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Assessment of methane production from shredder waste in landfills: the influence of temperature, moisture and metals

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Abstract

In this study, methane (CH_4) production rates from shredder waste (SW) were determined by incubation of waste samples over a period of 230 days under different operating conditions, and first-order decay kinetic constants (k-values) were calculated. SW and sterilized SW were incubated under different temperatures (20-25 °C, 37 °C, and 55 °C), moisture contents (35 % and 75 % w/w) and amounts of inoculum (5 % and 30 % of the samples wet weight). The biochemical methane potential (BMP) from different types of SW (fresh, old and sieved) was determined and compared. The ability of metals (iron, aluminum, zinc, and copper) contained in SW to provide electrons for methanogens resulting in gas compositions with high CH_4 contents and very low CO_2 contents was investigated. The BMP of SW was 1.5-6.2 kg CH_4 /ton waste. The highest BMP was observed in fresh SW samples, while the lowest was observed in sieved samples (fine fraction of SW). Abiotic production of CH_4 was not observed in laboratory incubations. The biotic experiments showed that when the moisture content was 35 % w/w and the temperature was 20-25 °C, CH_4 production was extremely low. Increasing the temperature from 20-25 °C to 37 °C resulted in significantly higher CH_4 production while increasing the temperature from 37 °C to 55 °C resulted in higher CH_4 production, but to a lower extent. Increasing the moisture and inoculum content also increased CH_4 production. The k-values were 0.033-0.075 yr^{-1} at room temperature, 0.220-0.429 yr^{-1} at 37 °C and 0.235-0.488 yr^{-1} at 55 °C, indicating that higher temperatures resulted in higher k-values. It was observed that H_2 can be produced by biocorrosion of iron, aluminum, and zinc and it was shown that produced H_2 can be utilized by hydrogenotrophic methanogens to convert CO_2 to CH_4 . Addition of iron and copper to SW resulted in inhibition of CH_4 production, while addition of aluminum and zinc resulted in higher CH_4 production. This suggested that aluminum and zinc contribute to high CH_4 production from SW by providing H_2 for hydrogenotrophic methanogens. Gas compositions with higher CH_4 and lower CO_2 observed in landfilled SW are thus most likely

due to the consumption of existing CO₂ in the produced biogas and the produced H₂ by biocorrosion of aluminum and zinc by methanogens.

Keywords

end-of-life vehicles; anaerobic digestion; biogenic carbon; biochemical methane potential (BMP); biocorrosion; first-order decay kinetic constant

1. Introduction

An end-of-life vehicle (ELV) is a vehicle that is discarded by its owner as waste. Together with other metal-containing waste products, including white goods, ELVs are collected, dismantled and shredded by authorized shredding companies. The ferrous and non-ferrous metals are then recovered. The residual fraction after recovery of metals and dismantled parts is called shredder waste (SW). SW consists of mainly plastic, metals, rubber, textile, foam, glass and wood, and it constitutes approximately 20-25 % of an ELV's weight (Ahmed et al., 2014; Fiore et al., 2012; Morselli et al., 2010).

According to EU-Directive 2000/53/EC, a maximum 10 % of an ELV's weight may be incinerated, and a maximum of 5 wt% may be landfilled. However, the majority of SW is landfilled in most countries, including Denmark (Ahmed et al., 2014; Fiore et al., 2012). By deposition of SW in landfills, the biodegradable fractions produce landfill gas (LFG), which consists of methane (CH₄) and carbon dioxide (CO₂). Landfills are one of the main anthropogenic sources of CH₄ emission to the atmosphere. CH₄ is 28 times more powerful than CO₂ in terms of global warming potential (IPCC, 2013).

According to the European Pollutant Release and Transfer Register (E-PRTR), landfills—excluding landfills of inert waste—receiving more than 10 tons of waste per day or with a total disposal capacity of 25,000 tons are required to report their CH₄ emission (CEC, 2006). The reporting of CH₄ emissions from landfills is based on modeling of CH₄ generation in most countries, including Denmark. These models are based on the first-order decay (FOD) of organic matter, as shown by Eq. 1:

$$m_t = m_0 \times e^{-kt} \quad (\text{Eq. 1})$$

where m_t is the mass of organic carbon (g) after time t , m_0 is the mass of organic carbon (g) at $t = 0$, t is the degradation time (yr) and k is the FOD kinetic constant (yr^{-1}). The k -value (FOD kinetic constant) and biochemical methane potential (BMP) are two important parameters for estimation of the CH_4 generation by FOD models (Mou et al., 2015). Currently, knowledge of k -values and the BMP of SW is limited. Thus there is a need for more research about these parameters.

Although SW has passed through metal-separation technologies, the efficiency of separation is not 100 % and it still contains metals. The metal content of SW depends on the recovery technologies used and the initial amount of metals in the feed material. However, it is evident that due to an increase in metal scrap prices over time, metal recovery technologies are improving to recover more metals from SW (Ahmed et al., 2014).

Iron (Fe), aluminum (Al), zinc (Zn) and copper (Cu) are the most abundant metals in SW (Ahmed et al., 2014; Cossu et al., 2014; Fiore et al., 2012; Galvagno et al., 2001; Granata et al., 2011). Table 1 provides an overview of the metal content of SW. The fraction of these metals in SW varies significantly in previous studies. For instance, the percentage of Fe varied from 1.78 to 15.40 %. However, it can be observed that Fe is always the most abundant metal.

Table 1. Overview of the content (%) of Fe, Al, Zn and Cu in SW. The content is given per wet weight basis.

Reference	Fe (%)	Al (%)	Zn (%)	Cu (%)
Ahmed et al. (2014)	12.55-15.40	2.24-2.45	0.99-1.46	0.51-2.32
Fiore et al. (2012)	1.78	0.38	0.53	0.37
Granata et al. (2011)	9.30	1.50	1.10	1.50
Galvagno et al. (2001)	2.36-2.70	0.62-4.88	0.42-0.66	0.72-2.18

After sieving, the coarse fraction of SW consists of high amounts of metals and combustibles (plastic, rubber, foam, wood and textiles), while the fine fraction consists of more minerals and inert materials (Ahmed et al., 2014). This suggests that sieving SW could be an option for higher material and energy recovery from the coarse fraction, in order to reach the defined goal of

minimum 95 % reuse and recovery of the ELV's weight by the EU-Directive 2000/53/EC. If shredding companies apply sieving SW, the fine fraction will be landfilled, which could change the LFG production from SW significantly. Thus it would be interesting to know more about gas generation from the fine fraction of SW.

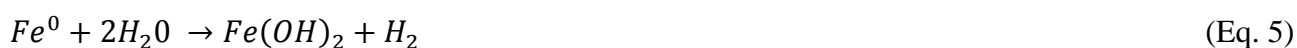
Generally, SW consists of about 20-30 wt% of plastic, 15-20 wt% of rubber, 20-40 wt% of paper and wood, and 10 wt% of inert materials (e.g. glass, and soil) and metals (Fiore et al., 2012). This indicates that SW contains low fractions of biodegradable waste and that the biodegradable fractions have a high content of lignocellulosic components such as paper and wood. However, relatively high production of CH₄ from SW (0.020-0.031 g CH₄ h⁻¹ ton⁻¹ of SW) has been observed in previous studies (Mønster et al., 2015; Scheutz et al., 2011). The reason for these relatively high CH₄ production rates from SW is unknown.

Conventional LFG consists of 55-60 % v/v of CH₄ and 40-45 % v/v of CO₂. However, previous studies have shown gas compositions in SW monofills, which differed from conventional landfill gas—having a high CH₄ content and very low or no CO₂ (Olsen and Willumsen, 2013; Scheutz et al., 2011). Moreover, high temperatures were reported inside SW monofills; 59 and 40 °C at 10 and 20 m depths, respectively (Olsen and Willumsen, 2013). The reason for the unusual gas composition and high temperatures are unknown. However, it is known that no aerobic reaction was taking place as there was no O₂ present in the sampled gas.

During anaerobic digestion, a part of the organic material is converted to CO₂ initially by fermentation and acetogenesis. Part of this generated CO₂ can be converted to CH₄ by hydrogenotrophic methanogens converting CO₂, using H₂ as the electron source as shown in Eq. 2 (Wise et al., 1978).



However, only around 30 % of the produced CH₄ is derived from this pathway due to limited H₂ supply (Gujer and Zehnder, 1983). Thus, theoretically it should be possible to increase CH₄ production by supplying H₂. A number of previous studies have investigated this approach in practice (Kim et al., 2013; Luo and Angelidaki, 2012; Luo et al., 2012). It was observed that supplying H₂ increased the CH₄ yield. H₂ can be produced by corrosion of the metals present in SW. For instance, H₂ production from Fe can be seen in Eq. 3-5 (Lorowitz et al., 1992).



The corrosion rate decreases as the corrosion products adhere to the surface of the metal, forming a protective layer. Microbial activity within the formed layer can influence the kinetics of the reactions. Accelerated deterioration of metals due to microbial activity is called biocorrosion or microbially influenced corrosion. In biocorrosion processes, the protective layer of H₂ formed on the surface of the metal can be used by biological reactions, such as hydrogenotrophic methanogenesis, and corrosion is accelerated (Beech and Gaylarde, 1999; Beech and Sunner, 2004; Lorowitz et al., 1992).

We hypothesized that high CH₄ production from SW and unusual gas composition could be due to H₂ production by biocorrosion of metals in the waste, supporting hydrogenotrophic methanogens to convert CO₂ to CH₄, resulting in higher CH₄ content and lower CO₂. The hypothesis is supported by microbial studies showing that biocorrosion of metals resulted in production of H₂ and enhancement of CH₄ yields by utilizing the produced H₂.

The objective of this study was to determine CH₄ production rates from SW with a focus on investigating the ability of metals contained in SW to provide electrons for methanogens. Moreover,

the BMP of different types of SW (i.e., fresh, old and sieved SW) was determined, and the impact of the age of the sample on the determined BMP was discussed. Finally, the impact of temperature, moisture and inoculum addition on biogas production from SW was evaluated and k-values at different operating conditions were calculated and compared to the literature.

2. Material and methods

2.1. Waste sampling, sample preparation and characterization

SW samples were collected from Odense Nord landfill located in Funen, Denmark. Odense Nord landfill was established in 1994 and is still in operation. Gas extraction facilities are installed in four cells of the landfill. An average of $19 \text{ Nm}^3 \text{ h}^{-1}$ LFG is collected from the SW cell. Different types of waste including SW, asbestos, sludge, soil and sand, and construction and demolition (C&D) waste are disposed of at this landfill. The landfill receives approximately 422,000 tons of waste per year, of which an average of 75,275 tons per year is SW. The SW is disposed of in individual cells dating back to 2000.

In total, four SW samples were obtained. SW samples were taken according to the year of deposition: 2009 (SW2009) and 2012 (SW2012). Fresh samples of SW (year 2015) were obtained by sampling the waste on the same day as it was deposited in the waste cell. This sample was referred to as fresh unsieved (FUS). A part of the fresh SW was sieved with a drum sieve (mesh size 10 mm) at the plant. A sample of the sieved SW (the fine fraction) was obtained and is referred to as fresh sieved (FS) hereinafter.

Samples were taken with an excavator or wheel loader, laid out in a long pile at the landfill, and subdivided three times using the long pile-alternate shovel method (EU Technical Report, 2004). Following this method, the sample was first laid out in a long pile. Then, using a shovel and placing alternate loads to either side, two equal piles were formed. One pile was then randomly

selected and the process was continued to reduce the sample size. Fifty kg of each SW sample was transported to the laboratory and kept at 10 °C.

In the laboratory, the samples were subdivided three times using the long pile-alternate shovel method, resulting in 5-7 kg of subsamples, which were then used in gas production rate experiments. Samples from 2009, 2012 and FUS were mixed together based on equal wet weight to make one composite sample (COM), representative of the whole landfill. Five kg of each sample was dried at 105 °C for 24 hours and total solids (TS) were calculated based on the difference in the weight of the sample before and after drying. Metals, wires and stones were separated manually from the dried samples. The resulting samples (of about 3-4 kg) were size reduced using a cutter mill with 1 mm sieve. The milled samples were analyzed for volatile solids (VS), total carbon (TC), total organic carbon (TOC), biogenic carbon (BioC) content and used in the BMP experiment (see section 2.2).

TS and VS were measured according to Standard Methods (APHA, 2005). TC and TOC were analyzed using a LECO Induction Furnace CS-200 oven on approximately 0.1 g of dried sample ground to 1 mm (EN 13137, 2001). All measurements were done in triplicate. The Biogenic Carbon (BioC) content of the waste samples was analyzed according to EN 15440 (2011), on 3.8 g dried and ground sample at a commercial laboratory (Beta Analytic, USA).

2.2. Biochemical methane potential (BMP)

2.2.1. Experiment set up and monitoring

BMP test was performed on all five SW samples: SW2009, SW2012, COM, FUS, and FS. The experiment was carried out in triplicate in 1 L glass bottles for 37 days in a 37 °C incubator. The inoculum to substrate ratio and organic loading rate (OLR) were 1 g VS/g VS and 5 g VS/L, respectively. Deionized water was added to get the final working volume of 300 mL. Iron particles

of 5 mm × 2.5 mm (16 % of the sample dry weight) were added to the SW2009 sample to investigate the effect of separated metals on BMP. Bottles were flushed with N₂ for 15 minutes to establish the anaerobic condition; then sealed with rubber septum.

CH₄ concentration in the headspace was measured two to three times per week by taking 0.2 mL gas samples from the headspace of the bottles and direct injection to a thermo-scientific trace gas chromatograph (TRACE 1310 GC, Q PLOT, 0.32 mm, 8 m) equipped with a flame ionization detector (FID). Helium was used as the carrier gas and the oven temperature was set at 160 °C. To avoid pressure build up, the produced biogas was released during the experiment. The amount of CH₄ generated was calculated based on the difference of CH₄ concentration before and after the release of excess gas from the reactor. Gas volumes from all incubations were converted to standard temperature and pressure conditions (STP; T = 273.15 K, P = 1 atm).

Mesophilic inoculum for the BMP experiments was collected from a biogas reactor located at Va Syd Sjölund wastewater treatment plant (WWTP), Malmö (SE). This plant treats residential and industrial (e.g. dairy industry) wastewater. Before use, the inoculum was stored in a 37 °C incubator for one week with an anaerobic headspace. Bottles containing only inoculum and water were used as a blank to determine CH₄ production from the inoculum alone; this was subtracted from the CH₄ production of substrates to calculate the CH₄ potential of the substrates.

No nutrients or buffer solution was added to the BMP bottles as digestate after co-digestion of residential and industrial wastewater was used as inoculum, which is rich in nutrients and has high buffering capacity. Avicel (Fluka, Sigma Aldrich, Vallensbæk Strand, Denmark) was used in control experiments to check the quality of the inoculum. According to Hansen et al. (2004), the BMP for the average of three Avicel samples should be in the range of 315-439 mL CH₄/g VS (at STP); otherwise the series should be disregarded.

Concentrations of volatile fatty acids (VFAs) were measured on the last day of the experiment to assess whether they had accumulated. Samples of 1 mL (diluted to 50 % with water) were extracted from the liquid phase, placed in Eppendorf tubes and acidified with 400 μ L ortho-phosphoric acid to pH < 2. Then it was centrifuged at 13,400 rpm for 10 minutes. After centrifugation, the 1mL sample was transferred to a GC glass vial and 100 μ L of internal standard (2.2 mM 4-Methyl valeric acid) was added. Concentrations of VFAs were quantified using GC Shimadzu GC-2010 equipped with and FID (flame-ionization-detector). VFA compounds were separated by a capillary column (ZB-FFAP, 30 m, 0.53 mm I.D x 1.0 μ m) and concentrations were determined by a linear calibration curve obtained by standard injections. The following VFAs were included in the analysis: acetate, propionate, iso-butyrate, butyrate, iso-valerate, valerate and hexanoate. In general, the detection limit was 1 mg/L. The pH of the last day's effluent was measured using a PHM 92 pH-meter according to ISO 10523 (2008).

2.2.2. Calculation of theoretical CH₄ generation and CH₄ recovery

The theoretical CH₄ generation potential of the waste samples was calculated assuming that all organic carbon of the waste samples could be degraded to equal volume fractions of CH₄ and CO₂. Eq. 6 was used to calculate the theoretical CH₄ potential (expressed as mL CH₄):

$$\text{Theoretical CH}_4 \text{ generation} = \frac{m_{\text{substrate}} \times \text{TOC} \times 50\% \times 16/12}{\rho/1000} \quad (\text{Eq. 6})$$

where $m_{\text{substrate}}$ is mass of substrate on a dry weight basis (dw) in the reactor (g), TOC is the total organic carbon content of the substrate (% dw), 50 % is the volume fraction of CH₄ in generated gas, 16 and 12 are the molar masses of CH₄ and carbon, respectively, ρ is the density of CH₄ (0.716 g/L at STP) and 1000 was the conversion factor from L to mL. The CH₄ recovery (%) in this study (Eq. 7) was defined as the ratio between the actual CH₄ generated in the BMP experiment and the theoretical CH₄ generation.

$$CH_4 \text{ recovery} = \frac{\text{Cumulative } CH_4 \text{ generated in BMP experiment}}{\text{Theoretical } CH_4 \text{ generation}} \quad (\text{Eq. 7})$$

2.3. Biocorrosion experiment

Biocorrosion incubation experiments were conducted to investigate the hypothesis of CH_4 yield enhancement by H_2 production from metals. Fe, Al, Zn and Cu are the main metals in SW (Ahmed et al., 2014; Cossu et al., 2014; Fiore et al., 2012; Galvagno et al., 2001; Granata et al., 2011) and thus were examined for their ability to provide electrons for methanogens. The experiment had two steps and both were carried out in duplicate in 1 L glass bottles for 20 days in a 37 °C incubator. Table 2 provides an overview of the two steps and the materials used in each step.

Table 2. Overview of materials used in the biocorrosion experiment.

Experimental step	Reactor name	Metals (g)				Inoculum (mL)	Water (mL)
		Fe	Al	Zn	Cu		
Step 1: H_2 generation by biocorrosion	Water+Fe	2.5	0	0	0	0	250
	Water+Al	0	2.5	0	0	0	250
	Water+Zn	0	0	2.5	0	0	250
	Water+Cu	0	0	0	2.5	0	250
Step 2: Impact of metal addition on CH_4 yield	Blank	0	0	0	0	250	0
	Inoc+Fe	2.5	0	0	0	250	0
	Inoc+Al	0	2.5	0	0	250	0
	Inoc+Zn	0	0	2.5	0	250	0
	Inoc+Cu	0	0	0	2.5	250	0

In the first step, H_2 production from elemental metals in contact with water was investigated. In this step, incubation bottles contained 2.5 g of elemental metals and 250 mL of tap water. In step two, the CH_4 yield enhancement of inoculum by addition of metals was investigated. In this step, 2.5 g of elemental metals and 250 g of inoculum were placed in the incubation bottles, resulting a concentration of 10 g/L of liquid for each metal. Bottles containing only inoculum were used as

blank to calculate CH₄ production from inoculum alone. Bottles were flushed with N₂ for 15 minutes to establish an anaerobic condition, and then sealed with rubber septum.

CH₄ and H₂ concentrations in the headspace were measured three times in the first week and two times per week for the rest of the experiment. Gas samples (0.3 mL) were taken from the headspace of the bottles and directly injected to a thermo-scientific trace gas chromatograph (TRACE 1310 GC, Molsieve, 0.53 mm, 30 m) with a thermal conductivity detector (TCD). Argon was used as the carrier gas and the oven temperature was 130 °C. Gas volumes were converted to STP conditions.

Mesophilic inoculum collected from Va Syd Sjölanda WWTP was used in this experiment. Powders of elemental metals were obtained from Sigma-Aldrich. Iron was described as “powder (fine)” with purity of ≥99 %. The purity and particle size of the rest of the metals were as follows: Al, 99.7 %, <1000 µm; Zn, 99 %, 600 ± 100 µm; and Cu, 99.5 %, <425 µm.

2.4. Gas production rate experiment

2.4.1. Experimental set up

Glass bottles with total volumes of 5 L were used for determining the gas production rate. All bottles were connected to 2 L aluminum gas bags by a PVC tube to collect the produced biogas. All PVC tubes were equipped with a rubber septum for sampling the produced biogas. At each measurement of gas composition, 5 mL gas samples were taken from the rubber septum with a syringe and injected immediately into evacuated glass vials equipped with rubber septa (Exetainer Vail, Labco Ltd, Lampeter, UK), which then were analyzed by a gas chromatograph (490-PRO Micro GC).

FS, FUS and COM samples were the substrates in this experiment. In order to investigate the impact of metals on the CH₄ production rate, metals (Fe, Al, Zn, and Cu) with dimension of 5 mm ×

5 mm and concentrations of 5, 2, 2, and 2 % of the substrate wet weight (25, 10, 10, 10 g/L of liquid), respectively, were added to the incubation bottles containing the COM samples. The concentrations of the added metals were estimated based on the metal contents of SW, shown in Table 1.

Abiotic control experiments were also conducted using sterilized samples to measure possible CH₄ production due to non-microbial processes. Abiotic experiments were performed on the COM sample and COM sample with addition of previously mentioned metals. Controls were sterilized by autoclaving three times for 1 h at 121 °C. All reactors were flushed for 20 minutes with nitrogen gas to make an anaerobic condition. An overview of the content of the incubation drums can be seen in Table 3.

Table 3. Overview of the gas production rate experiment conditions and phases.

Name of the reactor	Biotic/Abiotic	Inoculum addition (% of the samples wet weight)		Temperature (°C)		Moisture content (% w/w)	
		Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
FS1, FUS1, COM1, COM+Fe1, COM+Al1, COM+Zn1, COM+Cu1	Biotic	5	30				
Ste_COM1 ^a , Ste_COM+Fe1, Ste_COM+Al1, Ste_COM+Zn1, Ste_COM+Cu1	Abiotic	0	0	20-25	20-25	35	75
FS2, FUS2, COM2, COM+Fe2, COM+Al2, COM+Zn2, COM+Cu2	Biotic	5	30				
Ste_COM2, Ste_COM+Fe2, Ste_COM+Al2, Ste_COM+Zn2, Ste_COM+Cu2	Abiotic	0	0	20-25	37	35	75
FS3, FUS3, COM3, COM+Fe3, COM+Al3, COM+Zn3, COM+Cu3	Biotic	5	30				
Ste_COM3, Ste_COM+Fe3, Ste_COM+Al3, Ste_COM+Zn3, Ste_COM+Cu3	Abiotic	0	0	20-25	55	35	75

^a "Ste" in the beginning of the reactor name indicates the sterilized reactors

As can be seen from Table 3, the gas production rate experiment was carried out in two phases. During the first phase (day 1 to 100), all experiments were carried out in triplicate and at room temperature (20-25 °C). A small amount of mesophilic inoculum (5 % of substrate wet

weight) was added to biotic incubation bottles in the beginning of this stage and the moisture content of the samples was adjusted to 35 % w/w in all of the reactors.

In phase two (starting on day 101), due to very low biogas production, the reactors were opened and more inoculum (30 % of substrate wet weight) was added to the biotic incubation bottles and the moisture content of the samples was adjusted to 75 % w/w. Moreover, in this stage the impact of temperature on the gas generation rate was studied. Thus, incubation bottles (one replicate each) were placed at two different temperatures, 37 °C and 55 °C, and one replicate remained at room temperature. Bottles containing only inoculum and water (one replicate at each temperature) were used as blank to determine CH₄ production from the inoculum alone, which was subtracted from the CH₄ production of waste samples.

Thermophilic inoculum, collected from Snertinge biogas plant (DK), was used for incubation at 55 °C. This plant co-digests pig slurry with fat and flotation sludge from food industries. Before its use, the inoculum was stored in a 55 °C incubator for one week, with an anaerobic headspace. Mesophilic inoculum, collected from Va Syd Sjölanda WWTP, was used for incubation at room temperature and 37 °C. Mesophilic inoculum was stored in a 37 °C incubator for one week with an anaerobic headspace, before its use.

CH₄ and CO₂ concentrations were measured by a 490-PRO Micro GC (Agilent Technologies Denmark Aps, Glostrup, Denmark) with a TCD. The Micro GC was equipped with two columns (PoraPLOT Q PLOT, 0.25 mm, 10 m, and Molecular Sieve 5A PLOT, 0.25 mm, 20 m) with a detection limit of 0.1 %. Helium was used as the carrier gas. The biogas volume was measured using a water displacement method. Gas volumes in all the experiments were converted to STP conditions. VFAs and pH were measured on the last day of experiment. The analytical methods were the same as those for measuring VFAs and pH in the BMP experiment.

2.4.2. Determination of k values of waste samples

The kinetics of the experiment was studied by applying FOD equation (Eq. 8) to the experimental data obtained. The FOD equation was modified to take into account the experiment's long lag-time:

$$m_t = m_0 \times e^{-k(t-t_{lag})} \quad (\text{Eq. 8})$$

where m_t is the mass of organic carbon (g) after time t , m_0 is the mass of organic carbon (g) at $t = 0$, t is the degradation time (yr), t_{lag} is the lag-phase time (yr) and k is the FOD kinetic constant (yr^{-1}). Thus, the k -value can be calculated by Eq. 9:

$$k = \frac{-\ln\left(\frac{m_t}{m_0}\right)}{t-t_{lag}} \quad (\text{Eq. 9})$$

Assuming that all organic carbon of the waste samples could be degraded to equal volume fractions of CH_4 and CO_2 over a long period of time ($t = t_\infty$), the ultimate CH_4 potential and the cumulative CH_4 generation at time t can be determined by Eq. 10 and 11 (De Gioannis et al., 2009; De la Cruz and Barlaz, 2010; Mou et al., 2015).

$$\text{Ultimate } CH_4 \text{ Potential } (t_\infty) = m_0 \times 50 \% \times 16/12 \quad (\text{Eq. 10})$$

$$\text{Cumulative } CH_4 (t) = (m_0 - m_t) \times 50 \% \times 16/12 \quad (\text{Eq. 11})$$

where 16 and 12 are the molar weights of CH_4 and carbon, respectively. The

Ultimate CH_4 Potential (t_∞) is the theoretical CH_4 potential (g) from each incubation bottle at $t = t_\infty$, while the Cumulative $\text{CH}_4 (t)$ is the cumulative CH_4 generation from each incubation bottle in the gas production rate experiment over time t . By using Eq. 10 and 11, the ratio between m_t and m_0 can be determined, as shown in Eq. 12:

$$\frac{m_t}{m_0} = \frac{\text{Ultimate } CH_4 \text{ Potential } (t_\infty) - \text{Cumulative } CH_4 (t)}{\text{Ultimate } CH_4 \text{ Potential } (t_\infty)} \quad (\text{Eq. 12})$$

In this study, the Ultimate CH_4 Potential (t_∞) was calculated by multiplying the BMP of each waste sample (g CH_4 /kg waste) by the mass of waste samples (kg). Half-life time ($t_{1/2}$) can be calculated using Eq. 9 when $m_t = \frac{1}{2}m_0$ as shown in Eq. 13:

$$t_{1/2} = \left(\frac{-\ln \frac{1}{2}}{k} \right) + t_{lag} \quad (\text{Eq. 13})$$

where k is the FOD kinetic constant (yr^{-1}) and t_{lag} is the lag-phase time (yr).

3. Results and discussion

3.1. Waste characterization

Table 4 shows waste characterization in terms of TS, VS, TC, TOC and BioC. In general, low variation was observed in the TS content of different waste samples. FUS had the highest TS content (91 %), while COM had the lowest (82 %). TC contents of waste samples were from 12 to 24 % with FUS having the highest (24 %) and FS the lowest (12 %). The TS and TC content of the waste samples were comparable to previous studies (Pasel and Wanzl, 2003; Day et al., 1999; Morselli et al., 2010; Mou et al., 2014).

Table 4. Characteristics of different fractions of SW. Numbers in brackets give the standard deviation.

Shredder waste	TS (%, kg/kg wet waste)	VS (%, kg/kg wet waste)	TC (%, kg/kg dry waste)	TOC (%, kg/kg dry waste)	TOC/TC (%)	BioC (%, kg/kg dry waste)	BioC/TOC (%)
SW deposited in 2009 (SW2009)	89 (6.54)	18 (1.17)	14 (0.67)	11 (0.93)	80	6.0	53
SW deposited in 2012 (SW2012)	83 (1.48)	20 (0.35)	15 (0.82)	14 (0.57)	95	6.1	43
Fresh SW, unsieved (FUS)	91 (0.02)	32 (1.15)	24 (1.99)	21 (1.29)	88	8.3	40
Composite SW sample (COM) ^a	82 (0.71)	24 (0.92)	18 (1.24)	16 (0.60)	86	6.5	42
Fresh SW, sieved (FS)	88 (2.51)	15 (1.06)	12 (0.98)	11 (0.62)	90	4.2	39

^a Mix of SW2009, SW2012 and FUS.

FUS contained the highest amount of VS, TOC, and BioC (32 %, 21 %, and 8.3 %, respectively), which is reasonable as this sample was fresh and thus had not undergone anaerobic degradation in

the landfill. The COM sample was a mix of FUS, SW2012 and SW2009 and it had VS, TOC and BioC contents between these substrates. SW2012 and SW2009 had lower VS, TOC and BioC contents than FUS, most likely as a result of anaerobic degradation since their deposition in the landfill.

FS had the lowest VS, TC and BioC content due to the sieving process and a resulting higher content of mineral and inert material in this fine fraction (Ahmed et al., 2014). The VS contents of the waste samples were in line with the previous study on SW from the same landfill (Mou et al., 2014); however, the TOC contents were slightly higher. The TOC/TC and BioC/TOC ratios were 80-95 % and 39-53 %, respectively, meaning that although a high portion of the TC was organic, only a small part was biogenic carbon. This indicates that a high portion (47-61 %) of the organic carbon in SW originates from fossil sources, such as plastic and rubber.

3.2. BMP test

Fig. 1 presents cumulative CH₄ production curves over an incubation period of 37 days. All the substrates showed similar gas generation trends except the COM sample, which followed the blank until day 20. FUS had the highest CH₄ generation. FS had a lower CH₄ generation than FUS because of the fact that it is the fine fraction after sieving and contains more mineral and inert material. The CH₄ generation of COM sample was between the CH₄ generation of FUS, SW2012 and SW2009, of which it was composed. SW2012 had lower CH₄ generation than the FUS sample as it has lost part of its potential by being deposited and producing CH₄ in the landfill. The CH₄ generation from SW2009 and SW2009+Fe incubations was lower than the blank containing inoculum alone. The BMP of the control was 421 mL CH₄/g VS, which was in the accepted range (315-439 mL CH₄/g VS). This indicated a well-functioning inoculum and no nutrients limitation.

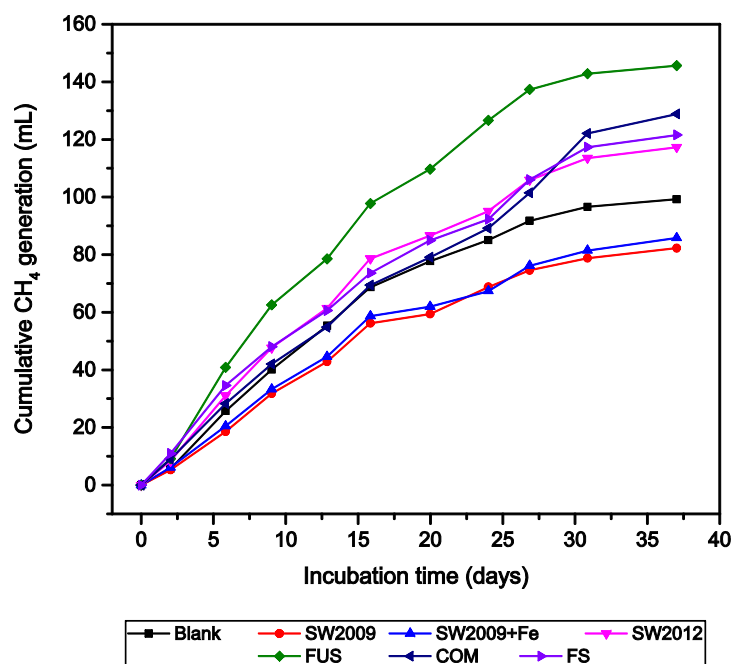


Fig. 1. Cumulative CH₄ generation of different fractions of SW over period of 37 days.

VFAs and pH were analyzed in all incubations. The results can be found in the Supplementary material (Table A.1.). Total VFAs (TVFAs) ranged from 3.1 to 9.7 mg/L with COM having the highest TVFAs and SW2009 having the lowest. The pH ranged from 7.4 to 8.1. As the CH₄ generation from SW2009 and SW2009+Fe incubations was lower than the blank containing inoculum alone, the VFAs and pH results for these two incubations are shown (Table 5) and discussed to assess inhibition.

Table 5. VFAs and pH values for the last day effluent of SW2009 and SW2009+Fe incubations. The numbers show the average value of three incubations (including duplicate analysis of VFAs) while numbers in brackets give the standard deviation.

SW fraction	Acetate (mg/L)	Propionate (mg/L)	Iso-butyrate (mg/L)	Butyrate (mg/L)	Iso-valerate (mg/L)	Valerate (mg/L)	Hexanoate (mg/L)	TVFA (mg/L)	pH
SW2009	2.1 (0.2)	0.0 (0.0)	0.0 (0.0)	1.0 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	3.1	8.0 (0.04)
SW2009+Fe	5.2 (3.0)	0.0 (0.0)	0.0 (0.0)	1.0 (0.2)	0.0 (0.0)	0.0 (0.0)	1.2 (0.4)	7.5	8.0 (0.03)

Average pH values of the triplicate reactors for both substrates (SW2009 and SW2009+Fe) were 8.0, which were higher than the optimal range of 6.5-7.5 for achieving the maximum CH₄

yield (Liu et al., 2008). However, these values were not significantly higher than the optimum range to cause inhibition. Acetate, butyrate and hexanoate were the only VFAs present. Acetate had the highest concentration (2.1 and 5.2 mg/L); however, it was still much lower than 2400 mg/L, which resulted in no significant inhibition of the activity of methanogens in Wang et al.'s (2009) study. Moreover, the concentration of butyrate (1.0 mg/L in both substrates) was significantly lower than 1800 mg/L, which showed no significant inhibition in Wang et al.'s (2009) study. Furthermore, TVFA concentrations were 3.1 and 7.5 mg/L, well below 1-6 g/L, which Siegert and Banks (2005) considered as inhibitory VFA concentration for biogas production. Overall, the pH and VFA analysis did not indicate inhibition of the incubations.

Table 6 provides an overview of the theoretical CH₄ generation (mL), cumulative CH₄ generated in BMP experiments (mL), calculated BMPs (kg CH₄/ton waste), BMP values in terms of mL CH₄/g VS to compare with reported BMP values in the literature and CH₄ recovery (%).

Table 6. Overview of BMP results in terms of theoretical and cumulative CH₄ generation, calculated BMP and CH₄ recovery. Numbers in brackets give the standard deviation of triplicate incubations.

	Theoretical CH ₄ generation (mL)	Cumulative CH ₄ generation (mL) ^a	BMP (kg CH ₄ /ton waste)	BMP (mL CH ₄ /g VS)	CH ₄ recovery (%)
SW2009	889	0	0 ^b	0 ^b	0
SW2009 + Fe	889	0	0 ^b	0 ^b	0
SW2012	975	18.0 (2.4)	1.7	12	1.8
FUS	1025	46.3 (5.3)	6.2	31	4.5
COM	908	29.6 (4.2)	3.4	20	3.3
FS	1051	22.3 (4.0)	1.5	15	2.1

^a CH₄ production from blank was subtracted.

^b CH₄ production was lower than blank and thus BMP was considered as 0.

The BMP of the waste samples was 1.5-6.2 kg CH₄/ton waste. The highest BMP was observed in the FUS waste sample, followed by COM, SW2012, FS and finally SW2009. The CH₄ recovery was 1.8-4.5 %, indicating that the majority of organic carbon in the waste sample was not released as CH₄. The CH₄ recovery rates seemed comparable with the BioC content of the waste samples, which were 4.2-8.3 %. The highest BioC and CH₄ recovery was observed from the FUS sample. The

calculated BMP and CH₄ recovery values were comparable with values reported in a recent study on SW (Mou et al., 2014).

The measured BMP values were significantly lower than the reported BMP of 500-600 mL CH₄/g VS for food waste (Fitamo et al., 2016; Labatut et al., 2011; Naroznova et al., 2016) and 180-400 mL CH₄/g VS for fruit and vegetable waste (Gunaseelan, 2004), while they were closer to the reported BMP values of 58-80 mL CH₄/g VS for newsprint (Jokela et al., 2005; Owens and Chynoweth, 1993), and 50-60 mL CH₄/g VS for some types of woody biomass (Turick et al., 1991). This is reasonable because food waste is rich in fats, proteins and carbohydrates, which are easily degradable organic matters, while SW, newsprint, and woody biomass consist mainly of biologically recalcitrant or lignocellulosic components.

3.3. Biocorrosion experiment

Fig. 2 presents the cumulative H₂ (2a) and CH₄ production curves (2b) over a 20-day incubation period. Please note that the H₂ production from Water+Cu, Blank, Inoc+Fe, Inoc+Al, Inoc+Zn, Inoc+Cu incubations (Fig. 2a), and CH₄ production from Water+Fe, Water+Al, Water+Zn and Water+Cu incubations (Fig. 2b) were all zero and thus the curves are on top of each other and not visible on the graph. As can be seen from Fig. 2a, Fe in water (Water+Fe incubation) showed the highest H₂ generation, followed by Al and Zn in water, respectively.

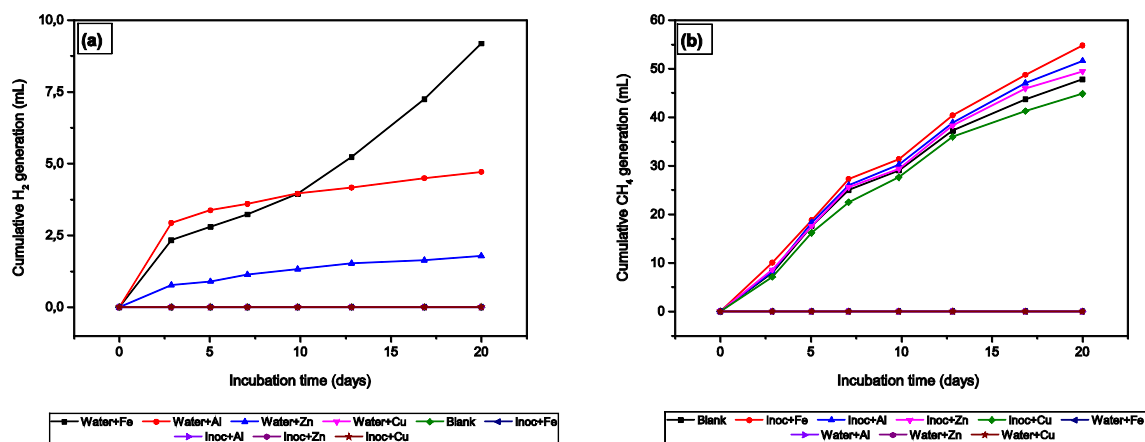


Fig 2. Cumulative H₂ (a) and CH₄ production curves (b) in biocorrosion experiment over period of 20 days. Please note that the H₂ production from Water+Cu, Blank, Inoc+Fe, Inoc+Al, Inoc+Zn, Inoc+Cu incubations (Fig. 2a), and the CH₄ production from Water+Fe, Water+Al, Water+Zn and Water+Cu incubations (Fig. 2b) were all zero and thus the curves are on top of each other and not visible on the graph.

Table 7 shows the redox potential for H₂ production from elements (Fe, Al, Zn and Cu) reacting with hydrogen ions (Belay and Daniels, 1990). A more positive ΔE^0 indicates that H₂ production from the specified metals is more favorable thermodynamically (based on Belay and Daniels, 1990). Thus Fe, Al and Zn with positive ΔE^0 have the potential to produce H₂ thermodynamically. However, H₂ production from Cu (with negative ΔE^0) is not thermodynamically possible. This is in line with the results of this study, as H₂ production was observed in incubation of Fe, Al and Zn in water, but not with Cu.

Al has higher redox potential than Fe (Table 7), while in the laboratory experiment Al produced less H₂ compared with Fe. The redox potential was only used to show if the reaction can take place thermodynamically, and it was not used as a measure to compare reaction rates. The reaction rate depends on many other factors including the specific surface area of the reactants. In our experiment, Fe was in the form of a fine powder, which had a smaller particle size (and a larger specific surface area) in comparison to Al, which had a particle size of < 1000 μm .

Moreover, disagreement between thermodynamic predictions and results measured in laboratory experiments has been observed in previous studies. For example, ΔE^0 for H_2 production from Cd and Ti (+0.40 and +1.63 V, respectively) is very close to those of Fe and Al (+0.44 and +1.66 V, respectively) and thus their H_2 production is thermodynamically favorable (Belay and Daniels, 1990). However, in the study by Belay and Daniels (1990) addition of Ti and Cd to methanogenic cultures did not result in higher CH_4 production, while in the study by Lorowitz et al. (1992) addition of Ti resulted in a higher CH_4 production whereas the addition of Cd resulted in a lower CH_4 production compared to blank.

Table 7. Redox potential for elemental metals used in this experiment (based on Belay and Daniels, 1990)

Element	Reaction	Oxidation-reduction potential ΔE^0 (V)
Fe	$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$	+0.44
Al	$Al + 3H^+ \rightarrow Al^{3+} + 3/2 H_2$	+1.66
Zn	$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$	+0.76
Cu	$Cu + 2H^+ \rightarrow Cu^{2+} + H_2$	-0.34

Accumulation of H_2 was not observed in biological (containing inoculum) incubations (Fig. 2a). This was expected, as hydrogenotrophic methanogenesis is a very fast process, meaning that the generated H_2 is consumed rapidly in the production of CH_4 . This helps to keep the H_2 pressure low, which is needed for successful anaerobic digestion processes to occur (Gerardi, 2003).

Fig. 2b shows that adding Fe, Al and Zn to inoculum resulted in higher CH_4 generation than inoculum alone. However, addition of Cu to inoculum (Inoc+Cu incubation) resulted in lower CH_4 generation compared to inoculum alone. These results indicate that H_2 generation from corrosion of Fe, Al, and Zn can be utilized by hydrogenotrophic methanogens to convert CO_2 to CH_4 . CH_4 generation was not observed in incubations containing water and metals, indicating there was no chemical production of CH_4 .

The average pH of the SW leachate was 7.6 in 2015 (supplied by the landfill operators). H₂ production by the corrosion of metals is more favorable at lower pH (Boopathy and Daniels, 1991). However, the reactions are still possible at higher pH. For instance, Boopathy and Daniels (1991) observed biocorrosion and CH₄ production by Fe as electron source at a pH of 7.5.

The results of this experiment were in line with previous studies. For instance, Belay and Daniels (1990), Hu et al., (2015) and Lorowitz et al., (1992) observed enhancement of CH₄ production from certain types of methanogenic cultures and waste activated sludge by addition of Fe, Al and Zn due to H₂ production by these metals. Inhibition of CH₄ production by addition of Cu was also observed in previous studies (Ahring and Westermann, 1985; Belay and Daniels, 1990; Jin et al., 1998; Lin, 1992). The toxicity of Cu is due to the replacement of naturally occurring metals in enzyme groups and binding of the metal with certain groups on protein molecules resulting in disruption of enzyme function (Chen et al., 2008).

3.4. Gas production rate experiment

Fig. 3 shows cumulative CH₄ production curves of all waste samples during 230-day periods at room temperature (Fig. 3a), room temperature to 37 °C (Fig. 3b) and room temperature to 55 °C (Fig. 3c). Sterilized reactors did not produce CH₄, indicating there was no abiotic production of CH₄ from SW. A lag-phase of 31 days was observed for all microbial active reactors. By day 31, gas generation was observed but occurred very slowly until the initiation of phase two of the experiment.

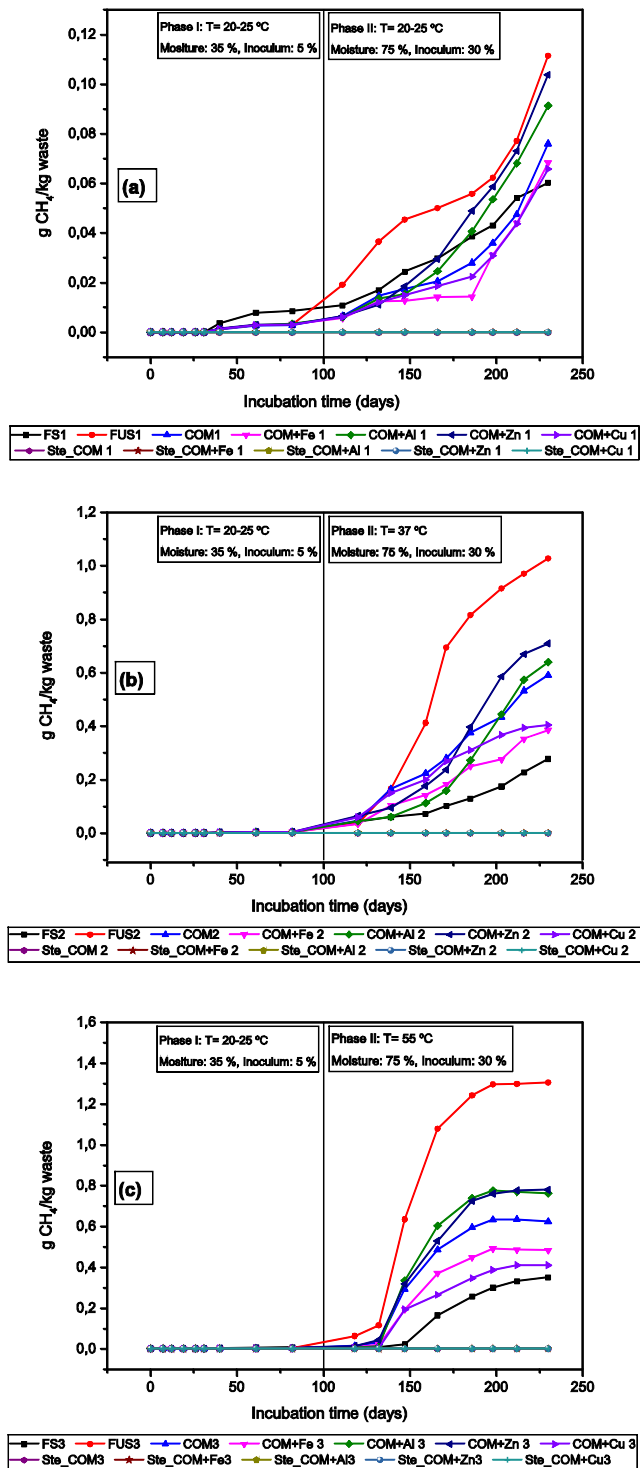


Fig. 3. Cumulative CH₄ generation from different types of SW, biotic and abiotic experiments, during period of 230 days and two experimental phases. Please note that the CH₄ production from sterilized reactors (starting with "Ste") were all zero and thus the curves are on top of each other and not visible on the graph.

Of the three SW samples studied, FUS had the highest cumulative CH₄ production at all three temperatures whereas FS had the lowest, which is reasonable as it is the fine fraction after sieving and contains more mineral and inert material (Ahmed et al., 2014). These results were in line with the BMP test, where FUS also showed the highest CH₄ production, followed by COM and FS, respectively.

At all three temperatures, adding Zn and Al to the COM samples resulted in higher CH₄ production in comparison to experiments with COM alone, while the addition of Fe and Cu resulted in lower CH₄ production. The obtained result for the impact of Al, Zn and Cu on CH₄ production is in line with the biocorrosion experiment. As discussed earlier, adding Al and Zn to inoculum can result in higher CH₄ generation, as these metals can produce H₂, which can be utilized by hydrogenotrophic methanogens to convert CO₂ to CH₄. Moreover, it was discussed that adding Cu can inhibit the AD process. However, adding Fe resulted in lower CH₄ production in this experiment, while it enhanced CH₄ production in the biocorrosion experiment. This could be due to a higher concentration of Fe in this experiment (25 g/L) compared to the biocorrosion experiment (10 g/L).

Iron (Fe⁰ and Fe²⁺) is an essential microelement for enzymatic reaction and can enhance anaerobic digestion by activating enzymes or H₂ production, or reducing sulfide toxicity (Feng et al., 2014; Hansen et al., 1999; Kayhanian and Rich, 1995; Zhang and Jahng, 2012). However, at high concentrations it can have an inhibitory impact on microorganisms and on the anaerobic digestion process (Gonzalez-Silva et al., 2009; Yang and Shen, 2006; You et al., 2005). Cumulative CH₄ production from the COM+Fe 1 reactor (Fig. 3a) stalled between day 132 and day 186; then increased again. This could be an indication of Fe inhibition, which was recovered after 54 days.

Table 8 shows the headspace CH₄ and CO₂ concentrations of the biotic reactors measured on the last day of the experiment. The CH₄/CO₂ ratio in the reactors was significantly different

compared to the CH₄/CO₂ ratio of conventional LFG. Unusual gas composition from SW (high CH₄ and low CO₂ content) has also been reported in previous studies (Olsen and Willumsen, 2013; Scheutz et al., 2011). When comparing the headspace CO₂ concentrations of COM reactors with COM+Al and COM+Zn reactors, it can be seen that COM+Al and COM+Zn reactors have lower headspace CO₂ concentrations. This could be due to utilization of produced H₂ by corrosion of Al and Zn and existing CO₂ in produced biogas by methanogens, resulting in higher CH₄ and lower CO₂ in the headspace of these reactors.

Table 8. CH₄ and CO₂ concentrations in the headspace of the biotic reactors measured on the last day of the experiment (day 230).

Reactor name	T (°C)	CH ₄ (%)	CO ₂ (%)	CH ₄ /CO ₂
FS1		19.9	1.6	12.4
FUS1		9.0	0.8	10.7
COM1		11.1	1.2	9.0
COM+Fe1	20-25	9.6	1.6	6.0
COM+Al1		11.9	1.2	10.1
COM+Zn1		13.0	1.1	11.8
COM+Cu1		9.6	2.0	4.9
FS2		58.9	3.0	19.4
FUS2		57.5	2.8	20.6
COM2		50.4	4.0	12.6
COM+Fe2	37	44.5	3.6	12.4
COM+Al2		53.3	3.2	16.5
COM+Zn2		52.9	1.7	30.7
COM+Cu2		44.7	3.8	11.7
FS3		51.3	3.9	13.1
FUS3		54.1	3.7	14.6
COM3		54.5	4.4	12.5
COM+Fe3	55	45.2	4.1	11.0
COM+Al3		55.4	2.6	20.7
COM+Zn3		57.3	3.7	15.7
COM+Cu3		39.6	2.1	19.3

Fig. 3a shows the CH₄ production curves at room temperature for the entire period of the experiment, but higher moisture and inoculum content in phase two. Increasing the moisture from 35 % to 75 % and inoculum from 5 % to 30 % resulted in significantly higher CH₄ production. It is

well discussed in literature that a high moisture content enhances the production of CH₄ by supporting bacterial movement, dissolving nutrients and substrate for microorganisms' assimilation, diluting inhibitory compounds, and limiting the transport of oxygen (Donovan et al., 2010; Fujishima et al., 2000; Khalid et al., 2011; Lay et al., 1997; Liotta et al., 2014). These results confirm that the moisture content of waste is a critical factor, which can affect CH₄ production significantly.

Addition of more inoculum in phase two resulted in more active biomass in the reactors and thus higher CH₄ production. Previous studies have also shown that the use of inoculum reduces the experimental time significantly and increases CH₄ production (Forster-Carneiro et al., 2007; Lopes et al., 2004). It should be noted that the moisture content in the second phase of this experiment (75 %) was higher than typical moisture levels for Danish landfills (Mou et al., 2015). Moreover, inoculum was added to the reactors, which does not happen in landfilling of SW, thus the CH₄ production rates may be overestimated in this study.

During phase two of the experiment, the moisture and inoculum content were the same in all the reactors, while the temperature was different (Fig. 3). The reactors running at 55 °C showed the highest CH₄ production, followed by those at 37 °C and 20-25 °C, respectively. As the sterilized reactors did not produce CH₄ at any of the operating temperatures and moistures, the impact of temperature and moisture content on CH₄ generation rate was biological.

When comparing phase two of Fig. 3a with Fig. 3b and 3c, it can be seen that increasing the temperature from 20-25 °C to 37 °C resulted in significantly higher CH₄ production, while increasing the temperature from 37 °C to 55 °C resulted in higher CH₄ production, but to a lower extent. For instance, FUS showed cumulative CH₄ production of 0.1114, 1.0274, and 1.3037 g CH₄/kg waste at 20-25 °C, 37 °C, and 55 °C, respectively, meaning approximately 10 times the CH₄ production at 37 °C compared with 20-25 °C, with just 1.3 times the CH₄ production at 55 °C

compared with 37 °C. Moreover, Fig. 3c indicates that the gas generation capacity of SW was depleted in a relatively short time (130 days in this experiment) at 55 °C and moisture content of 75 % w/w.

Many researchers have reported that lowering the temperature can result in lower microbial growth and substrate utilization rates and thus a lower gas production rate (Chen et al., 2008; Kim et al., 2006; Trzcinski and Stuckey, 2010), which is in line with the results of this experiment. As high temperatures (59 and 40 °C in 10 and 20 m depths, respectively) have been observed in SW monofills (Olsen and Willumsen, 2013), these results indicate that a high temperature is one of the most important reasons for high CH₄ production from SW.

VFAs and pH were analyzed in COM, COM+Fe, COM+Al, COM+Zn, and COM+Cu reactors, incubated at all three temperatures on the last day of the experiment. The results can be found in the Supplementary material (Table A.2.). TVFAs and pH ranged from 6.1-138.5 mg/L and 7.3-7.8, respectively, with COM+Cu1 having the highest TVFA. However, the results did not indicate inhibition.

Table 9 shows calculated k-values at 55 °C and 37 °C and room temperature. In general, the highest k-values were obtained for the experiment running at 55 °C, followed by 37 °C. Calculated k-values varied from 0.033 to 0.075 yr⁻¹ at room temperature, 0.220 to 0.429 yr⁻¹ at 37 °C and 0.235 to 0.488 yr⁻¹ at 55 °C. As discussed previously, a higher temperature can result in faster biogas production. Therefore, observing the highest k-values at the highest temperature (55 °C) was reasonable.

Table 9. Calculated k-values at 20-25 °C, 37 °C, and 55 °C.

Reactor name	T (°C)	t _{lag} (d)	t (d)	BMP (g/kg waste)	Waste mass in the reactor (kg)	Ultimate CH ₄ Potential (g)	Cumulative CH ₄ (g)	k (yr ⁻¹)	t _½ (yr)
FUS1		31	230	6.2	1.0	6.20	0.111	0.033	20.9
FS1		31	230	1.5	1.5	2.25	0.090	0.075	9.3
COM 1		31	230	3.4	1.3	4.42	0.099	0.041	16.8
COM+Fe1	20-25	31	230	3.4	1.3	4.42	0.088	0.037	18.9
COM+Al1		31	230	3.4	1.3	4.42	0.119	0.050	14.0
COM+Zn1		31	230	3.4	1.3	4.42	0.135	0.057	12.3
COM+Cu1		31	230	3.4	1.3	4.42	0.086	0.036	19.4
FUS2		31	230	6.2	1.0	6.20	1.027	0.332	2.2
FS2		31	230	1.5	1.5	2.25	0.416	0.375	1.9
COM2		31	230	3.4	1.3	4.42	0.769	0.350	2.1
COM+Fe2	37	31	230	3.4	1.3	4.42	0.500	0.220	3.2
COM+Al2		31	230	3.4	1.3	4.42	0.831	0.382	1.9
COM+Zn2		31	230	3.4	1.3	4.42	0.922	0.429	1.7
COM+Cu2		31	230	3.4	1.3	4.42	0.526	0.232	3.1
FUS3		31	230	6.2	1.0	6.20	1.304	0.433	1.7
FS3		31	230	1.5	1.5	2.25	0.525	0.488	1.5
COM3		31	230	3.4	1.3	4.42	0.810	0.371	2.0
COM+Fe3	55	31	230	3.4	1.3	4.42	0.628	0.281	2.5
COM+Al3		31	230	3.4	1.3	4.42	0.989	0.464	1.6
COM+Zn3		31	230	3.4	1.3	4.42	1.012	0.477	1.5
COM+Cu3		31	230	3.4	1.3	4.42	0.532	0.235	3.0

Table 10 presents a summary of the k-values reported in the literature. The reported k-values vary significantly depending on the type of substrate, applied methodology (modeling or laboratory experiment) and operating conditions (temperature, batch or continuous, with or without the addition of inoculum, etc.). The k-values obtained in this study are comparable to some of these studies. For instance, k-values obtained from room temperature incubations in our study (0.033 to 0.075 yr⁻¹) are close to the reported range of 0.0347-0.0803 yr⁻¹ by De Gioannis et al. (2009) for MBT waste incubated at 30 °C. Similarly, the k-values observed at 55 °C (0.235 to 0.488 yr⁻¹) are

comparable to the 0.3 yr⁻¹ k-value reported by modeling LFG data from a MSW landfill in Reinhart et al.'s (2005) study.

However, the calculated k-values are significantly lower than results obtained by Pantini et al., (2015); Jokela et al., (2005); Veeken et al., (2000); Veeken and Hamelers, (1999); and Mata-Alvarez et al., (1990). This difference is most likely due to the different substrates and operating conditions. The calculated k-values of 0.033 to 0.075 yr⁻¹ at room temperature in this study are higher than the k-values of 0.016-0.017 yr⁻¹ reported by Mou et al., (2015) for SW at room temperature. The higher k-values in this study are most likely due to the higher moisture content and the addition of inoculum, which can accelerate the biodegradation process.

Table 10. Overview of reported k-values in the literature at different temperatures for different types of substrates.

k-value (yr ⁻¹)	Temperature (°C)	Substrate/type of landfill	Method/experiment	Reference
0.016-0.017	20-25	SW from landfill	Anaerobic batch digester (no inoculum)	Mou et al. (2015)
2.555	20-25	MBT waste	Anaerobic batch digester (with inoculum)	Pantini et al. (2015)
10.95-21.90	37			
14.60-40.15	55			
0.14	35	MSW conventional landfill	BMP	Kim and Townsend (2012)
0.06	-	MSW conventional landfill	Modeling of LFG data	Tolaymat et al. (2010)
0.11	-	MSW bioreactor landfill		
0.0347-0.0803	30	MBT waste	Anaerobic batch digester (no inoculum)	De Gioannis et al. (2009)
7.66-39.05	35	Components of grey waste (residual MSW after source separation of biowaste, paper, metal and glass)	BMP	Jokela et al. (2005)
0.3	-	MSW landfill	Modeling of LFG data	Reinhart et al. (2005)
21.90-89.42	28	Biowaste	Anaerobic mixed batch digester (no inoculum)	Veeken et al. (2000)

10.95-54.75	20	Selected biowaste components	BMP	Veeken and Hamelers (1999)
87.60-171.55	40			
147.82	35	Mechanically sorted OFMSW	Continuously stirred tank reactor (CSTR)	Mata-Alvarez et al. (1990)

4. Conclusions

Different types of shredder waste (SW) were characterized in this study and CH₄ production from them was determined by performing anaerobic batch incubations. Moreover, the role of metals in CH₄ production from SW was investigated. Additionally, the impact of temperature, moisture and the addition of inoculum on gas production from SW was studied and first-order decay kinetic constants (k-values) were calculated at different operating conditions.

The characterization results indicated that a high portion (47-61 %) of the organic carbon in SW is fossil carbon. The BMP and k-value of the sieved fraction of SW indicated that if the sieving of SW and subsequently landfilling of the fine fraction is implemented by the industry, CH₄ production from SW in landfills will decrease significantly.

It was evident from the incubation experiments that CH₄ production from SW was not abiotic. Moreover, results of the incubation experiments indicated that the unusual gas composition (higher CH₄ and lower CO₂), and the relatively high CH₄ production rate from landfilling of SW is most likely due to the consumption of existing CO₂ in the produced biogas and H₂ produced by biocorrosion of Al and Zn by methanogens

Performing the incubations at different operating conditions indicated that the high temperature observed inside SW monofills is an important factor in high CH₄ production and if a higher moisture content is obtained (for instance by leachate recirculation), even higher CH₄ production rates can be expected. Additionally, it was observed that the lag-phase in biotic experiments depended on the moisture content and temperature. However, after the lag-phase, when the environmental conditions for methanogenesis become favorable, it is expected that the gas

production of SW is depleted in a relatively short period, if a high temperature and moisture content is maintained.

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Supplementary material

The Supplementary material contains VFAs and pH analysis of the BMP incubations (Table A.1.) and gas production rate experiment reactors (Table A.2.).

Table A.1. VFAs and pH values for the last day effluent of BMP incubations. The numbers show the average value of three incubations (including duplicate analysis of VFAs).

	Acetate (mg/L)	Propionate (mg/L)	Isobutyrate (mg/L)	Butyrate (mg/L)	Iso-valerate (mg/L)	Valerate (mg/L)	Hexanoate (mg/L)	TVFA (mg/L)	pH
SW2009	2.1	0.0	0.0	1.0	0.0	0.0	0.0	3.1	8.0
SW2009+Fe	5.2	0.0	0.0	1.0	0.0	0.0	1.2	7.5	8.0
SW2012	4.5	0.0	0.0	1.0	0.0	0.0	1.5	7.0	8.0
FUS	6.2	0.0	0.0	1.0	0.0	0.0	1.0	8.2	8.0
COM	6.4	0.0	0.0	1.0	0.0	0.0	2.4	9.7	8.1
FS	6.4	0.0	0.0	0.0	0.0	0.0	2.7	9.1	8.1
Blank	3.1	1.1	0.0	1.0	0.0	0.0	1.0	6.2	7.9
Control	4.2	0.0	0.0	0.0	0.0	0.0	1.6	5.8	7.4

Table A.2. VFAs and pH values for the last day effluent of gas production rate experiment reactors. The numbers show the average of duplicate analysis for each reactor.

	Acetate (mg/L)	Propionate (mg/L)	Isobutyrate (mg/L)	Butyrate (mg/L)	Iso-valerate (mg/L)	Valerate (mg/L)	Hexanoate (mg/L)	TVFA (mg/L)	pH
COM1	116.0	11.8	0.0	0.0	0.0	0.0	0.0	127.8	7.6
COM+Fe1	13.6	0.0	0.0	0.0	0.0	0.0	0.0	13.6	7.6
COM+Al1	20.1	0.0	0.0	0.0	0.0	0.0	0.0	20.1	7.7
COM+Zn1	20.8	0.0	0.0	0.0	0.0	0.0	0.0	20.8	7.7
COM+Cu1	125.6	12.9	0.0	0.0	0.0	0.0	0.0	138.5	7.4
COM2	8.6	0.0	0.0	0.0	0.0	0.0	0.0	8.6	7.3
COM+Fe2	6.1	0.0	0.0	0.0	0.0	0.0	0.0	6.1	7.4
COM+Al2	17.6	0.0	0.0	0.0	1.5	0.0	1.1	20.3	7.7
COM+Zn2	12.1	0.0	0.0	0.0	1.2	0.0	2.4	15.7	7.6
COM+Cu2	11.5	0.0	0.0	0.0	1.3	0.0	2.1	14.8	7.6
COM3	30.8	0.0	0.0	0.0	0.0	0.0	0.0	30.8	7.7
COM+Fe3	40.4	0.0	0.0	0.0	0.0	0.0	0.0	40.4	7.8
COM+Al3	24.5	0.0	0.0	0.0	0.0	0.0	0.0	24.5	7.7
COM+Zn3	37.2	0.0	0.0	0.0	0.0	0.0	0.0	37.2	7.8
COM+Cu3	22.3	0.0	0.0	0.0	0.0	0.0	0.0	22.3	7.7

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