



The impact of pressure, moisture and temperature on pyrolysis of municipal solid waste under simulated landfill conditions and relevance to the field data from elevated temperature landfill

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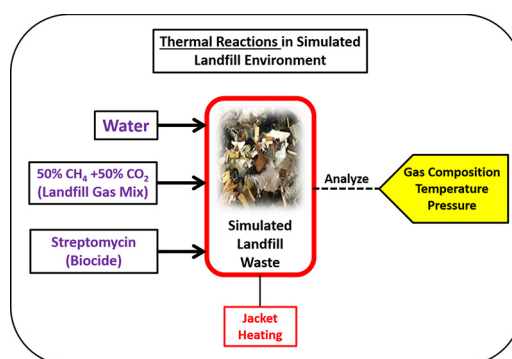
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HIGHLIGHTS

- Simulated landfill sample was tested under varying P and T conditions.
- CH₄/CO₂ ratio changed from 1 to 0.3 at 85 °C, closely matching field measurements.
- Higher pressure had greater impact on H₂ generation than higher temperature.
- Wood charred at a faster rate than other components of Municipal Solid Waste.
- The trends in CH₄/CO₂ ratio match closely to Elevated Temperature Landfills.

GRAPHICAL ABSTRACT



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ABSTRACT

Experiments were conducted with simulated Municipal Solid Waste (MSW) to understand the impact of pressure, moisture, and temperature on MSW decomposition under simulated landfill conditions. Three experimental phases were completed, where the first two phases provided baseline results and assisted in fine tuning parameters such as pressure, temperature, gas composition, and moisture content for phase three. The manuscript focuses on the results from third phase. In the third phase, the composition of the gases evolved from representative MSW samples was tested over time in two pressure conditions, 101 kilopascals (kPa) (atmospheric pressure) and 483 kPa, with varying moisture contents (38 to 55 wt%) and controlled temperatures (50 to 200 °C) in the presence of biological inhibitors. The headspace in the reactor in phase three was pressurized with gas mixture of 50/50 (vol%) of methane (CH₄) and carbon dioxide (CO₂) setting the initial CH₄/CO₂ gas composition ratio to 1.0 at time $t = 0$ days. The results established moisture ranges that affect hydrogen (H₂) production and the CH₄/CO₂ ratio at different temperature and pressure conditions. Results show that at 85 °C, there was a change in the CH₄/CO₂ ratio from 1.0 to 0.3. Additionally, moisture contents from 47 to 43.5 wt% caused the CH₄/CO₂ ratio to increase from 1.0 to 1.2, yet from 43.5 to 38 wt%, the ratio reversed and declined to 0.3, returning to 1.0 for moisture levels below 38 wt%. Thus, moisture levels above 47 wt% and below 38 wt%, for the system tested, allow thermal reactions to proceed without a measured change in CH₄/CO₂ ratio. H₂ generation rates follow a

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similar trend with moisture, yet definitively increase with increased pressure from 101 kPa to 483 kPa. The observed change in solid MSW and gas composition under controlled pressure, moisture, and temperature suggests the presence of thermal reactions in the absence of oxygen.

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1. Introduction

1.1. Background

Municipal solid waste (MSW) landfills accept a variety of material over the course of their operation. While the waste stream has changed over time, it is still mostly comprised of biogenic material such as wood, food waste, paper as well as plastics, metals and synthetic textiles. Under typical conditions, the waste is biologically decomposed in an oxygen-free environment, producing landfill gas composed of approximately 50% CH₄ and 50% CO₂. Recently a few landfills experiencing temperatures of 80 to 100 °C have been reported in the U.S. (Barlaz et al., 2016). These landfills have been referred to as elevated temperature landfills (ETLFs) and are characterized by elevated temperatures over a large surface area. ETLFs are a new phenomenon and have unique characteristics and challenges including substantial changes in the composition and quantity of landfill gas and leachate, rapid waste subsidence, and in some cases, elevated liquid and gas pressures. ETLFs contrast with typical MSW landfills that have been reported to operate in a temperature range of 35 °C to 55 °C (Hanson et al., 2005; Hanson et al., 2010, 2013; Yeşiller et al., 2005, 2015, 2016).

The types of reactions that occur in landfills are numerous and change over time. Furthermore, these reactions are dependent on the reacting material, which in a landfill is variable (Hao et al., 2017). While the biological decomposition of MSW to CH₄ and CO₂ in landfills is well understood, there is little published information on the types of abiotic (thermal) reactions of MSW that can occur in landfills in the absence of oxygen and how these reactions might contribute to heat accumulation. Consequently, to better understand possible reaction processes, we have conducted a series of laboratory experiments using synthetic MSW under carefully controlled anaerobic conditions. It should be noted that the present work focuses on the thermal decomposition reactions in a landfill rather than biological reactions. Biocides such as streptomycin were utilized to terminate the biological activities.

1.2. Previous studies

Previous studies have shown that pyrolysis reactions of biomass can transition from endothermic to exothermic conditions (Antal and Varhegyi, 1995; Ciuta et al., 2014) such that pyrolysis can occur under both conditions. However, even a homogeneous starting material like wood is not completely understood in terms of the reaction sequence and the initiation of exothermic reactions (Ciuta et al., 2014). Wood pyrolysis is a complex physiochemical process in which the reaction products are directly affected by several operating parameters, such as temperature, pressure, and moisture (Ciuta et al., 2014, 2018). Although, many experimental and modeling studies (Neves et al., 2011; Ratte et al., 2009; White et al., 2011) focused on explaining the pyrolysis mechanisms to transform feedstock into valuable products, a number of aspects are not fully understood including reaction rates. In particular, many studies are based on thermo-gravimetric analysis (TGA), that show different temperature profiles for similar materials (Casajus et al., 2009; Singh et al., 2012). Thus a robust connection between literature studies of pure components and field observations of landfill is lacking.

Macroscopic measurements and global calculations such as equilibrium analyses provide information about some reaction events (Baedecker and Back, 1979; Bridgwater et al., 2008, 2017; Bridgwater

and Peacocke, 2000). However, previous research has not resulted in any predictive capability regarding initiation and activity of ETLFs (Barlaz et al., 2016). This work is aimed at relating the landfill field data trends with simulated MSW sample experiments in lab.

1.3. Objective of the work

The objective of this study is to identify the effect of pressure, moisture, and temperature on the thermal pyrolysis decomposition reactions that occur in MSW under simulated landfill conditions to provide an initial understanding of landfills. A series of laboratory experiments was conducted using synthetic MSW under simulated landfill (anaerobic) conditions. To our knowledge, the data generated in our laboratory is the first that demonstrate that synthetic MSW under abiotic and anaerobic conditions produces H₂ and shifts the CH₄ to CO₂ ratio. It has been demonstrated in this paper that it is possible for pyrolysis reactions to occur within temperature ranges that are relevant to landfills experiencing elevated temperatures.

2. Materials and methods

The experimental campaign to investigate the decomposition of synthetic MSW was conducted in three phases. The MSW sample used for all the experiments was synthetic waste comprised of plastic, wood, metal, paper, fabric, and other wastes, consistent with the average MSW composition in the United States (U.S.) (Staley and Barlaz, 2009). The waste had a Carbon (C)/Hydrogen (H)/Nitrogen (N)/Oxygen (O) composition of 52.0, 7.6, 1.6, 38.8 wt%, respectively. The density of the uncompact waste was about 180 kg/m³. The weight of waste used in each phase in each reactor ranged from 200 g to 600 g. The composition of the simulated waste is specified in Table 1 and the experimental program is summarized in Table 2.

From phase 1, it was observed that there is a need for investigation over temperatures lower than 80 °C and higher than 120 °C, hence a broader temperature range of 50–200 °C was chosen for phase 2. Results from phase 2 indicated that it is necessary to study the decomposition at

Table 1
Composition of the simulated waste used in all the experiments.

Material	Component	Normalized discards composition (%)
Paper	Newsprint	1.63
	Office paper	0.76
	Magazines	0.40
	Corrugated containers	2.13
	Other paper	10.57
Metals	Aluminum cans	0.35
	Steel cans	0.34
	Other metals	6.05
Plastics	PET containers	1.22
	HDPE containers	1.01
	Other plastics	15.91
Glass	Glass containers	3.76
	Other glass	1.40
Other wastes	Rubber and leather	3.98
	Textiles	7.89
	Food waste	21.65
	Yard waste	8.36
	Wood	8.17
	Other	4.42
Total		100.00

Table 2
Three phases of the experimental campaign.

Phase	Temperature	Pressure (kPa)	Reactor gas env.	Biological inhibitor	Duration	Purpose
1	80 to 120 °C	483	N ₂	No	4 months	Establish initial understanding of MSW reactions in inert atmosphere at temperatures relevant to ETLF sites.
2	50 to 200 °C	483	N ₂	Yes	3 months	To explore a wider temperature range relevant to ETLFs.
3	50 to 200 °C	101 & 483	50% CO ₂ , 50% CH ₄	Yes	~1 year	To simulate decomposition under more realistic landfill conditions simulating different depths.

atmospheric pressure (101 kPa) to distinguish between the MSW at the surface of a landfill and MSW buried deep into the landfill. As a result, another reactor at atmospheric pressure (101 kPa) was added to the study in phase 3. A majority of the results and discussion in this paper focuses on phase 3 of the experimental campaign as it most realistically depicts the system of interest.

2.1. Experimental outline

Phases 1 and 2 were used as baseline experiments of shorter duration (3–4 months) to establish conditions for the longer duration study (~1 year) which evaluated a range of temperature, pressure and moisture conditions. In phase 1, tests were conducted in a high-pressure system (483 kPa) using a pure nitrogen (UHP grade, Praxair) atmosphere at 80 °C. The pressure (483 kPa) was selected based on field observations showing elevated pressures in landfills exhibiting elevated temperatures (Barlaz et al., 1990). The temperature was kept constant, and a N₂ environment was used to maintain an inert atmosphere, minimizing variables for the first phase. Biological inhibitors were not used in Phase 1 as biological activity was assumed dormant at 80 °C. In subsequent phases, biological inhibitors were used as an added precaution against biological activity.

The second phase used the same reactor pressurized with N₂ to 483 kPa but the temperature range was expanded to cover 50 °C to 200 °C. The maximum temperature in this phase was used to establish a baseline performance across a range that was determined relevant for ETLFs from the obtained field data (Barlaz and Castaldi, 2016).

The third phase replicated the high-pressure system in phases 1 & 2 but included a control reactor operated at 101 kPa. The headspace in phase 3 (in both reactors) was a 50:50 mixture of CO₂ and CH₄. The temperature was initially set to 50 °C and increased in steps to predetermined targets up to ~200 °C. A majority of the study was performed between 50 and 121 °C, however two higher temperatures (177 °C and 204 °C) were used to study the effect of extreme temperature on H₂ concentration as discussed later in the paper.

The synthetic MSW sample was soaked in deionized water for 2 h to obtain saturated material. The moisture content of the MSW tested was measured to be 55 wt% (mass water/total mass) which corresponded to a saturated condition. During the course of the experiment, as gas samples were extracted, some moisture was also removed. Moisture content was controlled by allowing it to decrease as gas samples were extracted and then re-adding precise amounts at pre-determined times. Water injections were done to either restore the water content to the initial 55 wt% or to flood the reactor with water (to study the impact of extreme moisture) using a high-pressure syringe pump. It should be noted that a majority of the experiments used the highest value of water content as 55 wt% with the exception when the goal was to flood the system with water. In which case, water contents as high as 75 wt% were used as discussed later. An equation used to calculate the water content is discussed in the next subsection under GC sampling.

Biological reactions were inhibited in the second and the third phases by the addition of 2,2-dibromo-3-nitrilopropionamide (DBNPA) (0.02 g (gm) per gm MSW) and streptomycin (0.0008 g/g MSW) (Lang et al., 2016).

2.2. Equipment and instrumentation

As stated previously, two reactors were used in phase three, one at high-pressure (483 kPa) and one at low-pressure (101 kPa) to simulate samples at various depths in a landfill (Fig. 1). Based on field data provided to the authors, a pressure of 483 kPa was determined to be the most relevant for the high-pressure tests (Barlaz and Castaldi, 2016). The high-pressure reactor was a stainless steel vessel assembly (Parr Instruments Model 4642). The same reactor was used in all the three phases for the testing at 483 kPa. The vessel has an internal volume of 2 L and has multiple ports for gas exchange. The vessel was sealed with a high-temperature flexible graphite gasket using 47 Newton-Meter of torque, allowing a maximum pressure rating of 13 MPa. The reactor pressure was maintained using a backpressure regulator (BPR) and measured using a transducer on the cover of the vessel. The waste temperature was measured by a J-type thermocouple (Omega Engineering, # HJQIN-18G-18) inserted into a thermowell of the reactor vessel. The thermocouple also served as the reference for the proportional-integral-derivative (PID) temperature controller (Parr Instruments Model 4835). The temperature controller served to heat and control the temperature via a heater assembly (Parr Instruments Model 4913) which encases the reactor vessel. For low-pressure studies, a glass reactor (Chemglass Life Sciences) was used with the same setup and instrumentation as the high-pressure reactor with the exception that there was no BPR required. The sample loading procedure was to charge the reactor with wet waste followed by a purge of the pressurizing gas to eliminate air from the vessel.

The outlets from the reactors were connected to a micro-gas chromatograph (model 3000, Inficon) used for online analysis of the evolved gas. Gas was extracted through a needle valve mounted on the reactor head assisted by the internal microGC pump. The microGC is equipped with a thermal conductivity detector and two columns, a Mol-Sieve column for the separation of Helium (He), H₂, O₂, N₂, CH₄ and CO and a Plot-U column for the separation of CO₂, ethylene (C₂H₄), ethane (C₂H₆) and propylene/propane (C₃H₆/C₃H₈). This provides the concentrations of all permanent gases that would be produced during the course of the experiment. The extracted gas was injected into the GC without any pretreatment/cleaning except condensation of trapped moisture. The gaseous measurements from the reactor were obtained twice daily during the testing campaign, however graphs presented here contain a subset of those measurements for clarity. It should be noted that there is no continuous flow of the gas in/out of the reactor. The small amount of gas extracted for GC sample is replenished (with 50:50 CH₄:CO₂) as soon as the sampling is complete.

As the experiments progressed, the moisture content in the systems decreased as water vapor was removed with gas sampling. The moisture content remaining in the reactor was calculated by subtracting the water loss through sampling from the initial water content. Assuming the gaseous sample was saturated with water vapor, the water loss through each gas sampling was calculated using the known temperature, pressure, gas composition, and the sampling volume. The following equations were used to calculate the water loss in the system

$$\text{Water loss through the GC sample (gm)} = H_{\text{abs}} \text{ gm/m}^3 \times Q_{\text{gc}} \text{ m}^3$$

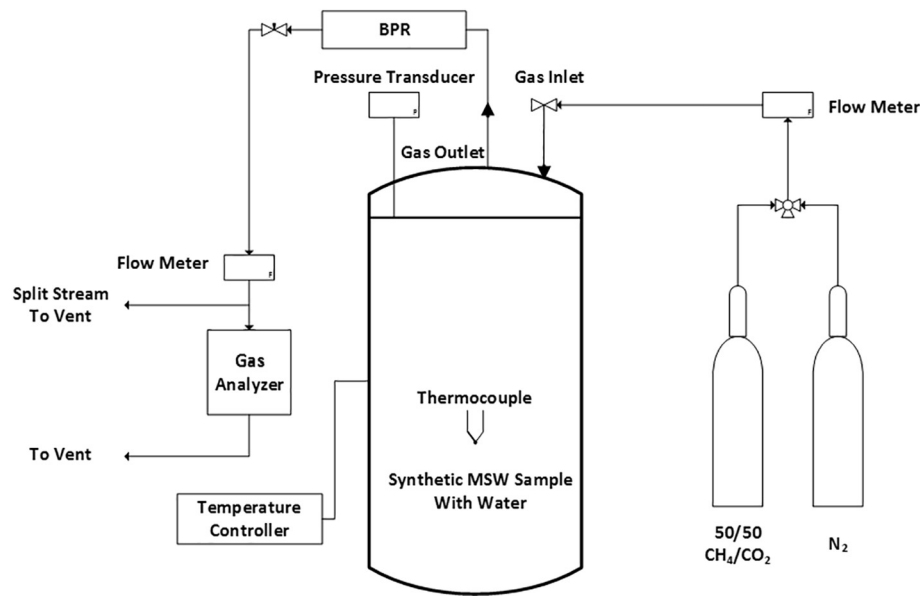


Fig. 1. Schematic of high-pressure reactor used for all experiments.

Water content of the reactor (gm) = $W_i \text{ gm} - [H_{\text{abs}} \text{ gm/m}^3 \times Q_{\text{gc}} \text{ m}^3]$

where,

H_{abs} = Absolute humidity of the gas in the reactors (gm/m³)

Q_{gc} = Total volume of gas extracted through the GC sample (m³)

W_i = Initial amount of water in the reactor (gm)

The absolute humidity of gas exiting the reactor is calculated using humidity tables with the assumption that the gas is saturated with water at the reactor temperature and pressure. The water content of the reactor at any point is calculated by subtracting the cumulative water loss due to each sample from the initial water content of the reactor. It should be noted that the total volume of gas extracted through GC sample (Q_{gc}) can be calculated easily by multiplying the GC gas flow rate with the time for which the gas was flowing.

3. Results and discussion

The only chemical species identified in the characterization of the gaseous product were H₂, CH₄, and CO₂. Trace amounts of carbon monoxide, ethane, ethylene and acetaldehyde were also detected but were not always present. Figs. 2 and 3 present the impact of temperature and moisture on the measured concentrations of CO₂, CH₄ and the ratio of CH₄/CO₂ for the high and low pressure conditions. These results indicate that transitions in the CH₄/CO₂ ratios are connected to the

critical reactions regimes. Presented next, using Fig. 4, are the H₂ production profiles, their behavior as a function of temperature and moisture for the high-pressure system. The H₂ production rates for both the high and low pressure systems are then compared. Observations of char formation from the experimental system, in the presence of 100% N₂, are also shown accompanied by a plausible explanation regarding its formation. The liquid product of the reaction was not extensively tested or quantified in this research because that would require opening the reactors and thus risk air infiltration and contamination.

3.1. Impact of moisture on CO₂ and CH₄ concentrations

The impact of moisture on the biodegradation rates for MSW is well known and is related to the microbial activity (Barlaz et al., 2016b). However, the effects of moisture on abiotic MSW decomposition are unknown. Fig. 2 shows the relationship between temperature, moisture, and the CH₄ and CO₂ concentrations. The gas composition originally charged into the reactors was 50/50 vol% CH₄/CO₂.

During the first 70 days (data not shown for brevity), the temperatures were initially set to 50 °C. The temperature was then increased to 71 °C on day 71 and maintained constant until day 96. During days 1 to 96, the moisture content was calculated to decrease from approximately 55 to 47 wt% for both the high (Fig. 2a) and atmospheric pressure (Fig. 2b) systems. This is due to the sampling protocol of

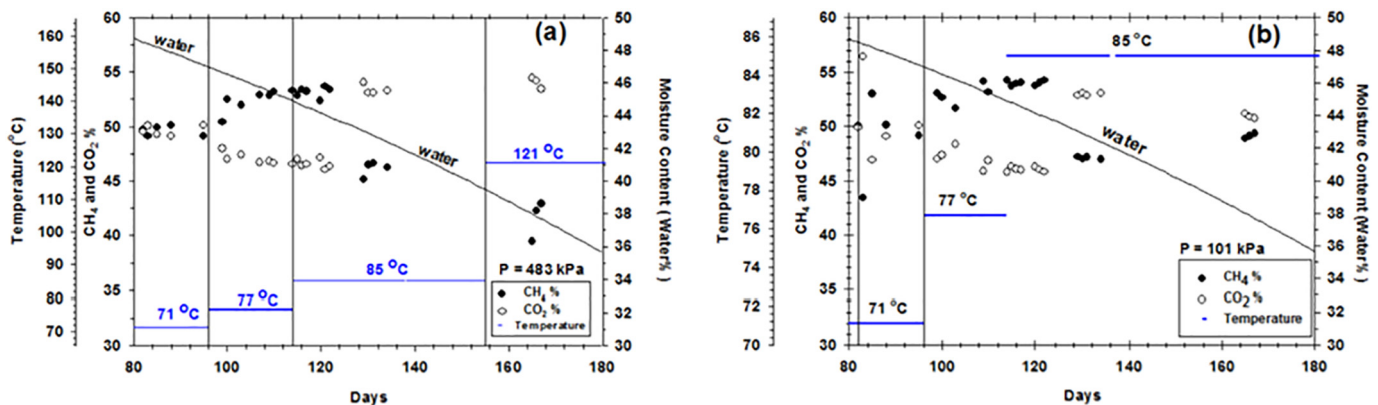


Fig. 2. a) High-pressure and b) low-pressure laboratory reactors demonstrating a temperature and water % dependence on CH₄ and CO₂ concentrations. The short gap in sampling between days 140 and 165 was due to GC malfunction.

withdrawing product gases, which were assumed to be water-saturated, for GC analyses and replenishing with dry CH_4/CO_2 to maintain pressure causing the non-linear decrease in moisture content. The temperature was then increased to 77 °C on day 96 and there was a corresponding increase in the CH_4 concentration and drop in the CO_2 concentration. The trend in the CH_4 and CO_2 continued as the temperature was increased to 85 °C on day 114 while the moisture content continually decreased to 43.5 wt% on day 125. There was an abrupt reversal in the CH_4 and CO_2 concentrations on day 125, when the moisture content reached 43.5 wt%, even though the temperature was constant at 85 °C until day 154. This measurement is the first reported in the literature that shows an abrupt change in the CH_4/CO_2 gas ratio for abiotic conditions. This suggests moisture may contribute to this gas composition reversal. Importantly these trends and the reversal occurred in the high and low pressure reactors on the same day. The high and low pressure data in Fig. 2 therefore serve to quantitatively identify regimes that are moisture independent that caused the initial 50/50 gas mixture to change.

The increase in CH_4/CO_2 ratio is a result of either CH_4 being produced, CO_2 being consumed or some combination of both. When the moisture content reaches a critical value of 43.5 wt%, (on day 125) there is a decrease in the CH_4/CO_2 ratio. The processes causing the change in gas ratio corresponds to the change in moisture concentration, as all other parameters were constant. Importantly these processes are pressure independent indicating that they are not dependent on the depth in a landfill as has been reported at some ETLFs literature (Castaldi et al., 2016).

Fig. 2 also shows that as the temperature was increased to 121 °C, there was a further divergence between the CO_2 (increasing) and CH_4 (decreasing), suggesting that temperature has an impact on the processes that caused that change. It must be noted that the low-pressure reactor required temperatures below 100 °C to maintain 101 kPa so it was kept at 85 °C for the remainder of the experiment, preventing a comparison at 121 °C. Moisture compositions greater than 43.5 wt% result in CH_4/CO_2 ratios above 1; however a moisture condition below 43.5 wt% moves this ratio towards values less than one. Although, a mechanistic understanding cannot yet be developed, it is apparent that elevated temperature resulted in an increased divergence in the concentrations of CO_2 and CH_4 , and that moisture conditions below 38 wt% or above 47 wt% suppress that trend. This becomes more evident when observing gas compositions in the low-pressure system. The low-pressure system temperature remained at 85 °C while the moisture continued to decrease and eventually the CO_2 and CH_4 concentrations return to the 50/50% that was used to recharge the reactors after each gas sampling. This divergence in the CH_4/CO_2 gas ratio will be discussed and compared with field observations later in Section 3.4.

Another way to visualize the change in CH_4 and CO_2 is by plotting the ratio of CH_4 to CO_2 , i.e. the primary gas ratio that is typically used in screening for ETLF conditions. Fig. 3 shows the variation in the CH_4/CO_2 ratio, demonstrating the performance change with changes in temperature and moisture for both the low and high-pressure reactor tests. The gas headspace (volume not occupied by solids) was charged with 50/50 CH_4/CO_2 , providing a constant ratio of 1.0 at temperatures up to 71 °C for nearly 100 days. In Fig. 3, the comparison of the CH_4/CO_2 ratios for the low and high pressure conditions provides further detail on critical temperature and moisture transitions that appear to be independent of pressure. When both reactors were increased to 77 °C, there was an abrupt increase in the CH_4/CO_2 ratio from 1.0 to 1.2. Increasing the temperature to 85 °C did not change the ratio as it was stable at 1.0 for 11 days (day 113 to 124). However, as the moisture decreases at a constant temperature of 85 °C, there is an abrupt decrease in the value of this ratio in both reactors on day 125. Again, when the temperature in the high-pressure system is increased to 121 °C, the ratio continued to decrease. Yet in the low-pressure reactor, where the temperature remained constant, but the moisture continued to decrease below 38 wt%, the ratio recovers to near 1.0. The ratio in the low-pressure reactor, which remained at 85 °C, eventually recovered to near 1.0 when the moisture dropped below 38 wt%. However, the high-pressure reactor was able to accommodate higher temperature and thus was increased to 121 °C. That increase in temperature caused a continued decrease in the ratio indicating that the processes responsible for the ratio change are accelerated with increasing temperature and decreasing moisture.

Specific to the high-pressure reactor, although the moisture was below 38 wt%, the CH_4/CO_2 ratio did not recover to 1.0. Yet near day 200 the ratio began to plateau and eventually reached a low of approximately 0.25 with an increase to 0.4 at day 230. Given our limited understanding of the mechanisms of the shift in CH_4/CO_2 , it is not clear why the plateau occurred. It was anticipated that the ratio in the high-pressure reactor would eventually return to 1.0. Therefore, on day 232 (data not shown), additional water was introduced into the high-pressure reactor to return the moisture content to 55 wt% which corresponded with the ratio to returning to 1.0.

3.2. Impact of moisture and pressure on hydrogen production

The effect of moisture content (i.e. degree of saturation) on H_2 production is slightly more complicated but trends can be identified. Overall, there appears to be a relationship where higher temperatures require higher moisture content to maintain H_2 production. However, once the moisture content reaches significantly above 55 wt%, the

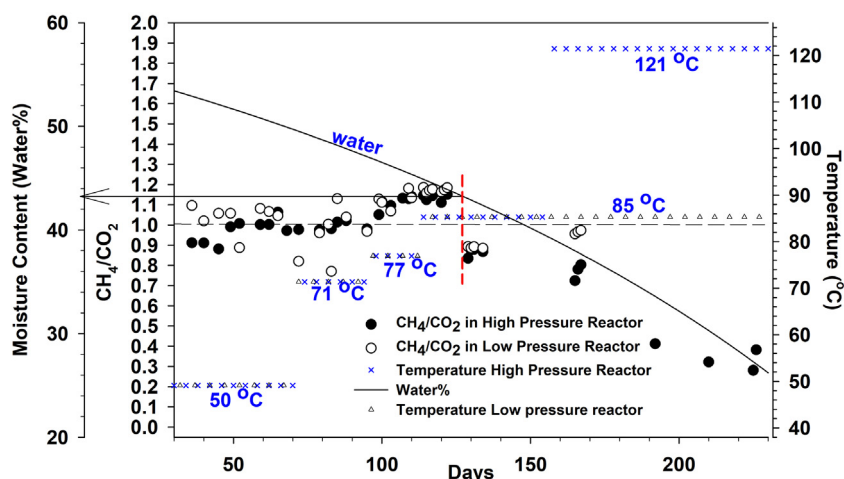


Fig. 3. CH_4/CO_2 ratio measured in low and high pressure reactor conditions.

processes producing H_2 appear to shut down. This is consistent with the CH_4/CO_2 ratio, where higher moisture content did not manifest in a measured change in the ratio. These data provide evidence that within a moisture range, certain processes are initiated or become dominant, compared to other processes, and produce measurable changes in gas phase compositions. Outside of that moisture window (identified later) the processes are likely continuing but do not significantly change the CH_4/CO_2 ratio or release a sufficient volume of permanent gases to be measured. It is hypothesized that reactions occurring outside the “gaseous production/consumption window” yield products that remain in the liquid phase for reactions above the window and the solid phase for those below the window. To test this hypothesis, water was added to the system (during the course of the reaction) to increase the moisture content in controlled dosages. The initial time-dependent decline in moisture followed by the water injection intervals are shown in Fig. 4 with the solid red line curves serving as guides for the trends. It should be noted that a higher temperature (177 °C) is used in Fig. 4 to get a trend over a wider range.

Overall, the H_2 generation rate increases with temperature which is expected for thermal reactions (Fig. 4). The H_2 production rate was calculated from the gas composition and flow rate. Beginning at day 95 at a temperature of 71 °C (not shown) there was no production of H_2 , however when the temperature was increased to 77 °C, there was an increase in H_2 generation observed on day 100. Subsequently as the moisture content declines, at a constant temperature of 77 °C, there was a commensurate decline in H_2 generation. Another increase in temperature to 85 °C on day 114 shows a recovery in the H_2 generation beginning on day 120 followed by a decline as the moisture continued to decrease. As seen in Fig. 4, the elevated temperatures are associated with increased H_2 production. However, as the moisture content decreased elevated temperatures coincided with suppressed H_2 production.

In the same test campaign, temperature was also held constant at 121 °C and the moisture content was allowed to decrease to 26 wt% then increase to 68 wt%, revealing the “moisture window” that results in H_2 production. In Fig. 4, starting on day 155, the temperature was increased to 121 °C and the moisture was allowed to continually decrease. The measurements showed the expected increase in H_2 generation rate, due to the initial increase in temperature, followed by a decline as the moisture content decreased to 26 wt% on day 231. On day 232, the moisture content was adjusted to near 55 wt% (using water injection), after which the H_2 generation rate increased, albeit with some lag. Again, as the moisture level decreased, due to the sampling procedure, there was the anticipated decrease in the H_2 production rate. Importantly a further increase in water addition (to 65 wt%) did not lead to

an increase in the H_2 generation rate at the constant temperature of 121 °C, instead the additional moisture appears to further suppress the rate to nearly zero from days 255 to 270. When the moisture decreased, the H_2 production began to recover from days 270 to 278. Finally, an increase in temperature to 177 °C with a simultaneous increase in moisture to 74 wt% displayed an initial increase in H_2 production that probably corresponded to the higher temperature. The sharp decline that followed coincided with the increased moisture content that returned the system to the initial moisture level.

Although, the data are not conclusive regarding the moisture window, there is definitely a trend related to moisture. Conditions that are either too wet or too dry coincided with changes in H_2 production (Fig. 4). However, as illustrated in Fig. 4, within a moisture window (identified here as between 38 and 47 wt%) the H_2 production increased, where the CH_4/CO_2 ratio decreased (Fig. 3). The quantitative identification of this zone is novel to our knowledge and is consistent with field observations from ETLFs where the hottest temperatures often appear in wet waste (Barlaz et al., 1990, 2016a). Hence it is hypothesized that the reactions causing elevated temperatures are likely related to the higher moisture content of the waste, close to 50% in this study.

To demonstrate the impact of pressure, the H_2 concentrations are presented in Fig. 5. Also included in Fig. 5 is moisture content as a reference to provide a more complete view of the experimental conditions. It is observed that H_2 concentrations increased as temperature increased, however the effect of pressure is significantly more pronounced. This finding is consistent with Mok and Antal (Mok and Antal Jr., 1983; Mok and Antal, 1983) where it is shown that higher pressures resulted in an increased rate of reaction for biomass pyrolysis. The synthetic MSW tested here has a biomass component, specifically wood; that we show (later in Fig. 6) reacted at a lower temperature relative to the other components. The data establishing the enhancement of H_2 production at 483 kPa compared to atmospheric pressure (101 kPa) completes the description of the roles of temperature, pressure, and moisture on pyrolysis performance.

The comparison of $H_2\%$ at atmospheric and elevated pressure and the trends with temperature indicate that H_2 production is favored at higher temperature and higher pressure. The trends observed between CO_2 and CH_4 are not conclusive. The reactions that generate H_2 and change the CO_2 and CH_4 concentrations are the subject of active experimental investigation. H_2 production is nearly four times higher in the high-pressure system compared to the low-pressure system. Both exhibit decreased H_2 production as moisture content declines with the low-pressure reactor ceasing production (or below detection limits) at a moisture content of 47 wt%. Even an increase in temperature to

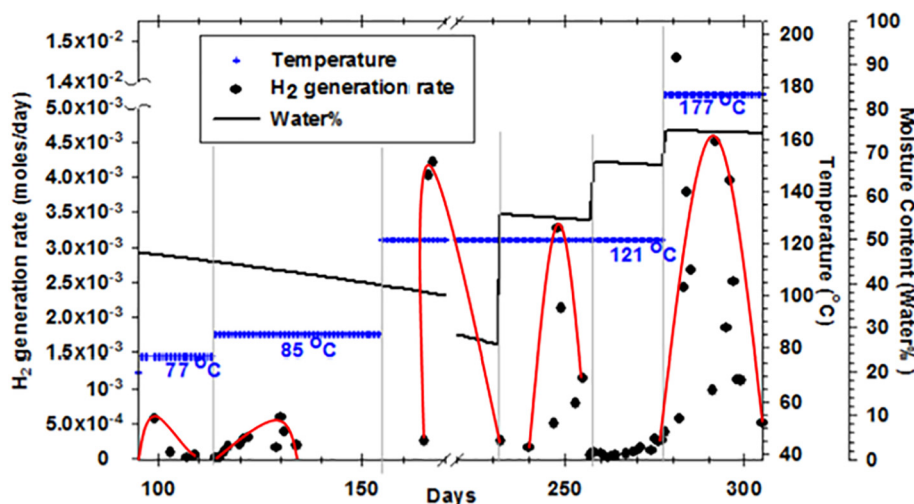


Fig. 4. Calculated H_2 generation rates in the high-pressure reactor highlighting the impact of temperature and moisture.

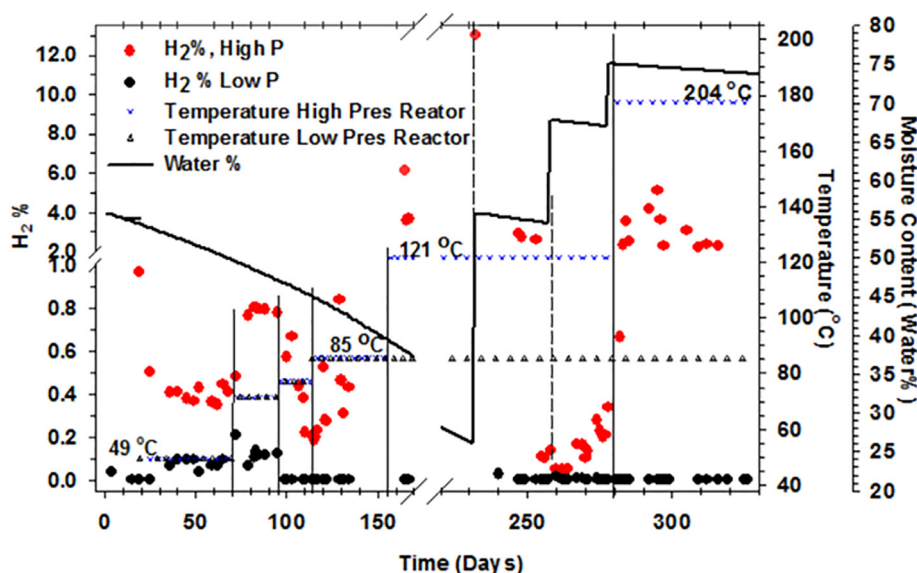


Fig. 5. $H_2\%$ as a function of temperature and pressure.

85 °C in the low-pressure reactor did not promote H_2 production as it did for the high-pressure condition. Only when additional water is injected, on day 232, to re-establish the initial moisture content of 55 wt% was there a brief time where a small amount of H_2 was produced in the low-pressure reactor. In the high-pressure reactor, H_2 decreased by an order of magnitude by day 255. Further increases in water, at the constant temperature of 85 °C, for the low-pressure system did not result in recovery of H_2 formation.

3.3. Char production in the absence of oxygen

During the experimental campaign, a series of tests were conducted to provide information on different aspects of thermal MSW decomposition in an inert (N_2) environment. One of the tests conducted was to expose synthetic MSW to an inert environment for a fixed time frame followed by sample characterization. That test confirmed the formation of char in a pyrolysis (O_2 free) environment. The temperature was initially set at 80 °C and maintained to provide an initial understanding of the reaction products as a function of temperature. Fig. 6a shows a sample of synthetic MSW as initially placed in the reactor containing plastics, textiles, wood, and other non-putrescible waste. Fig. 6b shows a sample of completely charred wood recovered from the reactor after being subjected to 80 °C for 4 months. Importantly the fresh MSW did not contain any charred material, only wood, along with the other waste components. The remaining MSW components did not show

visible signs of degradation, thus pointing to an ability of the wood to begin reaction at lower temperature compared to the other MSW components. The synthetic MSW also contained paper waste that did not appear to burn or char during the course of this experiment. It is possible that the volatile matter in the wood that is not present in paper may be the cause of the charring of the wood.

The observations and discussions present evidence that pressure accelerates gas production as indicated by the H_2 production data. The divergence of the CO_2 and CH_4 in an abiotic, pyrolysis environment is independent of pressure, yet follows the expected trend for thermal reactions where increases in temperature accelerate the reactions. The data also reveal that a moisture “window” exists that promotes CH_4/CO_2 ratio changes and gas phase H_2 production. Outside that window, either higher or lower moisture content diminishes the processes that caused the ratio changes and H_2 production within a small temperature range. Importantly, some of these experimental data match field observations from a representative ETLF as shown in the next section.

3.4. ETLF field observations and laboratory measurements in the absence of oxygen

There has been a concern that the elevated landfill temperatures are due to the presence of a fire or smoldering combustion event (Jafari et al., 2017). The discussion in this section attempts to provide more evidence that combustion or smoldering is not occurring in the landfill

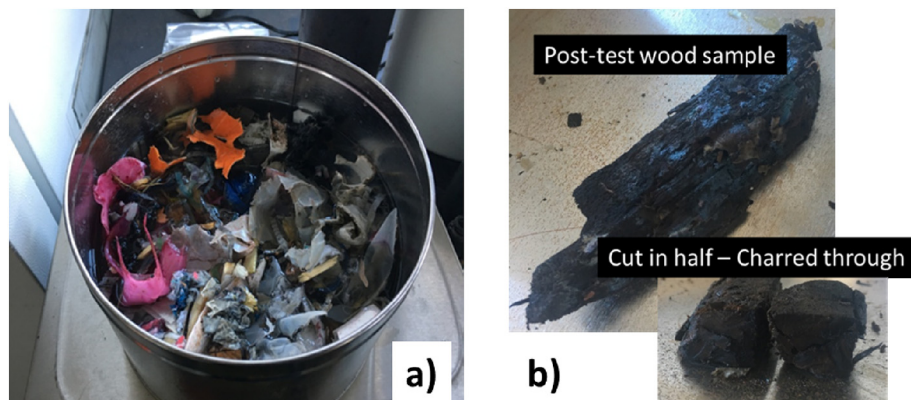


Fig. 6. a) Synthetic MSW (left image) and b) post-test confirmation of char from wood (right image).

studied by making use of N_2/O_2 and CH_4/CO_2 ratios of the field data. Fig. 7 shows that measurements from a gas well in a landfill (Barlaz et al., 2016) indicate normal stable operation for four years at a temperature of approximately 54 °C and CO_2 and CH_4 concentrations at typical values. Importantly the gas measurements also show nearly no oxygen as expected. The lower temperature observed in the field, 66 °C, coinciding with the gas composition change is due to the averaging effects associated with well head measurements (Barlaz and Castaldi, 2016). The laboratory measurements of 80 °C are likely more indicative of the waste temperature required to affect the composition change. These field measurements have been incorrectly associated with the possibility of a sub-surface fire or smoldering event. Yet the experimental data presented aligned with Fig. 7 and data discussed below indicate the reactions are anaerobic and display a pyrolysis character.

The elevated temperature landfill measurements that have been reported have been erroneously attributed to a sub-surface fire or smoldering event. If there was a fire, then large amounts of oxygen would be required that can only be supplied from air. The oxygen content from air brings an associated amount of nitrogen at a fixed ratio. The nitrogen is 3.73 times the amount of oxygen in the air. During a fire oxygen is consumed and CO and CO_2 are produced. Any unreacted oxygen remains as O_2 . It should be noted that during a combustion event (fire) the nitrogen is only slightly consumed, typically on the order of 0.00001–0.0001%. This is not enough to materially change a calculation done to determine the N_2/O_2 ratio. Therefore, measurements in landfill wells that contain accurate readings of CO, CO_2 , O_2 and N_2 enable a determination of the N_2/O_2 ratio. The data shown in Fig. 8 compares the N_2/O_2 ratio of gas well data, using laboratory chemical analyses, to that required for a fire. The data show nitrogen to oxygen ratios below 0.5 which precludes air infiltration sustaining a fire or smoldering.

To illustrate how this calculation can be used in a quantitative manner, consider MSW combustion.

MSW can be approximated as $C_6H_{10}O_4$ (Themelis et al., 2002). This will adjust the N_2/O_2 ratio slightly from 3.73 to 2.85 due to the oxygen present in the MSW. The following reaction can be written



The stoichiometry of Eq. (1) results in the N_2 to O_2 ratio in air reacting with MSW to be 2.85 – indicated by the dashed red line in Fig. 8. Specifically, the N_2 to O_2 ratio in the products of reactions is $6 \times (\text{molar amount of } CO_2) + \frac{1}{2} \times (\text{molar amount of } H_2O)$ or $\{6 + \frac{1}{2} \times 5 = 8.5\}$. Therefore, the molar amount of oxygen in the product (contained in CO_2 and water) is 8.5 and the molar amount of nitrogen in the product is 24.25. Thus the ratio of $N_2:O_2$ in the product gases is 2.85. Importantly, the excess oxygen in the reactants (i.e. more than required to completely convert the MSW) will be measured as O_2 in

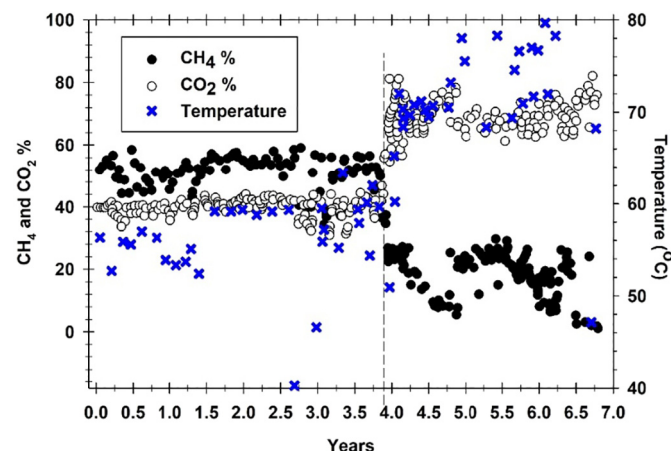


Fig. 7. Field measurements of ETLF gas well.

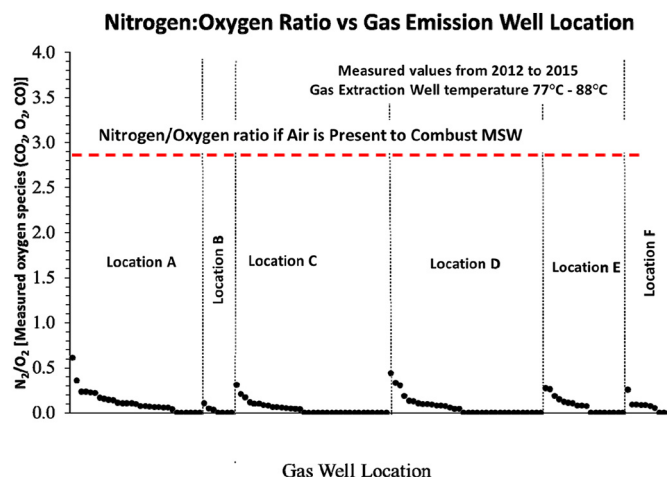


Fig. 8. Laboratory analyses of gas well samples from the Bridgeton MO landfill site.

product gas mixture giving a mixture of CO_2 , H_2O , N_2 , and O_2 . Any compounds that should be in the product mixture that contain oxygen (e.g. H_2O) that are not measured serve to increase the ratio. For example, if only CO_2 were measured, then the $N_2:O_2$ ratio would be 4.04. Thus field measurements of ETLFs that confirm there is no air infiltration likely have processes that are similar to the processes in our experimental campaign.

Finally, the laboratory observations related to the wood converting to char can be compared to field sample observations where some core samples have exhibited significant char (Barlaz and Castaldi, 2016). Fig. 9 shows one such core sample taken from an elevated temperature zone in a landfill. The core sample likely has many other MSW components, as opposed to the synthetic MSW used in the experiments and therefore definite correlations cannot be made, but from the visible observation it can be suggested that the char produced in the ETLF shown in Fig. 9 is consistent with the experimentally produced char seen in Fig. 6b. Further studies with individual MSW components under simulated landfill conditions are needed to formulate pyrolysis reaction mechanisms.

4. Conclusion

A laboratory test campaign that studied simulated Municipal Solid Waste decomposition (in the presence of biological inhibitors) was performed over temperature ranges and relevant pressures that corresponded to field measurements from Elevated Temperature Landfills. The experimental campaign focused on thermal reactions that take place under simulated landfill conditions, rather than biological reactions. Two reactors were setup using exact same process condition with the exception of pressure. The first reactor was maintained at



Fig. 9. Core sample of MSW from ETLF site showing similar char formation to inert lab tests.

483 kPa whereas the second reactor was kept at atmospheric pressure (101 kPa). This allowed investigation of the impact of pressure on the decomposition of the simulated municipal solid waste. The data from these tests suggest that the hydrogen generation rate is an order of magnitude higher at 483 kPa than at atmospheric pressure (101 kPa). Moisture content of the reactors was monitored during these tests. The laboratory test results revealed that within a moisture range of 47 wt% to 38 wt% the CH₄/CO₂ gas ratio decreased from an initial value of 1.0 to 0.3 with a corresponding increase in hydrogen generation. However, moisture levels above 47 wt% and below 38 wt% resulted in the CH₄/CO₂ gas ratio to remain at 1.0 and the hydrogen production to cease. Furthermore, the laboratory measurements of the changes in the CH₄/CO₂ ratio at 85 °C coincided with field measurements that have been connected to the onset of an ETLF event. An MSW test sample that was exposed to pure N₂ at 483 kPa and 80 °C, demonstrated that the wood portion completely charred while the other MSW constituents were nearly unchanged. This suggests that wood, which is one of the biomass components in MSW, is likely the first to decompose in an abiotic environment. Thus, the observed changes in solid MSW and gas composition under controlled pressure, moisture, and temperature conditions in the absence of oxygen provide insights into possible processes occurring in landfills that possess similar properties. Although the reaction mechanism is not clear, the experimental data provides evidence that pyrolysis, abiotic processes occurring in landfills can transition to elevated temperature conditions.

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CRediT authorship contribution statement

Swanand Tupsakhare: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Tasnuva Moutushi:** Data curation, Formal analysis, Writing - review & editing. **Marco J. Castaldi:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - review & editing. **Morton A. Barlaz:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - review & editing. **Scott Luetlich:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - review & editing. **Craig H. Benson:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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