler have to burn 12.2 t of wood, corresponding to 14

m^3. The boiler of the Institute works for 20 weeks per year and it needs around 50 m^3 per year of wood. The ashes will not be disposed in landfills but adopted as fertilizer, but first will be adopted as sorbent material, avoiding 30.55 €/cycle. The purchasing cost of the activated carbon quantity required is 2.53 € with a disposal cost around 0.31 €. The amount required, 389 g of activated carbon is compatible with the reactor volume installed. If we wanted to work with ashes, the reactor volume should be doubled and once a day, the spent catalyst should be removed and loaded in the second reactor to avoid the plant shutdown. These information and these results certify as ashes are not economically and, mainly technically exploitable to work with SOFC energy generators. This is due to two factors: the low cost of activated carbons and the low sulfur capacity of ashes.

4 Conclusions

Ashes from wood-chips as sorbent material for VOCs removal contained in a biogas from OFMSW were tested with a PTR-ToF-MS instrument for the first time. H$_2$S, VOSCs, terpenes, siloxanes, carboxylic acids and carbonyl compounds were tentatively identified and simultaneously monitored during the removal test. Results show how ashes are more efficient in removing H$_2$S, alcohols and some terpenes, compared to thiols, siloxanes and carbonyl compounds. Siloxanes were measured in biogas from an OFMSW anaerobic digestion batch by PTR-ToF-MS. This study tentatively identified siloxanes for the first time. The removal of siloxanes by ash was not attractive. Most of time wetting the ashes with nebulized water at the beginning of the removal test, increased the removal of the VOCs of interest. The best performance was achieved for H$_2$S, ethanol and propionic acid. Resuming results obtained certify how ashes are not economically and technically exploitable to work with SOFC energy generators. This is due to two factors: the low cost of activated carbons and the low sulfur capacity of ashes.

Acknowledgements

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Table captions

Table 1 - Starting values of digestion cycle – Initial biomass parameters.

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

Table 3 - Spectrometric peaks which has been used in this paper along with their experimental and expected m/z values, their chemical formula and tentative identification supported also by available literature.

Table 4 – Spectrometric sulfur peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Table 5 – Spectrometric ammonia peak: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Table 6 – Spectrometric alcohol peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Table 7 – Spectrometric carbonyl and carboxyl peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Table 8 – Spectrometric terpene peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with another AD batch.

Table 9 – Spectrometric siloxanes peaks: chemical formula and tentative identification, maximum concentration detected in the digester comparison with SMAT digester and another AD batch.

Table 1

	Volume (m^3)	Mass (t)	Water content (%)	Volatile Solids (%)	pH in	pH out
Inoculum	7.33 [±0.43]	6.67 [±0.52]	61.6 [±1.02]	55.3 [±3.1]	8.7 [±0.2]	
OFSMW + Wood	9.29 [±0.51]	5.34 [±0.53]	59.5 [±0.75]	82 [±3.2]	5.8 [±0.2]	
Mix	14.95 [±0.52]	12.01 [±0.46]	58.8 [±1.19]	59.8 [±3.3]	7.8 [±0.2]	8.3 [±0.2]

Where:

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

* Mix was left at ambient temperature for 4 days prior to loading into the digester, thereby probably changing the pH e.g. via CO_2 escaping into the atmosphere.

Table 2

Element	Atomic % virgin	Atomic % tested
C	7.73	17.65
O	39.99	54.18
Mg	2.74	0.56
Al	4.07	0.50
Si	9.09	19.46
Cl	-	0.15
K	10.82	6.65
Ca	10.87	0.86
Fe	11.68	-
Ti	0.85	-
Na	0.68	-
Mn	0.73	-
Total:	100.00	100.00

Table 3

Measured m/z	Theoretical m/z	Protonated chemical formula	Tentative identification	References for PTR-MS spectra	References for biogas from waste management
18.033	18.0338	NH_4^+	Ammonia	[26]	[3,34,35]
31.018	31.018	CH_3O^+	Formaldehyde	[36]	[3,35]
34.995	34.995	H_3S^+	Hydrogen sulfide	[2,37]	[3,35,38]
41.038	41.039	$C_3H_5^+$	Propyne	[39]	[15]
45.033	45.033	$C_2H_5O^+$	Acetaldehyde	[26,36]	[34,35,40,41]
47.013	47.013	$CH_3O_2^+$	Formic acid	[26]	[15]
47.049	47.049	$C_2H_7O^+$	Ethanol	[36]	[34,35,40]
49.01	49.011	CH_5S^+	Methanethiol	[2]	[35,38,40]
55.054	55.054	$C_4H_7^+$	Butadiene	[39]	[15]
57.07	57.07	$C_4H_9^+$	Butene	[39]	[15]
59.049	59.049	$C_3H_7O^+$	Acetone	[36]	[34,35,40]
61.028	61.0284	$C_2H_5O_2^+$	Acetic acid	[36,42]	[34,35,40]
63.022	63.0284	$C_2H_7S^+$	Dimethylsulfide (DMS)	[25]	[35,38]
67.054	67.054	$C_5H_7^+$	Cyclopentadiene	[43]	[44]
69.035	69.0335	$C_4H_5O^+$	Furan	[25]	[35]
69.069	69.07	$C_5H_9^+$	Isoprene	[25]	[6]
71.086	71.086	$C_5H_{11}^+$	Cyclopentane	[45]	[2]
73.028	73.028	$C_3H_5O_2^+$	Acrylic acid	[43]	[44]
73.065	73.065	$C_4H_9O^+$	2-butanone/butanal	[36]	[34,35,40]
75.044	75.044	$C_3H_7O_2^+$	Propionic acid/propanoates	[36,42]	[34,35,40]
77.041	77.042	$C_3H_9S^+$	Propanethiol	[2]	[46]
79.054	79.054	$C_6H_7^+$	Benzene	[25]	[34,35,40]
81.068	81.07	$C_6H_9^+$	Cyclohexadiene		[15]
83.049	83.049	$C_5H_7O^+$	Cyclopentenone		[44]
83.085	83.086	$C_6H_{11}^+$	Cyclohexene	[43,45]	[15]
87.081	87.080	$C_5H_{11}O^+$	2-Pentanone/Pentanal	[36]	[34,35,40]
89.059	89.059	$C_4H_9O_2^+$	Butyric acid/butyrates	[36,42]	[35]
91.057	91.057	$C_4H_{11}S^+$	Butanethiol	[2]	[46]
93.07	93.07	$C_7H_9^+$	Toluene	[25,26]	[6,35]
95.086	95.085	$C_7H_{11}^+$	2,5-Dihydrotoluene	[45]	[44]
101.096	101.096	$C_6H_{13}O^+$	2-Hexanone/hexanal	[36]	[34]
105.07	105.07	$C_8H_9^+$	Styrene	[25]	[34,35,40]
107.086	107.086	$C_8H_{11}^+$	Xylene	[25]	[34,35,40]
109.065	109.065	$C_7H_9O^+$	Benzyl alcohol	[43]	[44]

115.113	115.112	$C_7H_{15}O^+$	2-Heptanone/heptanal	[36]	[34]
119.086	119.085	$C_9H_{11}^+$	Methylstyrene	[45]	[44]
121.101	121.101	$C_9H_{13}^+$	Cumene	[26]	[3,34]
135.117	135.117	$C_{10}H_{15}^+$	p-Cymene	[25]	[3,34,35,40]
137.126	137.132	$C_{10}H_{17}^+$	Monoterpenes	[25]	[3,34,35,40]
143.143	143.143	$C_9H_{19}O^+$	2-Nonanone/nonanal	[36]	[3,34]
205.195	205.195	$C_{15}H_{25}^+$	Sesquiterpenes	[25,26]	[3,44]
223.061	223.064	$C_6H_{18}O_3Si_3H^+$	D3	[37]	[15]
297.075	297.082	$C_8H_{24}O_4Si_4H^+$	D4	[37]	[15]
311.162	311.135	$C_{10}H_{30}O_3Si_4H^+$	L4	[37]	[15]
371.092	371.101	$C_{10}H_{30}O_5Si_5H^+$	D5	[37]	[15]

[2] = Papurello et al., (2012); [3] = Mata-Alvarez et al., (2000); [6] = Staley et al., (2008); [15] = Papadias et al., (2012); [25] = Biasioli et al., (2011); [26] = Jordan et al., (2009); [34] = Scaglia et al (2011); [35] = Font et al., (2011); [36] = Buhr et al., 2002; [37] = Singer et al., (2011); [38] = Lomans et al., (2002); [39] = Knighton et al., (2012); [40] = Orzi et al., (2010); [41] = Wang and Wu (2008); [42] = Aprea et al., 2007; [43] = Brilli et al., (2014); [44] = Demirbas et al., (2007); [45] = Yuan et al., (2013); [46] = Vairavamurthy and Mopper (1987).

Table 4

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
H_3S^+	Hydrogen sulfide	1673	1730	482000
CH_5S^+	Methanethiol	778	19.4	29180
$C_2H_7S^+$	Dimethylsulfide (DMS)	13.4	15.3	22490
$C_3H_9S^+$	Propanethiol	64	2066	3780
$C_4H_{11}S^+$	Butanethiol	1685	-	1855

Table 5

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))
NH_4^+	Ammonia	2613.4	2781

Table 6

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_2H_7O^+$	Ethanol	1691.5	1006	792100
$C_7H_9O^+$	Benzyl alcohol	7.3	17.5	9246

Table 7

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
CH_3O^+	Formaldehyde	190	183.4	57020
$C_2H_5O^+$	Acetaldehyde	819	728	256800
$CH_3O_2^+$	Formic acid	370.4	53.8	955200
$C_3H_7O^+$	Acetone	2542.7	1691	219900
$C_2H_5O_2^+$	Acetic acid	226	571.4	475900
$C_4H_9O^+$	2-butanone/butanal	24728.6	25666	76100
$C_3H_7O_2^+$	Propionic acid/propanoates	20.6	141.4	173600
$C_5H_7O^+$	Cyclopentenone	187.9	148	32190
$C_5H_{11}O^+$	2-Pentanone/Pentanal	689.4	287.3	21230
$C_4H_9O_2^+$	Butyric acid/butyrates	15.3	15	66060
$C_6H_{13}O^+$	2-Hexanone/hexanal	272.3	86	7745
$C_7H_{15}O^+$	2-Heptanone/heptanal	116	175	2145

Table 8

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_5H_9^+$	Isoprene	618	873.4	338.6
$C_9H_{13}^+$	Cumene	77.3	222.4	75.3
$C_{10}H_{15}^+$	p-Cymene	6574	13400.5	28
$C_{10}H_{17}^+$	Monoterpenes	7728	20017	4.6
$C_9H_{19}O^+$	2-Nonanone/nonanal	29	49	170.6
$C_{15}H_{25}^+$	Sesquiterpenes	12.7	26.7	0.1

Table 9

Protonated chemical formula	Tentative identification	Maximum concentration detected -15th day (ppb(v))	Smat digester (ppb(v))	Batch T2 FEM at 13th day (ppb(v))	Solubility in water at 25 °C, p atm (mg/l) [47]
$C_6H_{18}O_3Si_3H^+$	D3	63.5	187	67	1.6
$C_8H_{24}O_4Si_4H^+$	D4	47	129	39.8	0.1
$C_{10}H_{30}O_3Si_4H^+$	L4	26.7	415		0.0
$C_{10}H_{30}O_5Si_5H^+$	D5	255	482	310	0.0

Figure captions

Figure 1 – Biogas to gas cleaning section – experimental set up.

Figure 2 – A SEM image of the ash sample tested, B SEM image of the activated carbon sample, C SEM image of the virgin ash sample.

Figure 3 – 34.995 H_2SH^+, 49.01 CH_4SH^+, 63.02 $C_2H_6SH^+$, 77.041 $C_3H_8SH^+$, 91.057 $C_4H_{10}SH^+$, VOCs pass through ratio for sulfur compounds.

Figure 4 – 18.033 NH_3H^+, VOCs pass through ratio for ammonia.

Figure 5 – 47.049 $C_7H_8OH^+$, 109.06 $C_2H_6OH^+$, VOCs pass through ratio for alcohol compounds.

Figure 6 – 31.017 CH_2OH^+, 45.033 $C_2H_4OH^+$, 47.013 $CH_2O_2H^+$, and 59.049 $C_3H_6OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

Figure 7 – 61.028 $C_2H_4O_2H^+$, 73.065 $C_4H_8OH^+$, 75.044 $C_3H_6O_2H^+$, and 83.049 $C_5H_6OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

Figure 8 – 87.08 $C_5H_{10}OH^+$, 89.059 $C_4H_8O_2H^+$, 101.096 $C_6H_{12}OH^+$, and 115.11 $C_7H_{14}OH^+$, VOCs pass through ratio for carbonyl and carboxyl compounds.

Figure 9 – 69.07 $C_5H_8H^+$, 121.101 $C_9H_{12}H^+$, 135.12 $C_{10}H_{14}H^+$, 137.13 $C_{10}H_{16}H^+$, VOCs pass through ratio for terpene compounds.

Figure 10 – 143.14 $C_9H_{18}OH^+$, 205.19 $C_{15}H_{24}H^+$, VOCs pass through ratio for terpene compounds.

Figure 11 – 223.064 $C_6H_{18}O_3Si_3H^+$, 297.082 $C_8H_{24}O_4Si_4H^+$, 311.13 $C_{10}H_{30}O_3Si_4H^+$, 371.1 $C_{10}H_{30}O_5Si_5H^+$, VOCs pass through ratio for siloxane compounds.

Figure 1
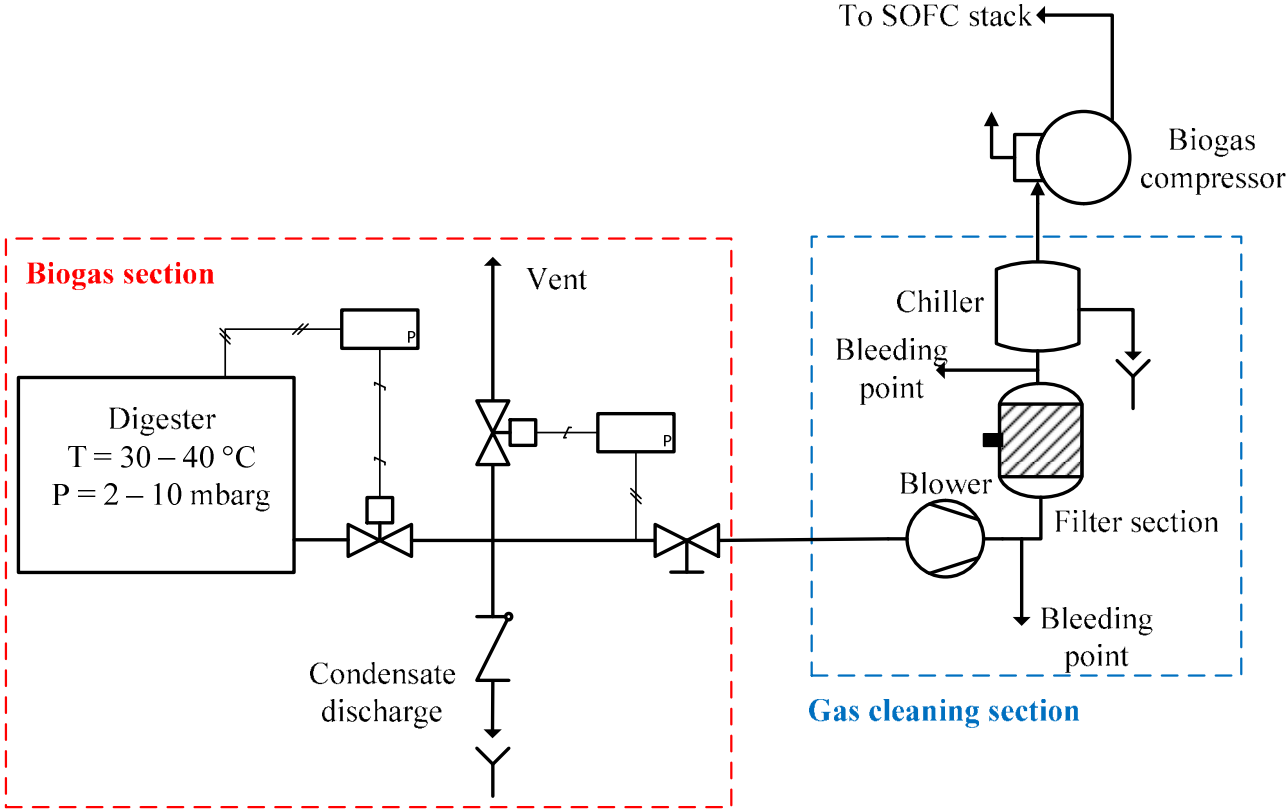
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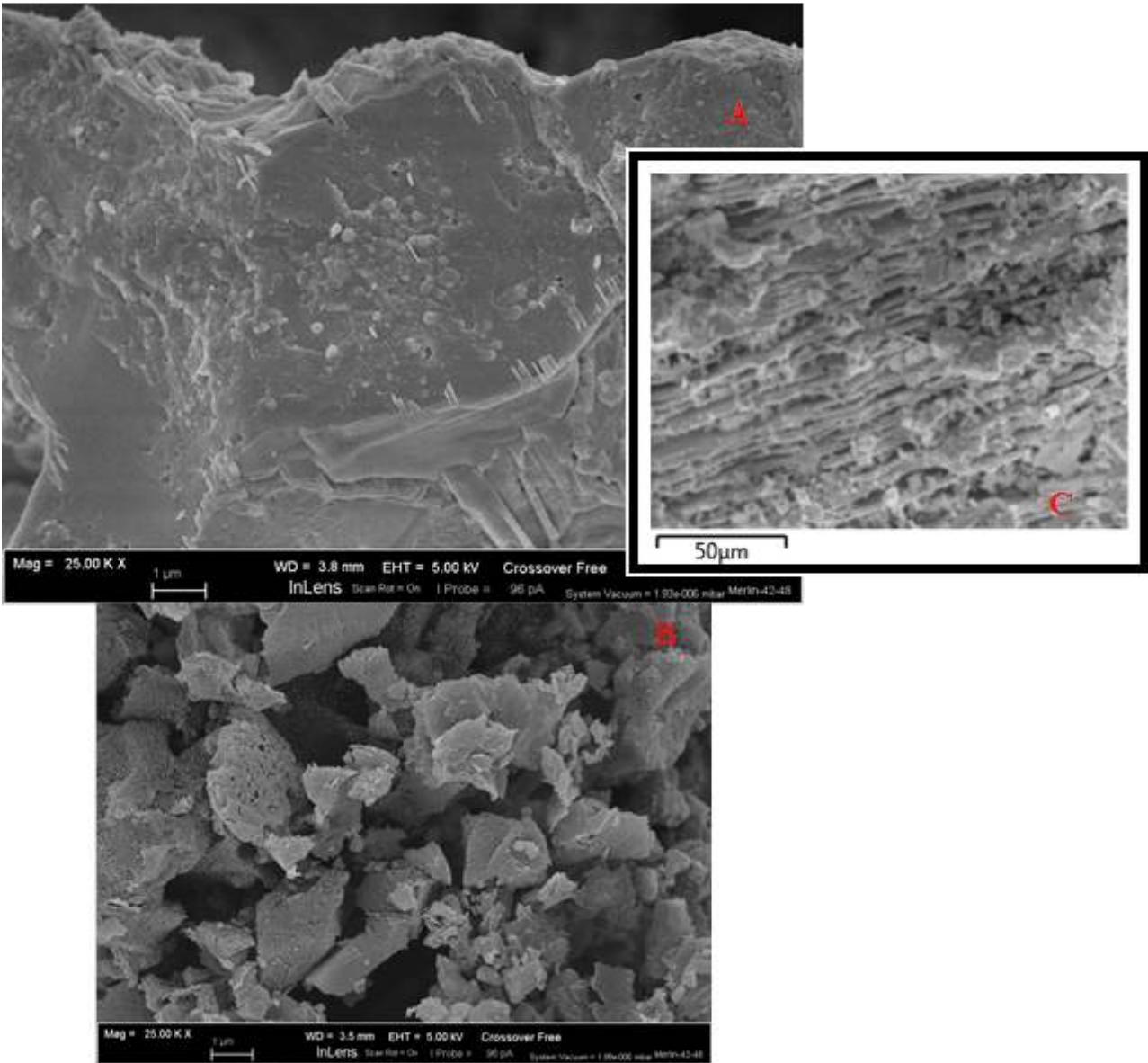
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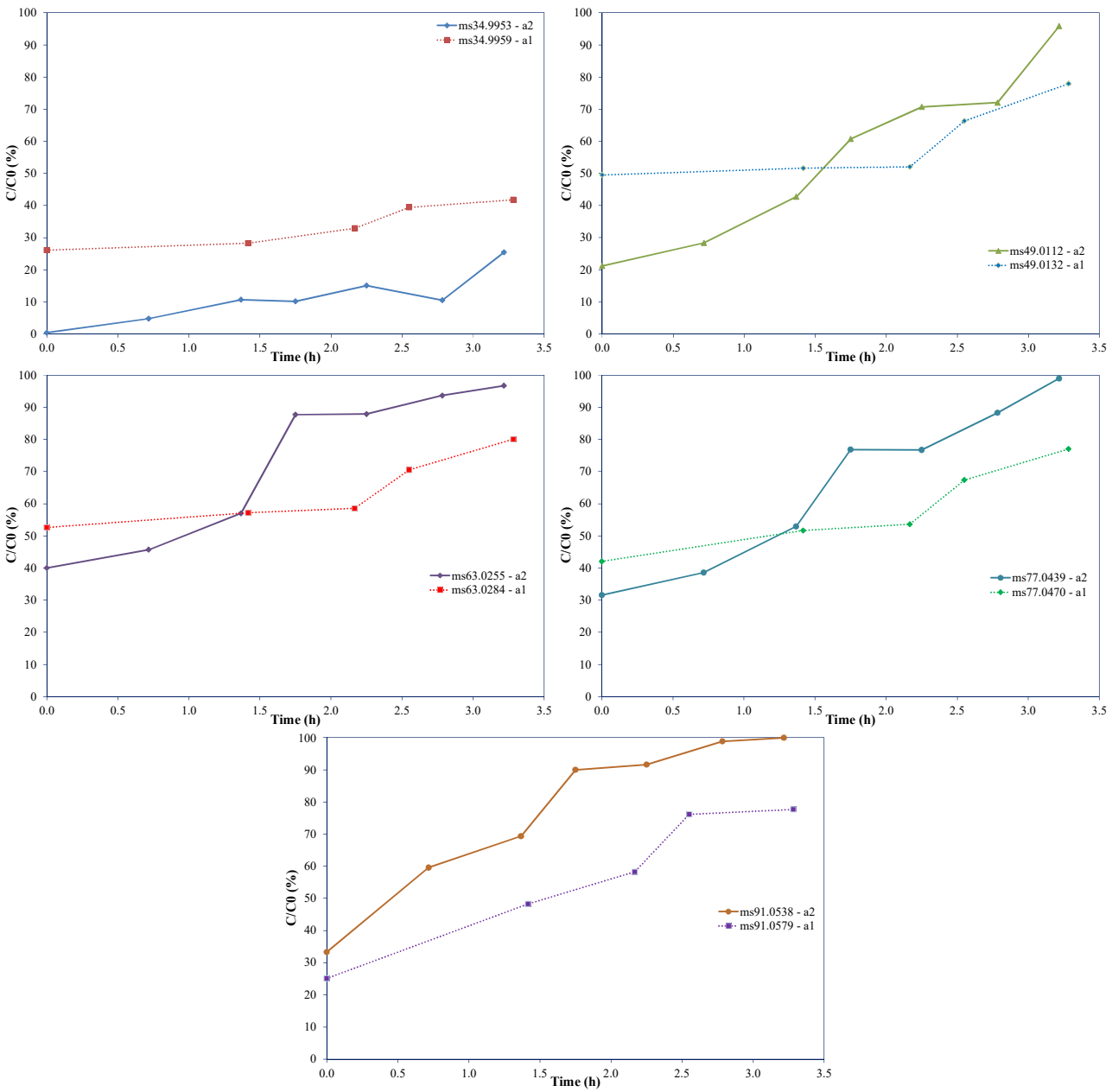
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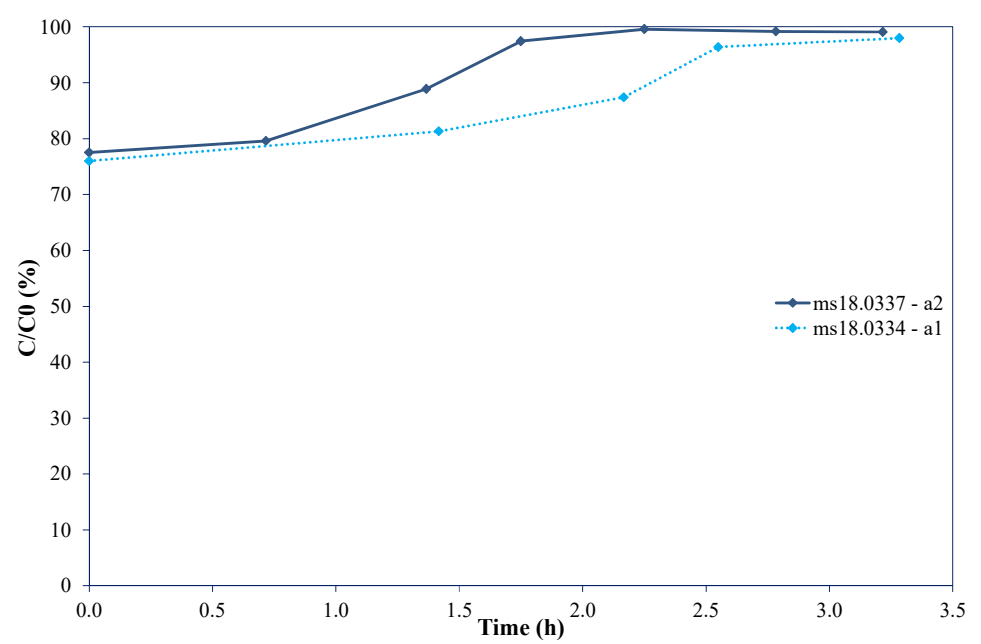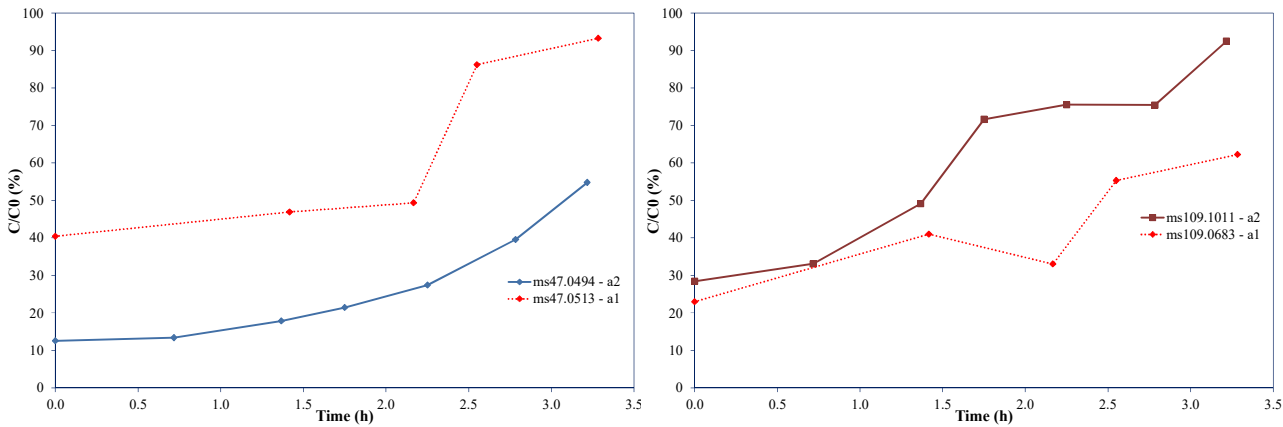
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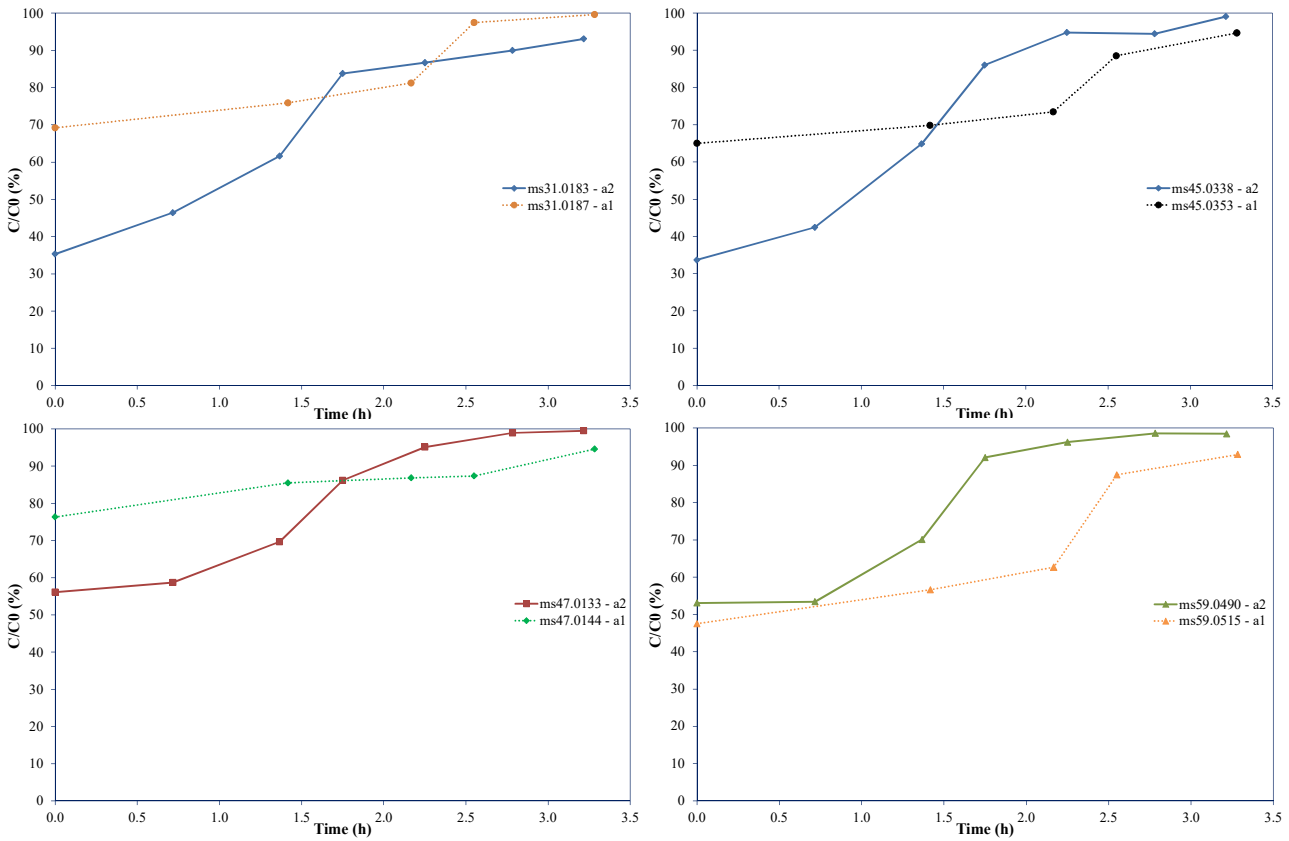
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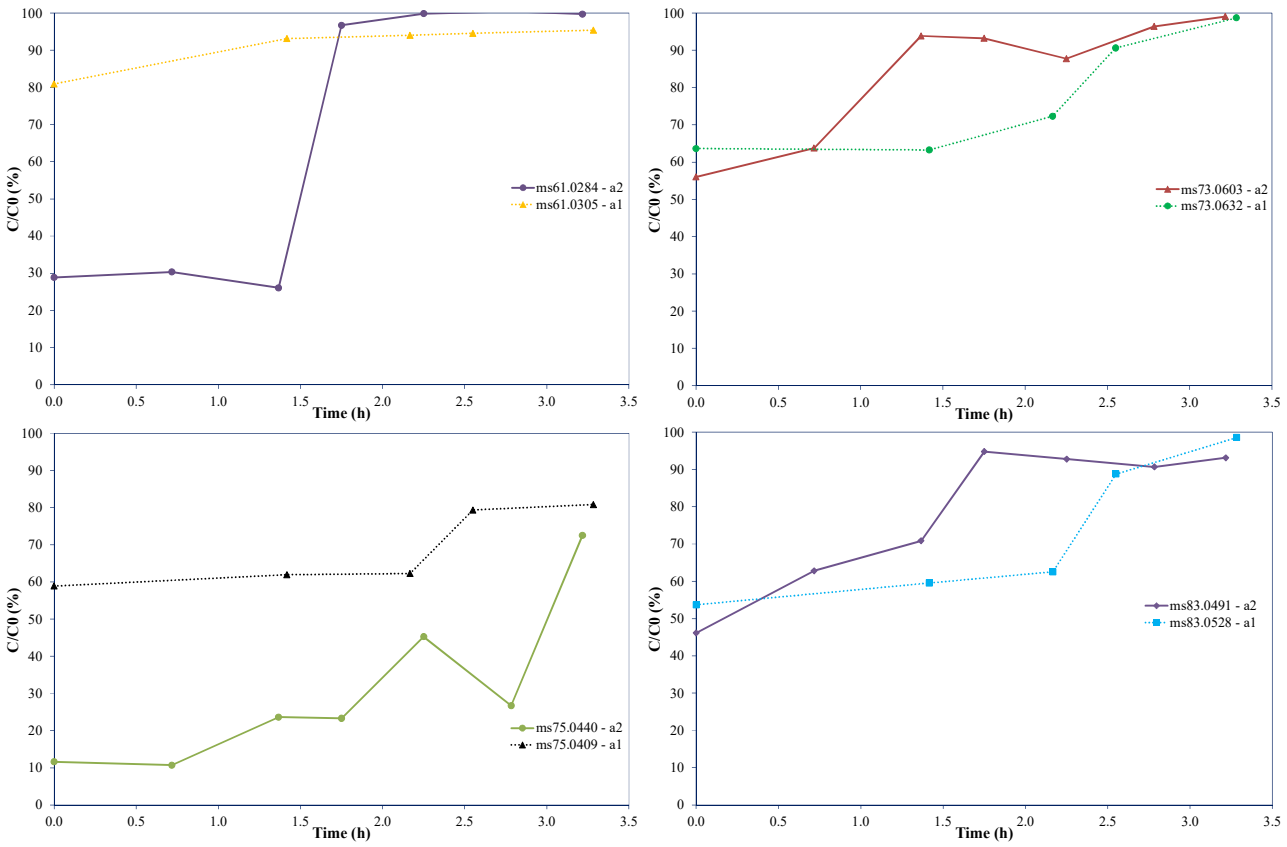
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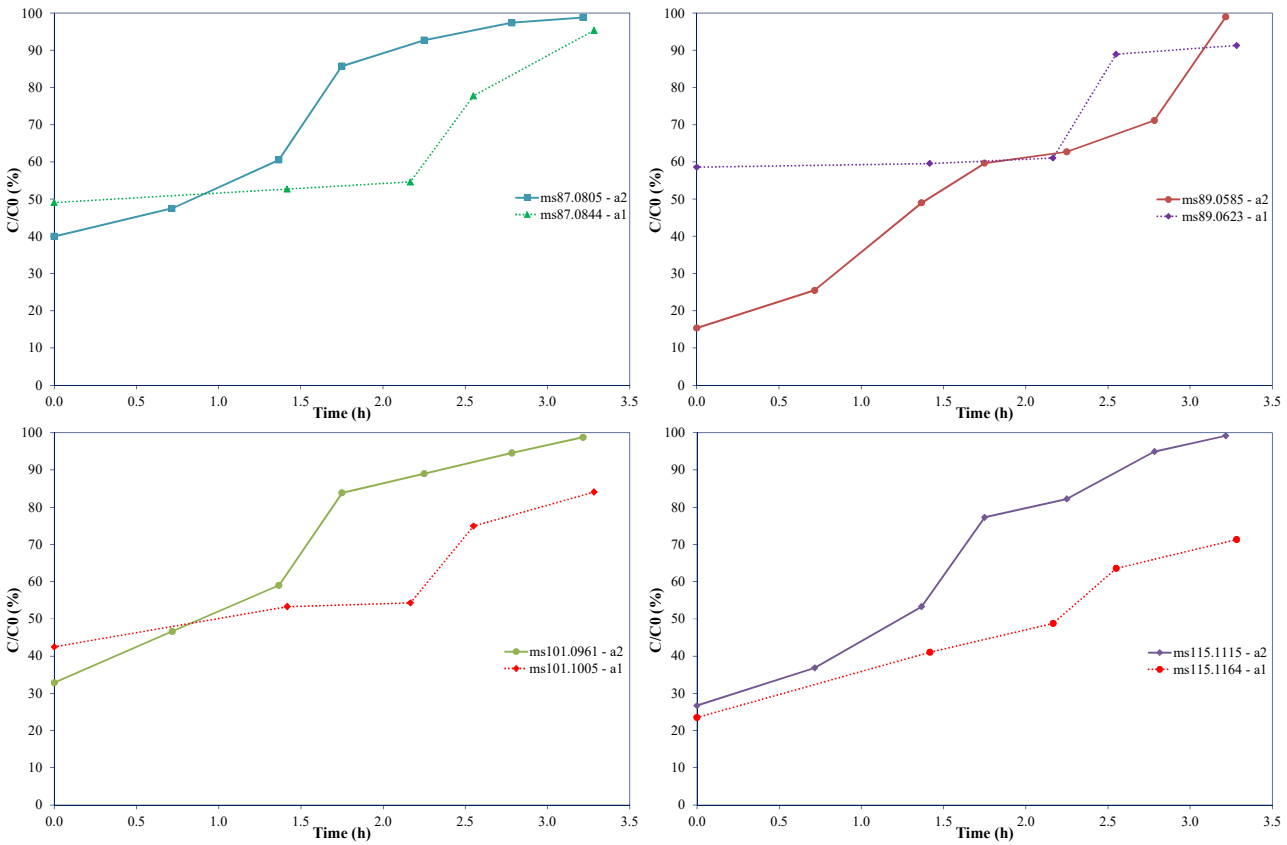
Figure 9

Figure 10

Figure 11