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Assessment of biogas production from MBT waste under different operating conditions

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Abstract

In this work, the influence of different operating conditions on the biogas production from mechanically-biologically treated (MBT) wastes is investigated. Specifically, different lab-scale anaerobic tests varying the water content (26-43 %w/w up to 75 %w/w), the temperature (from 20-25 °C up to 55 °C) and the amount of inoculum have been performed on waste samples collected from a full-scale Italian MBT plant. For each test, the gas generation yield and, where applicable, the first-order gas generation rates were determined. Nearly all tests were characterised by a quite long lag-phase. This result was mainly ascribed to the inhibition effects resulting from the high concentrations of volatile fatty acids (VFAs) and ammonia detected in the different stages of the experiments. Furthermore, water content was found as one of the key limiting factor of the anaerobic biological process. Indeed, the experimental results showed that when

the moisture was lower than 32 %w/w, the methanogenic microbial activity was completely inhibited. For the higher water content tested (75 %w/w), high values of accumulated gas volume (up to 150 Nl/kgTS) and a relatively short time period to deplete the MBT waste gas generation capacity were observed. At these test conditions, the effects of temperature became evident, leading to gas generation rates of 0.007 d^{-1} at room temperature that increased to 0.03-0.05 d^{-1} at 37 °C and to 0.04-0.11 d^{-1} at 55 °C. Overall, the obtained results highlighted that the operative conditions can drastically affect the gas production from MBT wastes. This suggests that particular caution should be paid when using the results of lab-scale tests for the evaluation of long-term behaviour expected in the field where the boundary conditions change continuously and vary significantly depending on the climate, the landfill operative management strategies in place (e.g. leachate recirculation, waste disposal methods), the hydraulic characteristics of disposed waste, the presence and type of temporary and final cover systems.

KEYWORDS

mechanically biologically treated waste; biochemical methane potential test (BMP); anaerobic tests; gas generation model; first-order kinetic constants

1 Introduction

Landfills still represent the dominant option for waste disposal in many parts of the world (Laner et al. 2012). However, as known, this option may pose a threat to groundwater pollution, soil contamination and global warming effects due to the potential emission of leachate and landfill gas to the surrounding environment (Pantini et al., 2014; Scaglia et al., 2010; Thomsen et al., 2012; White and Beaven, 2013). Indeed, landfill has been recognized as one of the main source of anthropogenic methane emission and a significant contributor to global warming (Bogner et al., 2008). Gas emissions from landfills are mainly dominated by methane and carbon dioxide that are generated from the anaerobic conversion of organic matter contained in waste as a result of biological processes naturally occurring in landfill sites. Moreover, due to the generally high nitrogen content in wastes, there is also a considerable potential for nitrous oxide

emissions from municipal solid waste (MSW) landfills that can further enhance the global warming effects (Harborth et al., 2013).

In view of these concerns, throughout the world, new regulations in waste management and treatment strategies of municipal solid waste (MSW) have been introduced. For instance, in Europe, the Landfill European Directive 1999/31/EC imposes member states only landfill wastes that have been preliminary subjected to treatment or incineration. The directive aims at limiting the amount of biodegradable waste in landfills while encouraging alternative strategies in order to move towards more sustainable waste management system, according to the waste hierarchy approach (De Gioannis et al., 2009; Sormunen et al., 2008). To meet the European targets, member states have adopted different options, such as separate collection and recycling of organic waste stream, MSW incineration with energy recovery, biological treatments of source separated organic wastes or Mechanical Biological Treatment (MBT) plants of residual MSW (Lornage et al., 2007; Pantini et al., 2015; Scaglia et al., 2010). Among these, the MBT technology is playing a key role in the waste management system of unsorted MSW wastes (Adani et al., 2004; Farrell and Jones, 2009; Pantini et al., 2015; Siddiqui et al., 2013;). All over Europe, MBT facilities can apply different combinations of mechanical sorting, bio-drying, and biological processes depending on the specific target, that may be a pre-treatment before incineration or a pre-treatment to produce a bio-stabilized product that has a lower impact when disposed of in landfills (Adani et al., 2004; Di Maria et al., 2013; Farrell and Jones, 2009; Montejo et al., 2013). In the latter case, the MBT plant consists of a mechanical pre-processing stage including crushing, sieving and recovering of recyclable materials (such as metals, glass and plastics). This stage leads to two distinct flows: the oversize fraction, which is further processed to produce refuse-derived fuel, and the undersize fraction, rich in organic putrescible matter, which is biologically treated using an anaerobic/aerobic process in order to stabilize it. The main distinction between different MBT systems concerns the sequence of process steps and the type and duration of the biological treatment (Pan and Voulvoulis, 2007; Pantini et al., 2015). The specific technology and process applied may strongly affect the long-term behaviour of MBT wastes in landfills in terms of both liquid composition and gas generation (Boldrin et al., 2011; Siddiqui et al., 2013). However, gas emissions from MBT waste have been rarely measured on full scale MBT landfills (Harborth et al., 2013). Hence, the current

state of knowledge on biogas emissions is based either on laboratory tests or on large scale experiments such as lysimeters (Sormunen et al., 2008). Depending on the specific aim of the test, lab scale studies on gas emissions from MBT wastes and solid organic wastes are usually carried out using different procedures and operative conditions (see Table 1). As highlighted by Lornage et al. (2007), the differences in the experimental procedure adopted may modify the biogas yield and kinetics, thus leading to results that are not always comparable. The anaerobic process is indeed sensitive to several factors such as pH, water content, temperature, particle size, as well as by the presence of inhibitors such as of volatile fatty acids (VFAs), ammonia and heavy metals (Cabbai et al., 2013; Elbeshbishy et al., 2012; Labatut et al., 2011; Lornage et al., 2007; Raposo et al., 2011). Among these, pH is recognised as the key parameter to be maintained in an appropriate range (6.4-7.5) in order to enhance the methane yield (Adani et al., 2004; Argun et al., 2008; Lo et al., 2010). High pH values would result in increased toxicity due to the shift to higher concentrations of ammonia, which is identified as one of the most toxic agent for methanogenic bacteria (Chen et al., 2008; Vigneron et al., 2007). In contrast, low pH values are indicative of the accumulation of VFAs within the system (Bouallagui et al., 2005; Li et al., 2011). VFAs represent the main intermediate products during the initial acidogenic stage of the anaerobic process that are successively converted into methane and carbon dioxide. However, VFAs concentrations at high level may result in an inhibition of the methanogenic activity, as observed by several authors (Argun et al., 2008; Borzacconi et al., 1997; Cabbai et al., 2013). Regarding the other operative conditions, an increase of temperature has a positive effect on the microbial growth and activity (Chen et al., 2008) thus leading to a faster gas generation process. Similarly, increasing the water content of incubated waste is beneficial for methane yield since it enhances the solute transport of nutrient, the organic matter solubilisation and the microorganism mobilization within micro-environments, as well as dilutes the concentration of inhibitors (Donovan et al., 2010; Mora-Naranjo et al., 2004). Finally, the particle size of materials exerts a relevant influence on the process kinetic; it is well accepted that particle size reduction results in higher methane generation rate (Esposito et al., 2012; Lesteur et al., 2010, Mata-Alvarez et al., 2000), whereas its effect on biogas yield is still not completely elucidated (Mshandete et al., 2006; Nopharatana et al., 2007).

Table 1

The objective of this work was to evaluate the effects of temperature, water content and inoculum addition on biogas generation from mechanically-biologically treated waste by performing anaerobic batch tests at different operating conditions. Furthermore, in order to determine the potential gas generation capacity under optimal conditions, biomethane potential tests (BMP) were carried out. All these tests were then compared in terms of cumulative biogas yield and rates. Besides, where applicable, a first-order kinetic model was used to compute the biogas rate constants from the cumulative gas generation curves observed in each experiment. Finally, the obtained results were addressed to assess the possible implications resulting from the different environmental conditions expected in the field.

2 Materials and Methods

2.1 MBT waste material

Mechanically-biologically treated waste samples were collected at the belt discharge point of the secondary refinement unit of a full-scale MBT plant operating in Italy. This MBT plant receives residual municipal solid waste (226,000 ton/y in 2013), with the average composition shown in Table 2.

Table 2

In this plant the incoming wastes are subjected to a mechanical pre-processing consisting of pre-sorting of bulky materials, shredding and size separation. From these processes two flows are obtained: the light fraction with particle size>80 mm (96,500 ton/y in 2013), which is further processed to produce refuse derived fuel (55,500 ton/y in 2013), and the undersize fraction (126,000 ton/y in 2013), which is sent to the biostabilization basins; the remaining flow is represented by recovered metals (3500 ton/y in 2013). In the biostabilization basins, the aerobic process occurs for 28 days at forced ventilation condition, with daily water addition and waste turning. Then, the stabilized output goes to a secondary sieving process to remove improper materials. The undersize fraction (<20 mm) is the organic MBT waste analysed in this study. The MBT waste sample was collected in May 2014 using standard procedures (UNI 10802:2013). A final MBT waste sample of about 80 kg was sent to the laboratory and stored at 4 °C for few days until the physico-chemical analyses were performed. In the laboratory, three representative sub-samples were

obtained by the "coning and quartering" method. One sub-sample was analysed to determine the moisture content (W), total (TS) and volatile solids (VS), pH, total (TC) and organic carbon (TOC) content, total Kjeldahl (TKN) and soluble nitrogen (NH_4-N), the Chemical Oxygen Demand (COD) and the water content at field capacity (FC) of waste (i.e. the water-retaining capacity including both the hygroscopic and capillary water). All measurements were performed at least in triplicate; initial waste water content, dry matter and waste field capacity are expressed as percentage of wet weight whereas the other parameters are computed on dry weight basis. Average values and standard deviations are reported in Table 2. A sub-sample (3-4 kg) was used for BMP tests. Before to perform the BMP analysis, the sub-sample was dried at room temperature (25 °C) to avoid losses of volatile organic compounds and then shredded to 1 mm particle size. The last sub-sample was used in the incubation tests as received since, currently, the MBT waste is not subjected to further treatment before landfilling it.

2.2 Analytical Methods

In order to characterize the MBT waste with regards to its physical and chemical properties, different analytical methods were applied. These tests provide basic information that are essential for the interpretation of the biological test results.

Moisture content (W), total (TS) and volatile solids (VS), total carbon (TC) and organic carbon (TOC) content, pH

Moisture (W) and total solid (TS) content were determined according to the standard method UNI EN 14346 (2006). Volatile solids (VS) were measured by loss-on-ignition (LOI) at 550 °C for 8 h (UNI/TS 11184, 2006). Total carbon (TC) and organic carbon content (TOC) were analysed by Shimadzu SSM-5000A instrument according to UNI EN 13137(2001). The own pH of MBT waste was determined after elution following the standard method UNI EN 12457-2 (2004).

Total (TKN) and soluble nitrogen (NH_4-N)

Total Kjeldahl Nitrogen (TKN) was measured on solid waste samples (2.5-3 g) by mineralization with a strong acid medium (97% sulphuric acid) followed by steam distillation and titrimetric determination, as

150 proposed by Mohajer et al. (2010) and Tremier et al. (2005). Blank and control tests were performed
151 simultaneously, in triplicate. In blank tests, 4 ml of deionized water were used whereas in control tests, to
152 evaluate the efficiency of ammonia recovery, 4 ml of L-glutamic acid (1000 mg/l) were utilized. Samples
153 were digested in FOSS 2020 Digestor at 180 °C for 1 h and thereafter at 350 °C for 1-2 hours (warm-up time
154 excluded). After cooling, samples were distilled using FOSS Kjeltec 8100 distillation unit. In the distillation
155 method, 30 ml of deionized water and 70 ml of the alkaline solution (32 %w/w NaOH) were added to each
156 tube. The steam supply was set to 60% and the distillation time was 5 minutes. A solution consisting of 50
157 ml deionized water, 4 ml boric acid (40 g/l) and 3 drops of Kjeldhal indicator (mixture of methyl red
158 indicator and Bromocresol green indicator, MERCK KGaA) was used as absorbent solution during
159 distillation. The ammonia content was determined by tritation of distillate with 0.1 M H_2SO_4.
160 Determination analyses of soluble nitrogen (NH_4-N) were carried out on 2.5-3 g using the same procedure
161 of TKN. For the distillation method, 30 ml of deionized water and 50 ml of the alkaline solution (32 %w/w
162 NaOH) were added to each tube. Steam supply and distillation time were the same as mentioned above, as
163 well as the titration method. The ammonia recovery of the instrument was evaluated by adding 4 ml of a
164 known solution (1000 mg/l NH_4-N) to 50 ml of deionized water. An efficiency up to 100% was detected.

165 ***Chemical Oxygen Demand (COD)***

166 To determine the COD of wet solid samples, the modified method proposed by Raposo et al. (2008) was
167 adopted. This method consists of a wet oxidation with potassium dichromate as the oxidant and silver
168 sulphate as the catalyst in a strong sulphuric acid solution (Raposo et al., 2008). COD measurements were
169 carried out on 1.0 g of MBT waste sample, adding 6 ml of 97% sulphuric acid and 30 ml of deionized water
170 to the flask while stirring it for 30 minutes. Then, 2.0 ml of Potassium Dichromate 0.025 M (for high range
171 detection) and 4.5 ml of silver sulphate sulphuric acid solution were added to each flask containing 3.5 ml
172 of initial solution. The reaction mixtures were boiled in a Holm & Halby Techne Dri Block at 148 ± 2 °C for
173 110 minutes. After cooling, 5.0 ml of deionized water and 3 drops of ferroin indicator were added and
174 samples were titrated with 0.035 M Ferrous Ammonium Sulphate solution. COD measurements were

175 performed in triplicate. Five blanks (3.5 ml of deionized water) and three control tests (3.5 ml of 500 mg
176 COD/l standard solution) were carried out simultaneously.

177 ***Volatile Fatty Acids (VFAs)***

178 VFAs were measured in fresh solid waste as well as in waste samples at different incubation time. Samples
179 were prepared weighing about 5 g of MBT waste, adding 12.5 ml of deionized water and acidifying them
180 with 0.4 ml of 97% sulphuric acid to ensure pH<2. A magnet was inserted and samples stirred for
181 approximatively 10-15 minutes to homogenize them. Then, 1.5 ml of each sample was placed in an
182 Eppendorf tube and centrifuged at Eppendorf mini spin table centrifuge at 13,400 rpm for 10 min. After
183 centrifugation, 1.0 ml sample was transferred to a GC glass vial and 0.1 ml of internal standard (2.2 mM 4-
184 Methyl valeric acid) was added. Concentrations of acetate, propionate, iso-butyrate, butyrate, iso-valerate,
185 valerate, hexanoic acids were determined by using GC Shimadzu GC – 2010 equipped with and FID (flame-
186 ionization-detector). VFA compounds were separated by a capillary column (ZB – FFAP, 30 m, 0,53 mm I.D x
187 1,0 µm) and concentrations were computed by means of a linear calibration curve obtained after standards
188 injection (range: 5-1500 mg/l). All measurements were performed in triplicate.

189 ***MBT waste field capacity (FC)***

190 Water content of MBT waste at field capacity was determined by performing column test. A Plexiglas
191 column with an inner diameter of 3.5 cm and a total height of 15 cm was packed with about 70 g of as
192 received MBT waste (water content at 19.4% w/w), corresponding to initial wet density of 0.5 g/cm^3 (dry
193 bulk density of 0.4 g/cm^3). The packed column was weighted (M_{in}) and then saturated from the bottom
194 section until a water head of few millimeters formed at the top and the pump was stopped. After
195 saturation, the column was let drain until no significant outgoing flow was detected and weighted again
196 (M_{end}). The difference in weight (M_{end} - M_{in}) is the adsorbed water ($M_{w,ads}$). The ratio between the total
197 water in the column at the end of the experiment (i.e. sum of adsorbed water and initial moisture water,
198 W) and the final mass of MBT material in the column ($M_{in,MBT}$ + $M_{w,ads}$), shown in Eq. (1), represents a rough
199 estimation of the field capacity of MBT waste (expressed as percentage of wet weight):

$$FC(\%w/w) = \left(\frac{M_{w,ads} + W(\%) \cdot M_{in,MBT}}{M_{in,MBT} + M_{w,ads}} \right) * 100 \quad (1)$$

2.3 Gas production tests

Biochemical Methane Potential test (BMP)

Different BMP assays, experimental set-ups and employed protocols can be found in literature due to a lack of harmonization and standardization of biochemical methane potential methods. Indeed, some methods are designed to evaluate the biodegradability of chemical substances under methanogenic conditions (ISO 14853, 1999; ASTM E2170-01, 2008 (withdrawn 2013); ASTM D5210-92, 2007; DIN 38414-8, 1985) while others aim at quantifying the ultimate biodegradability and gas generation of complex organic substrates (ISO 11734, 1995; ISO/DIS 14853, 1999) using different experimental set-ups. Additionally, these methods were applied differently or modified by researchers (Angelidaki et al., 2009), making the inter-comparison of BMP test results quite difficult. In this study, the BMP protocol proposed by Hansen et al. (2004) was adopted. Glass bottles (1 l) with a thick rubber septum were used as reactors. Approximatively 1 g of air dried waste sample (particle size < 1 mm), 80 ml of deionized water and 320 ml of a fresh de-gased inoculum were used in the experiments in order to achieve an organic load of 1.4 gVS/l (weight of VS in substrate per unit volume of inoculum). Tests were carried out for 30 days with six replicates, due to the relatively high heterogeneity of the MBT material. Thermophilically digested material from a full-scale biogas plant was used as inoculum. Three blanks with only water and inoculum were run to test the biogas production from the inoculum itself. Control tests, containing 0.8 g of AVICEL (Fluka, Sigma Aldrich, Vallensbæk Strand, Denmark) as a standard substrate, were performed to check the quality of the inoculum. After set-up, the reactors were flushed with N_2 for 10 minutes, to ensure the establishment of anaerobic conditions in the headspace of the glass bottles, then sealed and placed in the incubator at 55 °C (± 1 °C). The methane concentration in the reactors was measured every two days during the first two weeks, and later once per week. Gas samples (0.2 – 0.5 ml) were taken from the headspace of the reactors by using a syringe with a pressure lock and directly injected into the gas chromatograph for methane determination (Shimadzu GC 14A) and for qualitative analysis of gas composition in terms of $\%CH_4$ and

225 %CO_2 (Mikrolab GC Aarhus). In order to avoid build-up of high pressure inside the reactors, the gas was
226 released during the experiment. Based on the difference of CH_4 concentration before and after release of
227 excess gas, the generated amount of CH_4 was computed.

228 ***Anaerobic gas generation tests***

229 In order to evaluate the effects of temperature and water content on the gas generation rate and yield,
230 anaerobic batch tests were performed at three different temperatures: room temperature (20-25 °C), 37 °C
231 and 55 °C. In tests at room temperature and 37 °C, a mesophilic inoculum derived from a biogas plant
232 carrying out mesophilic co-digestion of manure and organic waste was utilized whereas in tests at 55 °C the
233 same inoculum of BMP tests (thermophilically digested material) was used.
234 Before starting the anaerobic tests, different amounts of water were added to four MBT sub-samples (as
235 received material with 19.4% water content) in order to achieve four values of the initial water content in
236 waste: 26%, 32%, 38%, 43% (expressed on wet weight basis). After homogenizing the samples, an aliquot of
237 each sub-sample at the specific water content was weighted and introduced into reactor and then
238 incubated at the corresponding temperature. The values set for temperature and water content aimed at
239 covering the actual ranges generally observed at real scale landfill sites (Mor et al., 2006; Mora-Naranjo et
240 al., 2004). Note that the operating conditions of anaerobic tests were selected in order to simulate
241 different disposal scenarios and, hence, they differ from the optimal ranges usually set in biogas plant
242 treating MSW waste organic fractions. Namely, in these plants, the anaerobic digestion of incoming
243 feedstock, usually mixed with a large amount of digester effluent or sewage sludge, may be carried out in
244 dry systems (60-80% water content) or in wet systems (water content >90%) at thermophilic or mesophilic
245 conditions in continuous or static digesters (Braber 1995; Gunaseelan 1997; Schievano et al., 2010).
246 Incubation tests at 37 °C and 55 °C consisted of 1 l glass bottle filled with waste sample (0.5-0.7 kg), sealed
247 with a rubber septum and equipped with a PVC pipe, which connected it to a 3 l SKC Tedlar Sampling Bag
248 (SKC Inc., Eighty Four, PA, US) for gas collection. At each measurement, 5 ml of gas were sampled with a
249 syringe and injected into evacuated glass vials fitted with pierceable rubber septa (Exetainer Vail, Labco Ltd,
250 Lampeter, UK), which were then analysed for determining gas composition. A 490-PRO Micro GC (Agilent

Technologies Denmark Aps, Glostrup, Denmark) equipped with two columns (PoraPLOT Q PLOT, 0.25mm, 10m, and Molecular Sieve 5A PLOT, 0.25 mm, 20m) was used to measure CH_4, CO_2 and O_2 in gas samples with a detection limit of 0.1% for all gases. In the incubation tests at room temperature, 12 l steel drums with airtight lids were used as reactors. Drums were filled with MBT waste samples at three different water contents (26%, 34%, 43%) and flushed with nitrogen for 30 minutes before sealing them. Lids were equipped with T-shaped sampling ports and connected to 5 l SKC Tedlar Sampling Bags. More information about tests conditions and experimental activities are reported in Table 3.

As shown in this table, the anaerobic gas generation tests were carried out in three sequential stages. In the first stage, no inoculum was used. During the second stage of experimental activity, a low amount of mesophilic or thermophilic inoculum (20 g of inoculum, i.e. approximately 5 %w/w of the waste dry matter used in the test) was introduced into the incubation bottles with lower water contents (T1, T2, T5, T6) to enhance the microbial activity. In the following stage III, due to the unexpected very low biogas production, some reactors were opened (R2, T2A, T3A/B, T4B, T6A, T7A/B) in order to partially remove the material, which was then analysed with regard to pH, VFA, TKN and ammonia content. In this stage, inoculum (30 %w/w of waste dry matter in reactor) and water (230 %w/w of waste dry matter, to obtain a final moisture content of 75 %w/w) were introduced within these reactors that were successively purged with nitrogen and incubated again. A triplicate measurement of the biogas production from the added inoculum was performed on blank experiments and deduced from the biogas yield of waste samples.

Table 3

The gas volume produced by each reactor was computed timing the emptying of gas bags using a Fluid Metering Inc. laboratory pump (QG, Fluid Metering Inc., Syosset, NY, US). The flow rate of the pump was tested several times during the experiment and an average flow of 0.5 l/min was measured.

2.4 First-order gas generation model

To compute the biogas kinetic constants under different operating conditions, the widely adopted first-order kinetic model (Gunaseelan 1997; De Gioannis et al., 2009; Lo et al., 2010; Mou et al., 2015) was used

for the interpolation of experimental data. The generic formulation, which accounts for the lag-time observed in the test, is the following:

$$L(t) = L_0 \left[1 - \exp\left(-k \cdot \left(t - t_{lag}\right)\right)\right] \quad (2)$$

where L is the biogas accumulation (Nl/kgTS) at the time t (d), L_0 the potential biogas production (Nl/kgTS) for the tested conditions (at optimal conditions, L_0 approaches the potential gas generation capacity measured in the BMP experiments), t the time over the digestion period, t_{lag} the lag-phase (d) and k the first-order kinetic constant (d^{-1}).

3 Results and discussions

3.1 MBT waste characterization

Results of the characterization analysis performed on the MBT waste are reported in Table 4. Moisture content (W), as well as water field capacity, were slightly lower than the values usually measured for this type of waste (Di Lonardo et al., 2014; Pantini et al., 2015; Zach et al., 2000). Despite the waste underwent an aerobic treatment process in the MBT plant, the organic matter of waste is still quite high, as confirmed by VS, TOC and COD contents. As shown in Table 4, the pH was almost neutral and in the optimal range for the anaerobic process. It is also interesting to point out that values of TKN and NH_4-N were quite high, close to the range usually observed for untreated waste or poorly treated waste (Modin 2007; Pognani et al., 2010).

Table 4

3.2 Biochemical Methane Potentials

Figure 1 shows the cumulative CH_4 generation curve measured in control (red dots) and in MBT waste tests (green dots) as a function of the incubation time. The results reported in this figure, expressed as cumulative volume of methane per gTS at standard temperature and pressure (STP) conditions (0 °C, 1 atm), represent the average values measured in the different replicates obtained after subtracting the CH_4 measured in the blank experiments. The solid red line and the dotted green line depict the theoretical

methane potential for the cellulose substrate (control) and the MBT waste, respectively. The latter was estimated from the total organic carbon (TOC) of the substrate (Table 4), as shown in Eq. (3). Assuming that the biogas generated by a complete degradation of organic carbon contains 60% of methane (that corresponds to the average CH_4 concentration measured during the BMP test), a theoretical value of 268 $NmlCH_4/gTS$ was computed (i.e. 60% of CH_4 in biogas implies that 1 g of TOC generates 1.12 Nl of CH_4 at STP).

$$L_{theoretical,TOC}\left(\frac{NmlCH_4}{g_{TS}}\right) = 60\%CH_4 \cdot \frac{1}{12\frac{g_C}{mol_C}} \cdot 22.414\left(\frac{Nl}{mol}\right) \cdot 0.239\frac{g_{TOC}}{g_{TS}} \cdot 1000 \quad (3)$$

From Figure 1, it can be noticed that the cumulative CH_4 curves observed for control and waste samples showed a rapid increase in the first two weeks and then achieved an asymptotic value. The lag phase was absent, confirming that the BMP test was run under optimal conditions. The average cumulative methane generation in controls resulted in an average gas generation of 367 $NmlCH_4/gTS$ on the 13th day after starting the batch tests and reached the theoretical potential value of 415 $NmlCH_4/gTS$ in 27 days. Within the first two weeks, the methane generation curve observed in control tests appeared linear (R^2=0.99), with an average slope of 27.5 $NmlCH_4/(gTS \cdot d)$. Similarly, in the first stages of the MBT waste sample test a linear methane production rate of 8.4 $NmlCH_4/(gTS \cdot d)$ was observed. Thereafter, the slope rapidly decreased and the cumulative CH_4 generation curve asymptotically approached a constant level of 121 $NmlCH_4/gTS$. Hence, it seems that, on average, only 45% of the theoretical methane generation (i.e. 268 $NmlCH_4/gTS$) was achieved during the BMP experiment of the MBT waste sample, most likely due to the presence of non-biodegradable fractions (plastics), recalcitrant organic substances or lower degradable compounds. Moreover, it should be noted that the theoretical methane (Eq. 3) was computed neglecting the biomass synthesis and, thus, it could be overestimated. Some authors indicate that 5-10 % of organic matter is consumed by bacteria growth (Angelidaki and Sanders, 2004; Elbeshbishy et al., 2012; Labatut et al., 2011; Raposo et al., 2011) and, hence, does not contribute to CH_4 production. Even though the extent of degradation achieved in a BMP test is strongly dependent on the composition of the analysed substrate as well as on the test methodology applied (substrate to inoculum ratio, test duration, inoculum

325 characteristics), the 45% degradability estimated for the analysed MBT waste based on TOC content is
326 consistent with other previous studies on similar MBT materials. For instance, using experimental results
327 (TOC, BMP, % CH_4 in biogas) presented by Bayard et al. (2010) for different MBT wastes, the degradability
328 of MBT waste was estimated within the range 10% - 36% in 90-days BMP tests. An organic carbon
329 degradability of 42.4% was computed from results reported in Barrena et al. (2008) for aerobically treated
330 MBT waste.
331 Making reference to Figure 1, some variation of accumulated CH_4 volume was observed between the
332 replicate of MBT waste tests (coefficient of variation in the range of 12.4-23.3 %), probably due to its
333 relatively high heterogeneity and to the low amount of material tested in the BMP experiment. On the
334 contrary, both substrate (control) and inoculum (blank) showed a good internal homogeneity with
335 coefficients of variation in the range of 0.5-7.0% and 1.9-4.9%, respectively.
336 From the qualitative analyses of gas composition, an average value of 60.8 ± 1.1 % and 62.4 ± 1.4 % of
337 methane concentration in biogas was detected for sample and control, respectively. Assuming this
338 percentage, a potential CO_2 yield of 78 ± 25 NmlCO_2/gTS for MBT waste was computed. Hence, a maximum
339 potential gas production of 199.2±63 Nml/gTS was estimated for the analysed MBT waste. This result is
340 consistent with some previous BMP studies performed on aerobically treated MBT wastes. For instance,
341 Barrena et al. (2008) measured a total gas production of 187±16 Nl/kgTS, with an average methane content
342 of 57 %v/v, from MBT wastes after 32 days of aerobic treatment. Bayard et al. (2010) analysed the gas
343 generation potential of different flows in a French MBT plant; they observed that the intermediate fraction
344 (< 50 mm), after 6 weeks forced-aerobic treatment, still exhibited high gas generation potential (232±23
345 Nl/kgTS). Lornage et al. (2007) measured a gas potential of about 160 Nl/kgTS from MBT wastes subjected
346 to 4-weeks aerobic treatment process.
347 **Fig. 1**

348 3.3 Anaerobic gas generation tests

349 Figs. 2-4 show the cumulative generation curve of methane (red circles) and carbon dioxide (black squares
350 dots) obtained for the MBT waste samples at room temperature (Fig. 2), 37 °C (Fig. 3) and 55 °C (Fig. 4), and

for different initial water contents of waste, as a function of the incubation time. Results are expressed as cumulative volume of gas per kg of total solids (TS) at STP. For comparison purposes only, the potential CH_4 and CO_2 values computed in BMP test have also been reported in Figs. 2-4 as dotted lines. From Figs. 2-4 it can be noticed that in the first stage of experimental activities that were carried out at low water contents and without inoculum addition, a long lag-phase was detected for all operating conditions. During this stage, the microbial population needed to get adapted to the micro-environment and to be acclimatized to the organic substrate in order to be able to grow until a sufficient active population established and the anaerobic degradation could stably evolve. Results shown in Figs. 2-4 suggested that the duration of the lag-phase was strongly affected by both the water content of waste and the process temperature. Regarding the former parameter, it widely documented that water enhances nutrients and substrates solubilisation in the liquid phase as well as supports bacteria movement and facilitates substrate and products diffusion through the porous medium (Donovan et al., 2010; Khalid et al., 2011; Liotta et al., 2014). However, the water content of waste in a landfill disposal scenario could be quite far from the optimum value for degradation (60% -90%) and, thus, may become limiting for the anaerobic process due to the accumulation of inhibitors with adverse effects on bacteria population (Donovan et al., 2010). Indeed, experimental results confirmed that the water content of waste could be considered as one of the most important factors limiting methane generation and, the probability of achieving a stable methanogenic stage is significantly reduced for water contents below 32 %w/w (wet weight) at any temperature for this type of waste.

Fig. 2

Fig. 3

Fig. 4

Increasing the operative temperature would enhance both the substrate solubilisation and the microbial activity (Raposo et al., 2011). It is likely that higher temperature allowed moving from non-equilibrium state

towards more suitable conditions for methanogenic bacteria growth, thus favouring a more rapid establishment of the methanogenic phase (Lesteur et al., 2010; Li et al., 2011; Mata-Alvarez et al., 2000). Indeed, as shown in Fig. 2 in all the experiments at room temperature methane was not detected within the first three months but only CO_2 was generated at high levels (80 %v/v, see Fig. S1 in the Supplementary information). A similar behaviour was observed by Adani et al. (2004) during 90 days incubation tests carried out on fresh and partially treated wastes (10 days of aerobic treatment). The high CO_2 concentration without CH_4 generation suggested that the biological process was completely inhibited at every water content in tests at room temperature, probably due to acidification effects, and revealed the poor stability degree of the analysed MBT waste. Furthermore, even though the methanogenic activity was observed in tests at higher temperature and water content, a clear instability associated with the anaerobic process was still detected.

In fact, as reported in Fig. 3, reactors at 37 °C and water content of 38% (T3) - 43% (T4) started producing methane after 27 days, even though CH_4 concentrations were low (below 20%). A similar trend was observed for batch tests at 55 °C (Fig. 4) where methane generation started after 22 days and 13 days for tests at moisture content of 38% (T7) and 43% (T8), respectively. However, in all these reactors (except T8) just after few days, biogas generation slowed down. Only the experiment at higher water content and temperature (T8) managed to reach the stable methanogenic phase during the experiment (without inoculum addition), as confirmed by the CH_4 concentration measured in biogas, which was in the range 45-60 %v/v (see Fig. S3 in the Supplementary information). Even if a lag phase of 40 days was observed in these tests, the cumulative gas generation approached an asymptotic value of 29.1±2.2 Nl CH_4/kgTS and 32.6±2.1 Nl CO_2/kgTS within 100 days (Fig. 4). These values are in line with previous studies on treated MBT waste wetted to water holding capacity in which no inoculum was added (Adani et al., 2004; De Gioannis et al., 2009). However, compared to the measured BMP value, in this test condition, a very low conversion degree was achieved (30% of BMP value).

Overall, the results obtained during the initial experimental activity indicated that, in most of test conditions, the anaerobic process was slowed down either due to high levels of inhibiting factors or to a limited amount of active biomass inside the reactors. Hence, during stage II, a small amount of inoculum

405 (20 g) was introduced into reactors at lower water contents (T1, T2, T5, T6) and the evolvement of
406 degradation was monitored for 20 days. After the inoculum addition, methane started to be produced in all
407 reactors but its concentration still remained very low (below 10 %v/v) and then decreased again (see Tests
408 T2B and T6B of Fig. S2 in the Supplementary information). Thus, it seems that the microorganism
409 population inside the MBT waste was not sufficient to sustain the anaerobic degradation process. For that
410 reason, during stage III, in reactor T4B (W=43%, T=37 °C) a greater amount of inoculum was introduced (70
411 g) and, in two weeks, methane concentration achieved the range typical of a stable methanogenic phase
412 (50-70 %v/v, see Fig. S2 in the Supplementary information).
413 Results shown in Figs. 3-4 also highlight the different behaviour of tests with water content at field capacity
414 (w=43% at 37 °C and 55 °C, see T4 vs. T8). In fact, even if the water content was the same in these reactors,
415 only tests at 55 °C (see T8 in Fig. 4) managed to achieve the stable methanogenic phase without the
416 inoculum addition. Instead, at 37 °C, a very low methane volume was measured in test where no inoculum
417 was used (see T4A in Fig. 3), whereas methane was stably produced only after the addition of a significant
418 amount (70 ml) of mesophilic inoculum (T4B). This may be ascribed, on the one hand, to a lower active
419 mass of mesophilic bacteria in the MBT waste compared to the thermophilic ones, presumably due to the
420 type of biological process performed in the MBT facility. Indeed, temperatures up to 70 °C were achieved in
421 the biostabilization basin of the MBT plant during the aerobic treatment. This sanitation process may have
422 significantly reduced the microorganism population inside the waste mass, especially the mesophilic
423 bacteria, which are more sensitive to high temperatures than the thermophilic ones. On the other hand,
424 the lower gas generation measured in test T4A compared to T8 may be explained considering that the
425 methanogenic mesophilic bacteria could be more vulnerable to unfavourable environmental conditions
426 (higher toxic effects exerted by VFA and ammonia) and have lower growth rates (van Lier et al., 1997;
427 Amani et al., 2011) compared to the thermophilic bacteria, that implies the adapting period could last
428 longer. In conclusion, results obtained during stage I and II suggested that the capability of the MBT waste
429 to generate methane is drastically limited due to inhibition effects, which are emphasized at lower water
430 contents, also because the initial bacteria population inside the waste mass could not contain a sufficient
431 level of methanogens to sustain the anaerobic process under the specific test conditions (high organic

load). For a better understanding of these results, during stage III of the experimental activity, reactors were opened and waste was partially removed in order to measure pH, VFA and NH_4-N. Then, inoculum (30% of final TS) and water (up to a final moisture content of 75 %w/w) were added in reactors R2, T2A, T3, T6A, T7 and incubated again. The beneficial effects of water and inoculum supply were evident, resulting in an immediate growth of the biogas yield, with increasing gas generation rates at higher temperature. On the one hand, the supplemental water addition may have reduced the inhibitory effect by diluting potential toxic substances such as heavy metals (copper, chromium or zinc), ammonia and VFAs. (Chen et al., 2008; Yenigun and Demirel, 2013; Poggi-Varaldo et al., 1997). On the other hand, a proper balance between acidogens and methanogens could have been achieved by lowering the organic load (through waste removal) and increasing the active bacteria mass within the anaerobic reactors (through inoculum addition). Indeed, tests at 55 °C achieved the asymptotical value of 66.7 ± 6.3 Nl CH_4/kgTS and 50.0 ± 2.3 Nl CO_2/kgTS within 30-40 days after the inoculum and water addition. In tests performed at 37 °C, a cumulative volume of 73.1 ± 2.1 Nl CH_4/kgTS and 54.9 ±1.8 Nl CO_2/kgTS was measured after 60-70 days from inoculum and water supply. These results showed that the biodegradability of the MBT waste in terms of methane and carbon dioxide yields did not vary significantly between 37 °C and 55 °C when moisture conditions were not limiting, as also observed by other authors (Hejnfelt and Angelidaki, 2009; Liu et al., 2009; Veeken and Hamelers 1999). In fact, in both cases, the total biogas yield at the end of these tests was in the range of 55–60 % of the methane potential value (66.7 and 73.1 against 121 Nl CH_4/kgTS). However, from the results obtained at room temperature, it is evident that the temperature surely affects the gas generation rate but also seems to influence the gas generation capacity. Indeed, in test with water and inoculum addition (see R2 test in Fig. 2), the gas production achieved a value of 8.5 ± 1.0 Nl CH_4/kgTS and 19.3 ±0.3 Nl CO_2/kgTS after 70 days from inoculum addition but was still increasing, indicating that the stable methanogenic phase has not been reached yet (see Fig. S1 in the Supplementary information).

3.4 Estimation of biogas kinetic constants

Fig. 5 shows, for the tests that achieved the stable methanogenic phase, the cumulative biogas production simulated with the first-order kinetic model (lines) fitted to the measured data (dots). The best-fit

parameters used in the model are reported in Table 5. Making reference to Fig. 5, it can be noticed that, in all cases, the first-order kinetic model accurately reproduces the different shapes of accumulated gas volume curves, as confirmed by the R^2 values reported in Table 5. Modelling the experimental results revealed that the biodegradability of the MBT waste, which is expressed as ratio of cumulative gas volume to potential gas ($\%L_0$/BMP), ranged between 56% to 75% in tests at 75 %w/w water content and decreased to 34% in tests with water content at field capacity and without inoculum addition. This range is slightly lower than the typical values for solid state incubation tests of MBT residues, presumably due to the poor stability degree of the MBT waste analysed in this study. For example, Binner and Zach (1999) found that the gas generated within 90 days was about 75% to 90% of the potential gas generation capacity (e.g. gas volume measured after 240 days) for well treated wastes (duration of pre-treatment >10weeks).

Fig. 5

As already discussed above, higher operative temperature leads to a faster gas generation since temperature enhances both microbial growth and activity (Bouallagui et al., 2005; Gavala et al., 2003; Kim et al., 2002). Specifically, k-values vary from 0.007 d^{-1} at room temperature, 0.03-0.05 d^{-1} at 37 °C and 0.04-0.11 d^{-1} at 55 °C. Moreover, a linear correlation of k-values with the operative temperature was observed for tests at 75 %w/w water content.

These k-values were also used to estimate the time required to reach the 99% of the maximum biogas generation L_0, as follows:

$$T_{99\%} = \frac{\ln(1-0.99)}{k} \quad (4)$$

Due to quite high k-values, a relatively short time period $T_{99\%}$ (Table 5), ranging from few months up to 2 years, was computed.

Table 5

Table 6 reports a brief literature review of the kinetic constants and gas yields experimentally determined for different types of organic substrates. As shown in Table 6, these parameters vary substantially between different substrates, experimental procedures and tests conditions. Even if a direct comparison is not possible, the k-values obtained in this work are in line with most of these studies. For instance, the k-value

484 of 0.007 d^{-1} determined at T=20-25 °C and water content of 75 %w/w, is consistent with the results
485 obtained by Vavilin et al. (2004) for MSW waste at 65% of water content and T=30 °C (k=0.007-0.08 d^{-1}).
486 Similarly, the k-values range (0.028-0.054 d^{-1}) observed at 37 °C appears close to the one reported by Neves
487 et al. (2006), which refer to a co-digestion of organic waste and sewage sludge (0.035-0.063 d^{-1}). On the
488 contrary, significant differences can be observed referring to the results presented by De Gioannis et al.
489 (2009) and Mou et al. (2015). Indeed, the k-values reported by those authors are up to one-two orders of
490 magnitude lower than the ones obtained in this work. This difference can be due to the higher content of
491 readily degradable organic matter in the analysed MBT waste compared to the low-organic wastes of Mou
492 et al. (2015) and De Gioannis et al. (2009).
493 Nevertheless, it should be kept in mind that the high water content (75 %w/w) as well as the inoculum
494 addition had accelerated the biodegradation process during the anaerobic experiments. Hence, the gas
495 generation rate and yield listed in Table 5 may be overestimated in comparison to real landfill conditions
496 where the emplaced MBT wastes will not be able to retain the high water content (75 %w/w) simulated in
497 lab scale tests. For example, Heyer et al. (2013) stated that the biological conversion process within
498 lysimeters filled with MBT waste could be accelerated by a factor 3-10 compared to MBT landfills due to
499 water addition or leachate recirculation.
500 **Table 6**

501 ## 3.5 Inhibition of anaerobic digestion process

502 Analysis carried out on the MBT waste samples removed from the reactors at the different stages of the
503 tests revealed that pH was still suitable for the anaerobic digestion (6.6-7.0). Hence, in this specific case, pH
504 alone did not give a clear indication of process inhibition. However, it should be considered that pH
505 changes may be very small in highly buffered system even when the process is severely stressed (Ahring et
506 al., 1995). Thus, it is likely that pH was buffered due to contrasting effects of VFAs accumulation, which
507 could have led to acidic conditions, and proteins degradation that could have favoured an increase of waste
508 buffer capacity through the ammonia release (Veeken et al., 2000). In fact, as shown in Table 7, high VFAs
509 and ammonia concentrations were measured in all MBT samples. Specifically, Table 7 reports the average

values of total TKN and soluble nitrogen NH_4-N, the ratio between NH_4-N and TKN, and the total VFAs concentration measured in the fresh MBT sample and in the MBT samples removed from the anaerobic batch experiments carried out at room temperature (R2), at 37 °C (T2A and T3) and 55 °C (T6A and T7). As shown in this table, the ratio of NH_4-N/TKN exhibited a twofold increase compared to what measured in the fresh waste. Moreover, VFAs concentrations in all samples were more than one order of magnitude higher than the ones measured in the fresh sample. These results indicate that the analysed MBT waste still contains a certain amount of readily and medium-degradable organic matter, which was not expected, since the easily degradable fraction was supposed to be mineralised during the stabilization process in the MBT plant. The high biological reactivity of this MBT waste may be in part due to a limited efficiency, during the waste sampling campaign, of the aerobic decomposition process employed in this specific MBT plant. However, as also highlighted in previous researches, this poor stabilisation can be mainly ascribed to the fact that the wastes coming out from this plant are not subjected to a further ripening treatment that might be necessary in order to obtain a well stabilized waste with lower impacts in landfills (Di Lonardo et al., 2014). Referring to Table 7, it can also be noticed that total VFAs content, as well as ammonia, exhibited an increasing trend with temperature (T7,T6 > T3, T2 > R2) reflecting the different extent of the biological process reached at different operating conditions. Namely, a total VFAs content ranging from 5.4 to 7.9 g/l was measured and the acetate was found as the predominant compound (see Table S1 in supplementary information). Hence, it seems that the hydrolytic-acidogenic bacteria did not limit the substrate degradation and the process was held at the acetogenic and methanogenic stage (a similar result was obtained by Palatsi et al., 2011). Therefore, the inhibition was likely due to an imbalance in the growth rate of acidogenic bacteria, which led to an accumulation of degradation by-products in reactors, as also observed by Adani et al. (2004). On the other hand, the inhibition of methanogenic bacteria may be also due to the high TKN and ammonia content observed in the MBT samples (see Table 7). Thus, it is likely that the interaction between ammonia, VFA and pH could have led to an “inhibited steady state” condition in which the process was running stably but a very low methane yield (Chen et al., 2008).

Table 7

3.6 Experimental findings and practical implications

The BMP experiments, performed under optimal operating conditions, highlighted that for the analysed MBT waste, only 45 % of the theoretical gas generation potential can be achieved within 30 days. This may be due to the presence of less soluble/degradable or more recalcitrant organic substances in the solid matrix, which cannot be mineralized during the limited duration of the BMP experiment. Hence, BMP tests, with respect to a simple stoichiometric estimation from the organic carbon measured in the solid matrix, can provide useful indications on the expected potential gas generation capacity of landfilled waste under optimal conditions. On the contrary, the results obtained in this study highlighted that particular caution should be paid when the anaerobic batch tests are carried out under limiting operational conditions, e.g. low water content and temperature, high organic load, no inoculum addition. This is particularly true when the material of concern is, as in the present case, a waste with high organic matter content and a poor stability degree. In fact, although the tests performed under these limiting conditions may better resemble the environmental conditions expected in the field, the presence of inhibitory substances at high level (such as ammonia, VFA, heavy metals) may slow down or stop the anaerobic microbial process leading to an underestimation of the gas yield and generation rate. Indeed, as already shown in Table 7, in all experiments which exhibited very low gas generation rate and methane content, high concentrations of VFA and ammonia were measured within the systems, revealing an imbalanced kinetic between acid forming and acid consuming bacteria. Nevertheless, small pH changes were detected due to high protein degradation, which have increased buffer capacity of the analysed waste sample as a result of ammonia release. Hence, it is likely that the interaction between ammonia, VFA and pH lead to an “inhibited steady state” condition in which the anaerobic process may run stably but at a very low gas yield. In particular, the experimental results suggested that the microbial activity could be completely inhibited when the water content of MBT waste was less than 32% (on wet weight) and severely reduced for higher water content (up to the field capacity of approximately 43%) depending on the operating temperature. These findings suggest that a stable gas generation process could be delayed for a long time until the environmental conditions within MBT waste landfills become favourable to the establishment of a stable methanogenic

562 activity. Thus, it is not possible to predict how long the lag-phase can last in a landfill disposal scenario,
563 where the boundary conditions significantly vary depending on the climate, the landfill geometry (surface,
564 height), the operative management strategies in place (e.g. leachate recirculation, waste disposal
565 methods), the presence and type of temporary and final cover systems. Indeed, the experimental results
566 reported in this study revealed that, as soon as the anaerobic process starts, a relative short time period,
567 ranging from few months up to two years depending on the water content and temperature, is required to
568 deplete the gas generation capacity. However, small scale experiments performed under controlled
569 conditions may not provide a gas generation trend that is completely representative of full-scale landfill
570 sites. Here, higher heterogeneous and variable conditions are expected due to greater amounts of waste
571 mass, miscellaneous nature of emplaced waste as well as the heterogeneity of water flow patterns inside
572 the landfill body that are also affected by operational strategies (such as waste emplacement density,
573 permeability and thickness of daily cover). Moreover, landfilled waste are subjected to increasing
574 overloading pressure due to the emplacement of new waste layers. This condition surely influences the
575 water retention capacity of landfilled MBT waste so that the water content will be surely lower than the
576 ones simulated in the lab scale tests (e.g. 75 %w/w). This implies that the gas generation, in terms of both
577 gas yield and rate, measured in anaerobic experiments at high water contents may be significantly higher
578 than what expected in real scale MBT waste landfills.

579 # 4 Conclusions and perspectives

580 The gas production from MBT wastes was analysed by performing anaerobic batch tests under different
581 operating conditions. In order to characterize the MBT material regarding its long-term gas emission in
582 different landfill disposal scenarios, a wide range of water contents (26-43 %w/w up to 75 %w/w) and
583 temperatures (20-25 °C, 37 °C and 55 °C) were investigated. The obtained results suggest that the analysed
584 MBT material still contains a large amount of readily degradable organic matter, as confirmed by the long
585 duration of the lag-phase (several months), the high values of gas production potential (199.2±63 Nml/gTS),
586 the gas generation rates (ranging from 0.007 d^{-1} at room temperature, 0.03-0.05 d^{-1} at 37°C and 0.04-0.11

587 d^{-1} at 55°C), as well as by the strong inhibition effects observed due to high concentrations of VFAs and
588 soluble ammonia.
589 Based on the results presented in this paper, the following conclusions and perspectives can be drawn:
590 - it is very difficult to predict how long the lag-phase can last in MBT waste landfills where the
591 boundary conditions change continuously and vary significantly depending on the climate, the
592 landfill geometry (surface, height), the operative management strategies in place (e.g. leachate
593 recirculation, waste disposal methods) and the presence and type of temporary and final cover
594 systems.
595 - The water content of emplaced MBT waste is the most important factor limiting the anaerobic
596 biological process. Experimental results showed that when the moisture was lower than 32 %w/w,
597 the methanogenic microbial activity was completely inhibited whereas for higher values (43% w/w)
598 only a limited amount of the degradable organic matter was converted to biogas (34% of the
599 potential gas generation capacity).
600 - As soon as the environmental conditions inside the waste mass become favourable to the
601 establishment of the stable methanogenic phase, a relatively short time period, ranging from few
602 months up to two years is required to deplete the MBT waste gas generation. However, this result
603 provides just an indication of the actual lifetime of biogas production from MBT wastes disposed of
604 in landfills, where much higher amount of waste are emplaced and the environmental conditions
605 may be quite far from the experimental ones.
606 - The benefits of using the MBT technology within a sustainable waste management system strongly
607 depends on the efficiency of the biostabilization process in reducing the gas generation capacity of
608 the residual MBT waste. In this specific case, experimental data suggest that the aerobic biological
609 treatment carried out in this specific MBT facility was not properly managed and did not guarantee
610 a sufficient degree of stability for the produced MBT waste. Therefore, a further treatment of this
611 MBT waste might be desirable before landfilling it.

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Fig. 1. BMP cumulative methane production measured in control (red dots) and MBT waste (green dots) tests, expressed as Nml CH_4 per g of total solids. Solid red line: theoretical methane generation of control. Dotted green line: theoretical methane generation of MBT waste, computed according to Eq. (3). Bars: standard deviation. The results is the average of 6 and 3 bottles for MBT waste and controls, respectively.

Fig. 2. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at room temperature (20-25 °C) and different values of initial water content (26%, 34-75% and 43% w/w). Solid red line: CH_4 potential obtained from BMP tests. Dotted black line: CO_2 potential obtained from BMP tests. Dotted grey line: starting point of stage III.

Fig. 3. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at 37 °C and different values of the initial water content (26%, 32%, 32-75%, 38-75%, 43% and 43-48% w/w). Solid red line: CH_4 potential from BMP. Dotted black line: CO_2 potential from BMP. Solid grey line: starting point of stage II. Dotted grey line: starting point of stage III.

Fig. 4. Cumulative methane (red circles) and carbon dioxide (black square dots) curves as a function of the incubation time, obtained during anaerobic batch tests carried out on MBT waste samples at 55 °C and different values of the initial water content (26%, 32%, 32-75%, 38-75%,43% w/w).

Fig. 5. Cumulative biogas volume (Nl/kgTS) as a function of the incubation time: comparison between measured data (dots) and modelling results obtained with a first-order kinetic model (lines).

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842 **Table 1 (Line 94)**

Reference	*Amount*	*Particle size*	*Water addition*	*Inoculum*	*Temperature (°C)*	*Test duration (d)*	*Aim*
Binner and Zach (1999)	50 g TS	<20 mm	1 l demineralized water	Used	35	42	Cumulative gas
De Araujo-Morais et al. (2008)	20 g	<20 mm	1.2 l nutrient medium	Used	35	90	Cumulative gas
Sormunen et al. (2008)	2 gVS_w/gVS_{in}	<40 mm	up to 95%	Used	20-22	70-100	Methane potential
Barrena et al. (2008)	200 g	ns	Not added	Used	35	100	Gas production in solid state test
Barrena et al. (2008)	1 g TS	<1 mm	up to 50%	Used	35	75	Gas production in liquid state test
Binner & Zach (1999)	1 kg TS	<20 mm	up to water holding capacity	Not used	40	90	Determining gas generation in landfills
De Gioannis et al. (2009)	500 g	ns	up to water holding capacity	Not used	30	240-390	Modelling gas generation
Sormunen et al (2008)	96 t	<40 mm	ns	Used	40	640	Simulate landfill emissions

ns=not specified

(*) water added on wet weight basis

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Table 2 (Line 108)

Categories	*Mean*	*SD*
Fines < 20mm	13.4	3.8
Organic waste	28.0	7.3
Paper	16.0	4.6
Cardboard	7.7	3.2
Coupled packaging	1.8	0.5
Textiles	3.0	1.1
Diapers	4.8	2.0
Plastics	14.4	2.8
Rubber	0.4	0.3
Glass	3.7	1.9
Metals	2.9	1.1
Inert materials	1.2	1.0
Hazardous waste	0.4	0.3
Wood	1.9	1.7
Leather	0.1	0.2
Others	0.4	0.4

Table 3 (Line 250)

ID TEST	Reactor volume (l)	T°C)	MBT weight (kg TS)	Water content (% w/w)	Inoculum addition (g)	Duration (d)
R1A, R1B	12	20-25	4.0	26%	Not used	**Stage I**: 167
R2A, R2B	12	20-25	4.4	34% (**Stage I**) 75% (**Stage III**)	**Stage III**: 800 g mesophilic inoc. (TS=3.8% wet weight, VS=60%TS) + 6.1 kg water [(a)]	**Stage I**: 94 **Stage III**: 73
R3A, R3B	12	20-25	4.5	43%	Not used	**Stage I**: 167
T1A, T1B	1	37	0.37	26%	**Stage II**: 20 g mesophilic inoc. (TS=3.8% wet weight, VS=60%TS)	**Stage I**: 38 **Stage II**: 94
T2A	1	37	0.36	32% (**Stage I**) 75% (**Stage III**)	**Stage II**: 20 g mesop. inoc. **Stage III**: 70 g mesop. inoc. + 530 g water [(b)]	**Stage I**: 38 **Stage II**: 20 **Stage III**: 74
T2B	1	37	0.37	32%	**Stage II**: 20 g mesop. inoc. (TS=3.8% wet weight, VS=60%TS)	**Stage I**: 38 **Stage II**: 94
T3A, T3B	1	37	0.38	38% (**Stage I**) 75% (**Stage III**)	**Stage III**: 70 g mesop. inoc. + 530 g water [(b)]	**Stage I**: 58 **Stage III**: 74
T4A	1	37	0.38	43%	Not used	**Stage I**: 132
T4B	1	37	0.38	43% (**Stage I**) 48% (**Stage III**)	**Stage III**: 70 g mesop. Inoc. (same), no water addition [(c)]	**Stage I**: 50 **Stage III**: 82
T5A, T5B	1	55	0.36	26%	**Stage II**: 20 g thermophilic inoc. (TS=3% wet weight, VS=65%TS)	**Stage I**: 24 **Stage II**: 76
T6A	1	55	0.36	32% (**Stage I**) 75% (**Stage III**)	**Stage II**: 20 g thermop.inoc. **Stage III**: 70 g thermop. inoc. + 530 g water (d)	**Stage I**: 24 **Stage II**: 19 **Stage III**: 57
T6B	1	55	0.37	32%	**Stage II**: 20 g thermop. inoc.	**Stage I**: 24 **Stage II**: 76
T7A, T7B	1	55	0.39	38% (**Stage I**) 75% (**Stage III**)	**Stage III**: 70 g thermop. inoc. + 530 g water [(d)]	**Stage I**: 43 **Stage III:** 57
T8A, T8B	1	55	0.38	43%	Not used	**Stage I**: 103

(a) Waste removed from reactor before inoculum and water addition. TS content Stage III: 2.66 kgTS

(b) Waste removed from reactor before inoculum and water addition. TS content Stage III: 0.21 kgTS (T3A/B)- 0.24 kgTS (T2A)

(c) Waste removed from reactor before inoculum addition. TS content Stage III: 0.36 kgTS

(d) Waste removed from reactor before inoculum and water addition. TS content Stage III: 0.22 kgTS (T7A/B) - 0.24 kgTS (T6A)

Table 4 (Line 273)

	Mean	*Unit*
Initial water content, W [(*)]	19.4 ± 1.1	(%w/w)
Water content at field capacity, FC [(*)]	41 ± 5	(%w/w)
Total solids, TS [(*)]	80.6 ± 1.0	(%w/w)
Volatile solids, VS	47.3 ± 1.0	(%TS)
Organic carbon, TOC	23.9 ± 0.3	(%TS)
pH	6.7	--
TKN	14.1± 2.0	g/kgTS
NH_4-N	2.0 ± 0.2	g/kgTS
COD	520 ± 40	g/kgTS
Total VFA	0.18 ± 0.05	g/l

[(*)] expressed on wet weight basis

Table 5 (Line 427)

	T= 20-25°C	T= 37°C			T= 55°C		
	R2 (W=34%-75%)	**T4B (W=43%-50%)**	**T2A (W=32%-75%)**	**T3 (W=39%-75%)**	**T8 (W=43%)**	**T6A (W=32%-75%)**	**T7 (W=39%-75%)**
L_0 (Nl/kgTS)	75	140	150	129	68	130	111
t_{lag} (d)	103	75	73	69	39	59	52
k (d^{-1})	0.007	0.028	0.044	0.054	0.038	0.110	0.110
R^2	0.993	0.991	0.972	0.996	0.992	0.981	0.986
% L_0/BMP	37.7	70.3	75.3	64.8	34.1	65.3	55.7
$T_{99\%}$ (d)	658	165	104	85	121	42	42

Table 6 (Line 447)

Gas yield	*k-value(d^{-1})*	*Substrate*	*Experimental assay*	*Reference*
75 Nl/kgTS	0.007 (T=20-25°C)	MBT waste (different water contents)	anaerobic batch digester	*This work*
129-150 Nl/kgTS	0.03-0.06 (T=37°C)			
68(*)-130 Nl/kgTS	0.04(*)-0.11 (T=55°C)			
52 -70 gCH_4/kg	$4.3 \cdot 10^{-4}$-$5.2 \cdot 10^{-4}$	sludge	anaerobic batch digester	Mou et al. (2015)
107-117 Nl/kg	$6.6 \cdot 10^{-5}$-$6.8 \cdot 10^{-5}$	combustible waste		
37.6 lCH_4/kg	0.013 (T=55°C)	lignocellulosic biomass	batch reactor (BMP)	Ghatak and Mahanta (2014)
26.6 lCH_4/kg	0.004 (T=35°C)			
350 NlCH_4/kgTS	0.068 (T=35°C)	mixed waste from landfill	reactor with recirculation	Bilgili et al. (2009)
425 NlCH_4/kgTS	0.056 (T=35°C)	(44% w/w organic)	reactor without recirculation	
19 Nl/kg	$9.6 \cdot 10^{-5}$ (T=30°C)	MBT waste (water=50% w/w)	anaerobic batch digester	De Gioannis et al. (2009)
550 Nl/kgVS	0.1	hay (no comminution)	anaerobic batch digester	Vavilin et al. (2008)
590 Nl/kgVS	0.15	hay (comminution)		
240-280 NlCH_4/kgVS	0.035-0.063 (T=37°C)	co-digested organic waste and sewage sludge	anaerobic batch digester	Neves et al. (2006)
163 NlCH_4/kgVS	0.0311 (T=35°C)	grey waste (residual MSW, 41% w/w biodegradable)	batch reactor (BMP)	Vavilin et al. (2004)
---	0.007 - 0.08 (T=30°C)	MSW (water=65% w/w)	landfill reactors	Vavilin et al. (2004)
---	0.06-0.245 (T=28°C)	biowaste	continuous anaerobic digester	Veeken et al. (2000)
---	0.03-0.15 (T=20°C)	selected biowaste components	anaerobic batch digester	Veeken and Hamelers (1999)
---	0.24-0.47 (T=40°C)			
140 lCH4/kgVS	0.405 (T=35°C)	mechanically separated OF-MSW	continuous anaerobic digester	Mata-Alvarez et al. (1990)

(*) values refer to 103-days experiments performed at 55 °C and 43% (wet weight) water content, without inoculum addition.

Table 7 (Line 479)

SAMPLE	*TKN (g/kgTS)*	*NH_4-N (g/kgTS)*	*NH_4-N/TKN (%)*	*VFA (g/l)*
FRESH WASTE	14.1 ± 2.0	2.0 ± 0.2	14.4	0.18 ± 0.05
R2 (20-25 °C, W= 34 %w/w)	15.2 ± 1.2	3.4 ± 0.1	22.7	5.42 ± 0.24
T2A (37 °C, W=32 %w/w)	15.2 ± 0.6	4.2 ± 0.2	27.4	6.28 ± 0.58
T3 (37 °C, W= 38 %w/w)	14.1 ± 0.9	4.2 ± 0.3	30.1	7.57 ± 0.31
T6A (55 °C, W= 32 %w/w)	14.1 ± 1.4	4.6 ± 0.3	32.4	7.94 ± 0.93
T7 (55 °C, W= 38 %w/w)	15.0 ± 1.3	5.0 ± 0.2	33.6	7.56 ± 0.83

Figure 1 (Line 317)

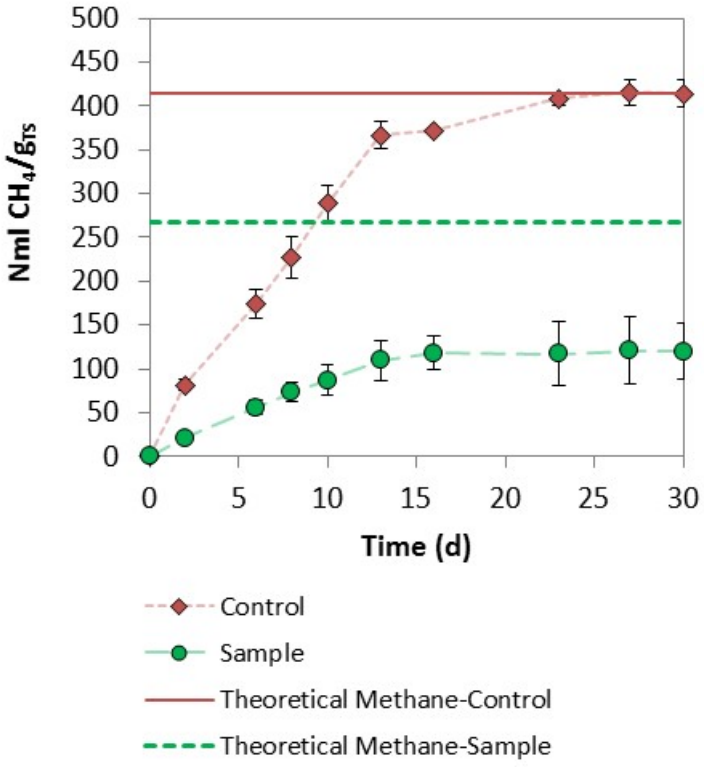


Figure 2 (Line 336)

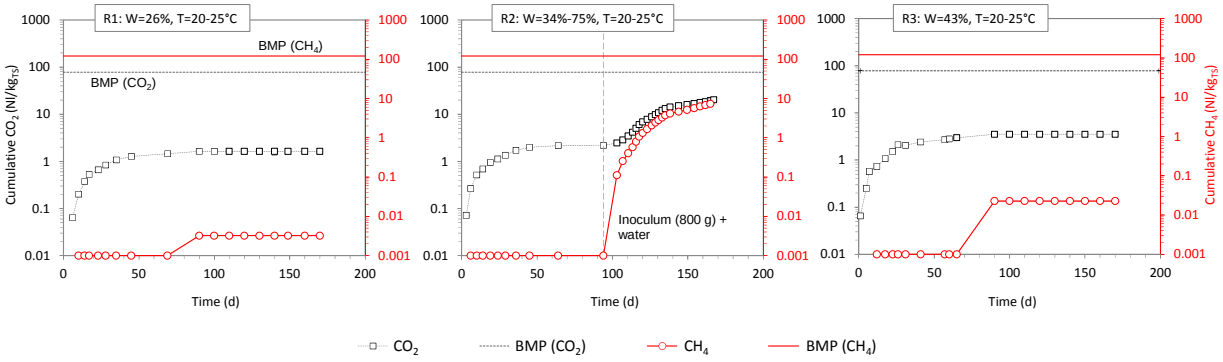
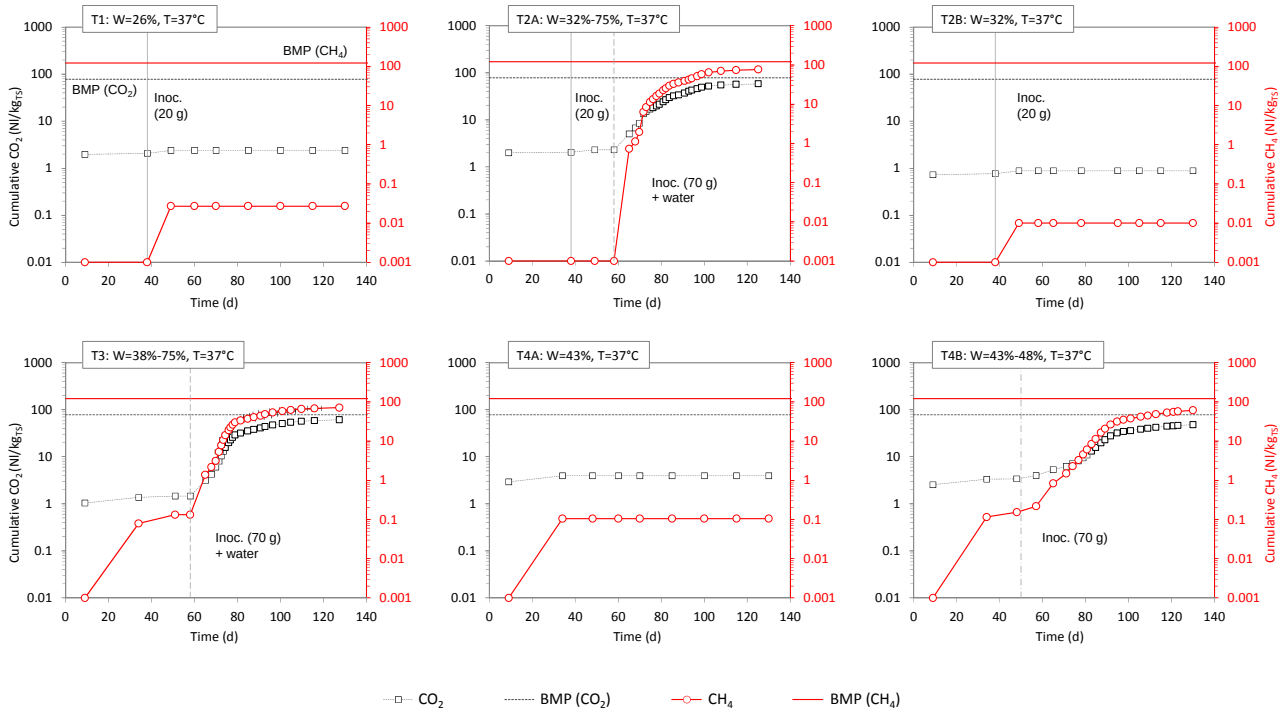


Figure 3 (Line 338)



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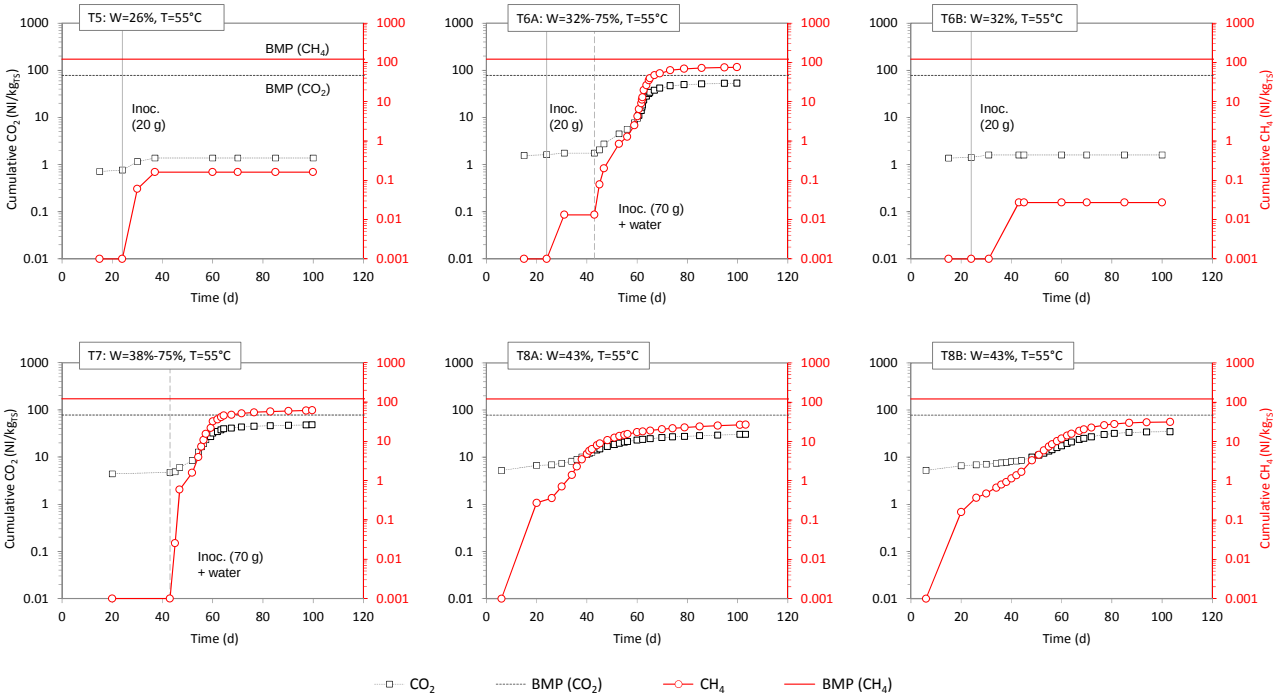
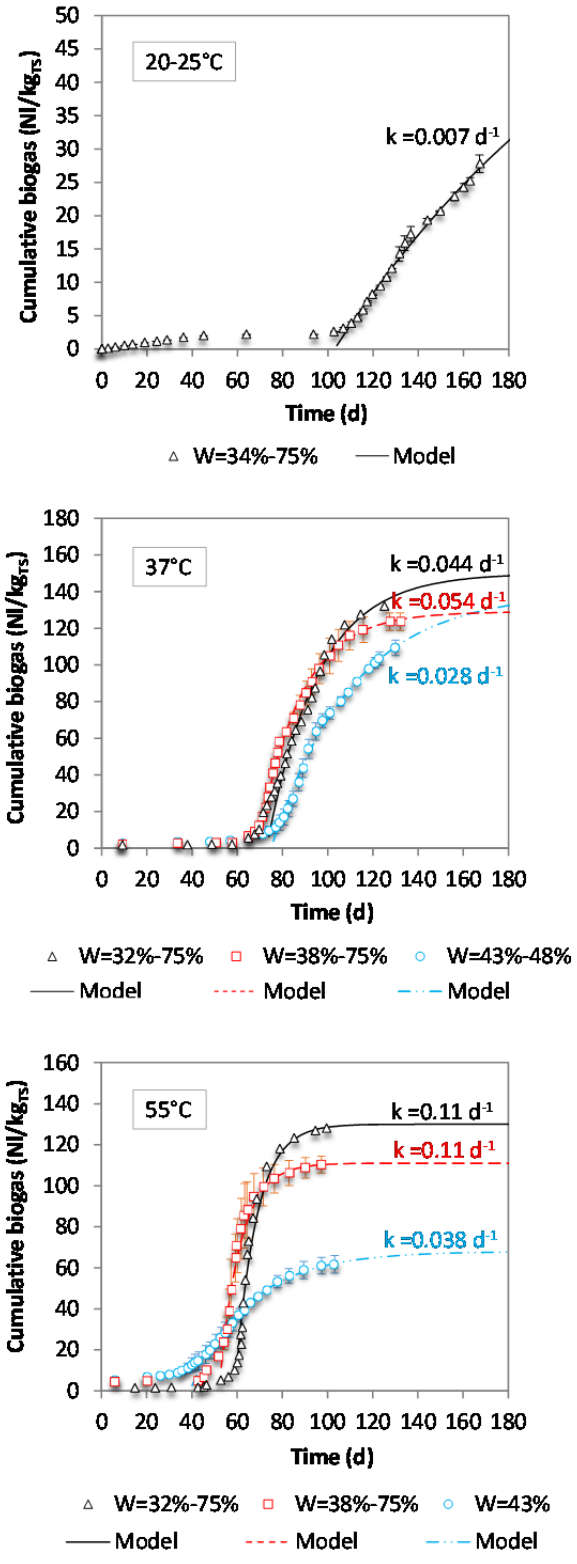


Figure 5 (Line 418)



5

Supplementary Material for:

Assessment of biogas production from MBT waste under different operating conditions

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Figure S1. Gas composition (percentage by volume) measured in tests at room temperature (20-25°C) and initial water content of 32%-75% (R2) and 43% (R3). Solid grey line: starting point of stage III.

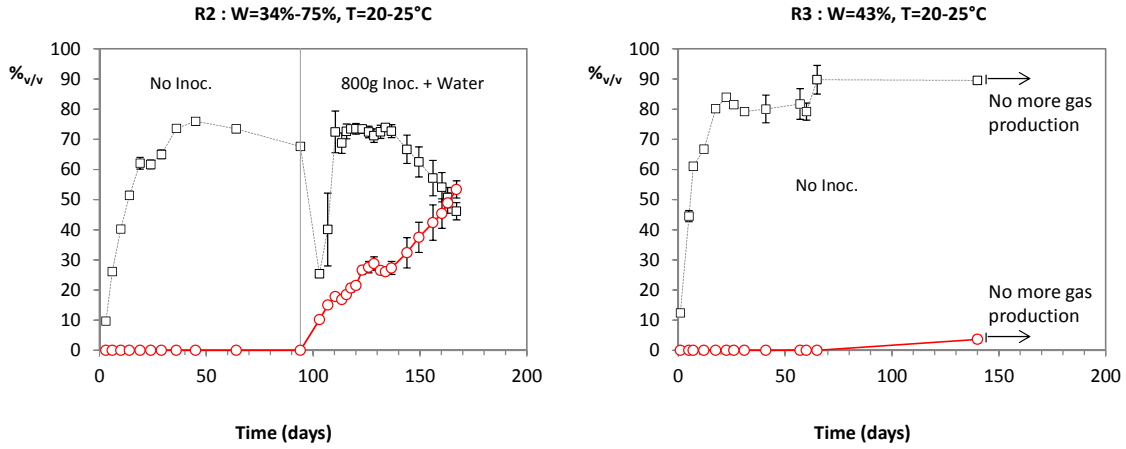

Figure S2. Gas composition (percentage by volume) measured in tests at 37°C and initial water content of 32%-75% (T2A), 32% (T2B), 38%-75% (T3A/B), 43% (T4A) and 43%-48% (T4B). Dotted grey line: starting point of stage II. Solid grey line: starting point of stage III.

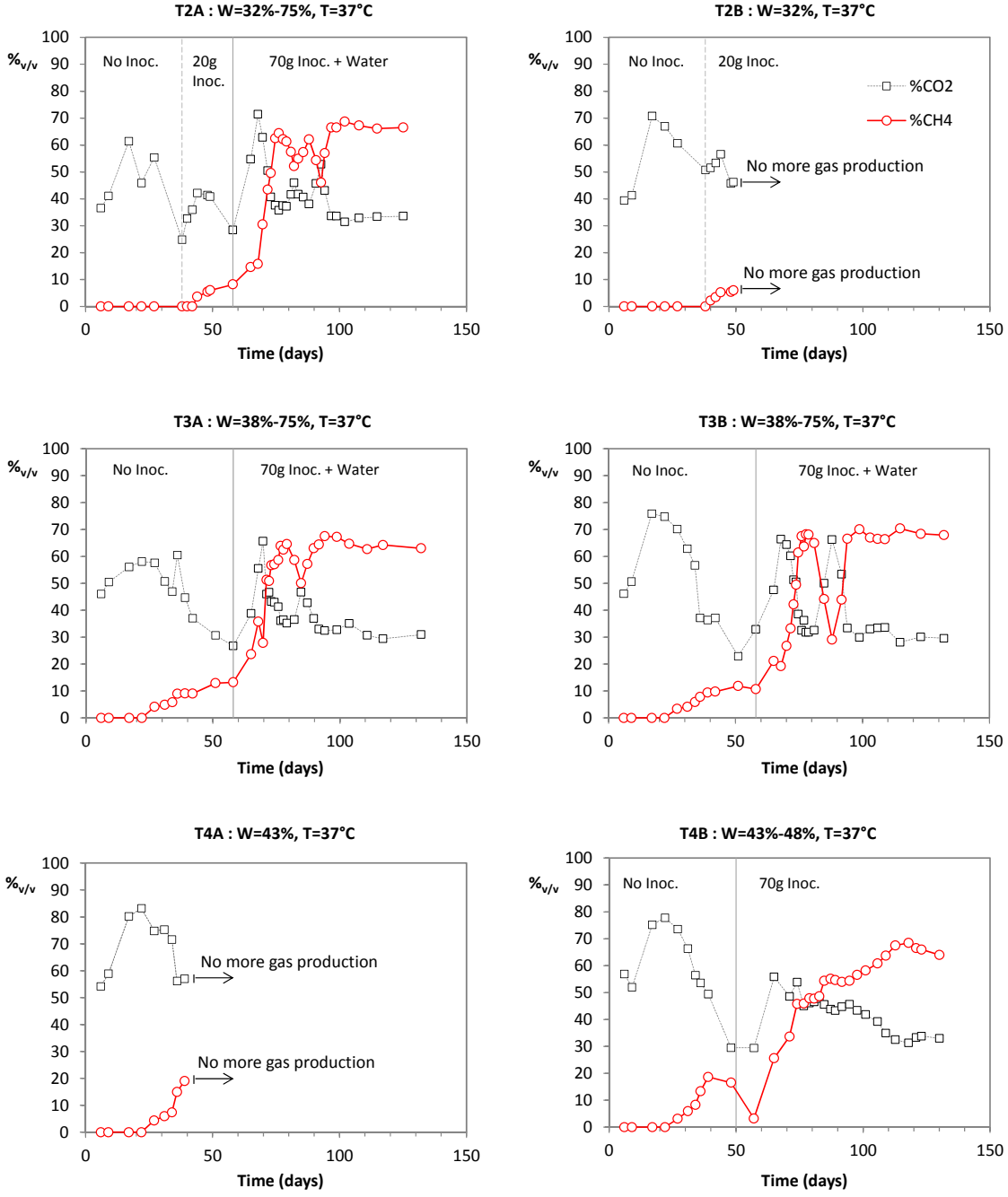

Figure S3. Gas composition (percentage by volume) measured in tests at 55°C and initial water content of 32%-75% (T6A), 32% (T6B), 38%-75% (T7A/B), 43% (T8A/B). Dotted grey line: starting point of stage II. Solid grey line: starting point of stage III.