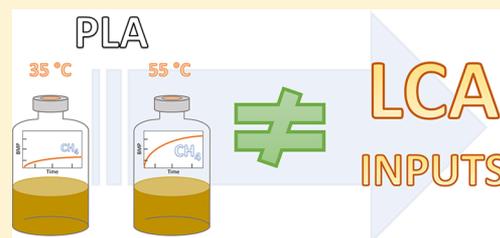


Life-Cycle Assumptions of Landfilled Polylactic Acid Underpredict Methane Generation

Max J. Krause and Timothy G. Townsend*

Environmental Engineering Sciences, University of Florida, 220 Black Hall, Gainesville, Florida 32611, United States

ABSTRACT: The life-cycle assessment (LCA) tool, Waste Reduction Model, currently applies no methane generation to landfilled polylactic acid (PLA), considering the carbon sequestered. A selection of PLA products were analyzed by the biochemical methane potential (BMP) assay, and the results were compared to LCA model values. BMPs were performed at 35 and 55 °C on a variety of single-use products that would be disposed alongside food scraps. No biodegradation was observed for any product after incubation at 35 °C for 60 days. PLA products generated 185–372 mL of CH₄/g of volatile solids at 55 °C after 60 days, some approaching the theoretical methane potential. The results here indicate that PLA may generate significant quantities of methane in an anaerobic landfill environment, which can reach thermophilic temperatures, and the current assumption of PLA as an absolute carbon sink in landfills is incorrect.



INTRODUCTION

Biodegradable PLA products are increasingly available as an alternative to petroleum-based plastic consumer products. Much of the biodegradation research on PLA has focused on aerobic conditions such as composting environments.¹ Because many of the products are food-related (e.g., disposable cups, cutlery, etc.), use of an aerobic standard is appropriate when food waste and PLA are comanaged using such a technology. However, anaerobic digestion (AD) is increasingly used as an energy recovery and waste treatment mechanism. Furthermore, source-segregated food waste management is uncommon in much of the world. PLA is not recyclable in the conventional sense and, in all likelihood, will be landfilled with other solid wastes.² Unlike petroleum-based plastics, which represent a carbon sink in landfills, though not a carbon credit, anaerobically biodegradable plastics may present a confounding issue by increasing landfill methane emissions to the environment.³

If all the carbon were anaerobically degraded, 1 g of PLA (C₆H₈O₄) would theoretically yield 467 mL of CH₄ based on the Buswell equation.^{4,5} However, the U.S. Environmental Protection Agency's (EPA's) Waste Reduction Model (WARM), a greenhouse gas accounting and life-cycle assessment (LCA) program, currently assumes no biodegradation of PLA in landfills.⁶ This is based on the finding that semicrystalline PLA will not anaerobically degrade at 35 °C and the assumptions that (1) landfill environment temperatures are 21–35 °C and (2) a large majority of PLA products have a semicrystalline structure.⁴ Experimentally, Kolstad et al.⁴ identified a methane potential of 260 mL/g of amorphous PLA after incubation at 35 °C for 180 days. Vargas et al.⁵ reported a methane potential of 187 mL of CH₄/g from a PLA cup after 56 days at 58 °C. Because of differences in temperature and structure, it is difficult to directly compare these results, but at least certain types of PLA are anaerobically degradable under mesophilic and thermophilic conditions.

The biochemical methane potential (BMP) assay has become a standard tool for engineers to predict anaerobic degradation of wastes.⁷ BMP assays are typically performed for 60 days to generate data in a timely manner. The current ASTM standards for assessing anaerobic biodegradability of plastics in the presence of sewage sludge (D5210) and under accelerated landfill conditions (D5526) direct incubation to occur at 35 °C.^{8,9} ASTM D5511 directs incubation to occur at either 37 or 52 °C.¹⁰ PLA's glass transition temperature, the point at which the crystalline structure begins to deform, is 55–60 °C, and degradation occurs more quickly once this temperature is reached.^{11–14} Each method identifies different experimental apparatus, and all instruct reporting cumulative biogas evolution, which has been reported for PLA.^{4,11–14} In conventional landfill modeling, whether for landfill gas (LFG) generation or LCA, generally only methane is evaluated because biogenic carbon dioxide is considered carbon neutral and methane drives energy recovery decisions.^{15,16} Hence, methane generation parameters are more valuable to solid waste engineers than total biogas. Although LFG can be assumed to be a 50/50 (v/v) methane/carbon dioxide mixture, this is not always accurate with regard to lipids or proteins.¹³

This research assessed the anaerobic degradability of advertised biodegradable PLA products at mesophilic and thermophilic temperatures according to the BMP protocol developed by Owen et al.¹⁷ and adopted in ASTM D5210. This method has been widely adopted by the solid waste community and was selected to allow for comparison to more conventional municipal solid waste (MSW) component methane potentials.¹⁸ Cumulative methane potentials (milliliters of CH₄ per

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Table 1. Advertised Biodegradability Standards and Physical Characteristics of PLA Products

sample	material	moisture content (MC)	volatile solids/total solids	BMP ^a (mL of CH ₄ /g of VS)	L ₀ ^b (m ³ of CH ₄ /Mg)
cup lid	PLA	0.4	90	243 ± 6	219
cup 1	PLA	0.5	100	274 ± 22	273
cup 2	PLA	1.8	100	372 ± 19	365
cup 3	PLA	0.5	100	344 ± 9	342
cutlery	70% PLA/30% talcum	0.3	71	185 ± 21	131
cutlery wrapper	PLA	0.5	100	326 ± 7	324
drink straw	PLA	0.3	100	238 ± 13	237
cellulose	cellulose	4.0	97	351 ± 2	322

^aBMPs are presented as the average ± standard deviation of triplicate samples incubated at 55 °C. ^bL₀ is an as-received (wet-weight) parameter used in LFG generation models and LCAs.

gram of volatile solids) of a selection of commercially available PLA products are presented after incubation with sewage sludge at 35 and 55 °C for 60 days. These experimental results were then compared to the values used in previously reported LCAs and WARM (version 13) to assess the model's ability to accurately account for the generation of methane from landfilled PLA.

EXPERIMENTAL METHODS

New, single-use PLA products such as cups, wrapped cutlery, straws, and lids that are now common alternatives to petroleum-plastic products were supplied by vendors and analyzed individually by the following methods. The cutlery was removed from the wrapper and analyzed as two separate products. Samples were first size-reduced in a commercial blender to <1 cm. The moisture content (MC) was evaluated as the percent mass loss after 24 h in a 105 °C oven. The volatile solid content was evaluated as mass loss from the dry mass after 4 h in a muffle furnace at 550 °C. The BMP assay followed the protocol developed by Owen et al.¹⁷ and adopted by ASTM D5210-92.⁹ Sludge was collected from a two-stage thermophilic–mesophilic sewage sludge anaerobic digester in Lakeland, FL, USA. After the sludge samples had been collected, they were incubated for an additional 5 days to reduce background activity.¹⁹ Triplicate samples of 0.2 g of volatile solids (VS) were inoculated with a 100 mL nutrient solution of anaerobic sludge, bulk and trace metals, and an oxidizing color indicator as defined by the method. The nutrient solution was sparged with high-purity nitrogen to remove oxygen. A positive (cellulose) control and blank control were used to evaluate inoculum performance. Samples were incubated in 250 mL serum bottles at 35 and 55 °C for 60 days with emission measurements taken at regular intervals. The total gas generation was measured volumetrically with gastight syringes. Gas composition was analyzed with a gas chromatograph equipped with a thermal conductivity detector (Shimadzu model GC-8A). Methane generation was normalized to standard temperature and pressure (0 °C and 1013 mbar, respectively) from the incubation temperature, and the blank control was subtracted from sample results.

RESULTS AND DISCUSSION

Biochemical Methane Potential of PLA. PLA products were first evaluated for their physical properties. As shown in Table 1, some products are made with a mix of other less volatile materials (e.g., cutlery 1), while others are almost completely volatile.

No gas generation was measured from the mesophilic assays over 60 days, and that experiment was subsequently terminated,

though cellulose reached a high methane yield within a few weeks. Previously reported experiments have shown mixed results regarding the ability to measure PLA degradation at mesophilic temperatures. Shi and Palfrey¹⁴ reported a significant decrease in gas generation from an extruded PLA sheet at temperatures below the glass transition temperature. Shin et al.¹¹ found no degradation of PLA film at 35 °C after incubation for 100 days. Kolstad et al.⁴ identified a methane potential of 260 mL/g of amorphous PLA pellets after incubation at the same temperature for 180 days but none in semicrystalline PLA. The time allowed in the mesophilic BMPs may have been insufficient to allow for the hydrolysis of PLA, and the physical structure (e.g., amorphous vs semicrystalline) of the product may also play a role.^{4,12} Regardless, the absence of methane generation from PLA under ideal mesophilic conditions after 60 days is notable. If a food waste stream with biodegradable plastics was digested by a typical mesophilic digester with a 30 day hydraulic retention time, it seems unlikely that any degradation or methane generation would occur from the PLA.

Whereas cellulose was rapidly consumed, peaking at 347 mL of CH₄/g of VS by day 27, many of the BMPs performed on the PLA products at the thermophilic temperature experienced a lag period of approximately 15 days before producing any gas. Thereafter, PLA products produced significant amounts of methane, suggesting the inoculum required a period of time to degrade the new material. As shown in Figure 1, after the lag phase, the thin cutlery wrapper film generated gas the quickest, whereas the thicker cup lids and cutlery were much slower. Decay rates (*k*) could not be reliably calculated from the data because of the infrequency of later measurements. If the lag period is ignored, Figure 1 shows that all PLA products

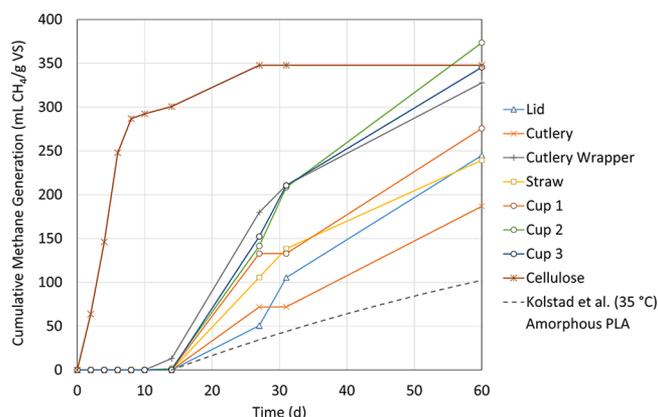


Figure 1. Thermophilic BMP time series of PLA products.

generated methane over approximately 45 days, similar to the results for other wastes analyzed by BMP. Table 1 presents the thermophilic BMPs of the products, showing a range of anaerobic biodegradability. PLA cups emitted 274–372 mL of CH₄/g of VS, indicating high anaerobic degradability compared to the theoretical value of 467 mL of CH₄/g predicted by Buswell.⁴ The greatest values are similar to those of cellulose (positive BMP control) and office paper, which exhibit among the highest methane potentials of MSW components.¹⁸ These values are also significantly higher than the value of 187 mL of CH₄/g reported by Vargas et al.,⁵ who similarly performed a thermophilic BMP on a PLA cup.

For solid waste engineers, the methane generation potential (L_0) is a parameter used to predict LFG generation and build greenhouse gas inventories. Because most LCA and LFG models import as-received tons of waste, L_0 is a wet-weight parametrization of BMP data, incorporating MC and VS data. L_0 values of PLA products ranged from 131 to 365 m³ of CH₄/Mg of product, with an average of 248 m³/Mg, in agreement with the value of 260 m³ of CH₄/Mg of amorphous PLA reported by Kolstad et al.⁴ Adjusting the start time to day 14 and superimposing the data of Kolstad et al. ($L_0 = 260$ m³/Mg and $k = 0.011$ year⁻¹ at 35 °C) in Figure 1 again emphasize that degradation of PLA is significantly quicker at thermophilic temperatures, indicating a significantly shorter half-life. The lack of well-defined cumulative methane curves, showing exponential growth and an asymptotic plateau, prohibited an evaluation of the decay rate.

The results here further support the notion that while degradation of many biodegradable MSW fractions is limited by moisture content,⁷ degradation of PLA is more temperature-dependent.^{4,12–14} If these products were semicrystalline, then the resistance to degradation observed at 35 °C would not hold true at temperatures near the glass transition temperature, and all PLA products would be readily anaerobically degradable under thermophilic conditions.

Landfills are generally known to exist under mesophilic and thermophilic conditions with internal temperatures being a function of local climate, waste temperature at disposal, landfill size, and depth. Townsend et al.²⁰ reported landfill temperatures of 30–55 °C in Florida. Hanson et al.²¹ reported temperatures of 30–55 °C in a Michigan landfill and 10–49 °C in a Canadian landfill. Maciel et al.²² reported mesophilic and thermophilic temperatures of LFG in Brazil, and Sormunen et al.²³ noted internal leachate temperatures as high as 50 °C in a Finnish landfill. Thus, some MSW landfills will exhibit temperatures suitable for semicrystalline PLA degradation. Additionally, thermophilic anaerobic digesters may be able to capture at least some portion of the released methane within a 30 day retention time if the microorganisms are adapted to the substrate.

The current anaerobic standards that dictate incubations at 35 °C may limit samples from producing methane or biogas in a short (i.e., 60 day) time frame.^{8,9} Increasing the temperature to 55 °C may allow for methane generation to occur in a timelier manner and is a condition observed in landfills. It is possible that digestion is rate-limited by hydrolysis and preincubation of the inoculum with PLA to acclimatize the microorganisms may quicken analyses.

In contrast to the samples analyzed here, Kolstad et al.⁴ performed the incubations with PLA pellets rather than finished products. PLA is a semicrystalline polymer, but its final physical form (amorphous or semicrystalline) is dictated by manufactur-

ing conditions and product requirements. Kolstad et al.⁴ indicated that approximately 96% of all PLA products are semicrystalline, and thus, the majority of PLA products would not degrade at 35 °C. It is unknown if the PLA would generate methane in the mesophilic BMP assays given enough time (>180 days). Across several studies, it is not currently possible to determine if PLA degradation is more a function of structure or temperature.^{4,5,11–13}

Comparison to LCA Inputs. LCAs assessing PLA, including end-of-life considerations, were reviewed to compare model values to experimental values reported in the literature as well as those reported here. In a comparison of PET and PLA bottles, Papong et al.²⁴ assessed PLA landfill methane generation based on the theoretical value of 467 mL of CH₄/g derived by Buswell. Vink et al.²⁵ did not identify a BMP value but did suggest PLA was a carbon sink in the landfill scenario, suggesting low or negligible degradability. Similarly, Madival et al.²⁶ assumed landfill emissions from PLA were identical to those of the disposal of mixed plastics, suggesting a carbon sink. WARM (version 13) evaluates PLA under four waste management schemes: landfill, compost, incineration, and source reduction.⁶ Using the work of Kolstad et al.,⁴ landfilled semicrystalline PLA is thought not to degrade and therefore generate zero methane, sequestering all carbon. If the landfilled products generated methane, even over a time period of 100 years, WARM would underpredict methane generation and overpredict carbon sequestration. Neither Britain's LCA tool WRATE nor Denmark's EASETECH includes PLA as a material. Table 2 includes BMP values of PLA from experimental values as well as inputs to LCA models, showing a clear discrepancy between the experimental findings and modeling assumptions.

Table 2. Experimental and Model Values of PLA Methane Generation

	Experimental Values	
	BMP (mL of CH ₄ /g)	temp (°C)
this study	0	35
this study	185–372	55
Kolstad et al. ⁴	0; 260 ^a	35
Vargas et al. ⁵	180	58
Values Used in LCA Models		
	BMP (mL of CH ₄ /g)	
Papong et al. ²⁴	467	
Vink et al. ²⁵	?	
Madival et al. ²⁶	0	
Posen et al. ²⁷	0	
WARM v13 ⁶	0	
WRATE	NA	
EASETECH	NA	

^aBMP values of 0 for semicrystalline PLA and 260 for amorphous PLA.

Landfill methane emissions associated with PLA would not necessarily undermine the environmental benefit of PLA products. The total environmental impact would be dictated by many more assumptions, such as if LFG was collected for energy recovery, if no LFG collection occurred, if biodegradable products were prohibited from landfilling, or local climate impacts on landfill behavior. The latter assumption may be particularly important as the majority of future landfills will be

constructed in warmer climates (i.e., in developing countries) and as global average temperatures continue to increase.

A more thorough understanding of the PLA product behavior at different temperatures while noting the physical structure will elucidate which has a greater effect, and this will better inform LCA models. Additionally, if the physical structure is dictated during the manufacture of products, then BMP data regarding products, and not raw pellets or resin, will be more valuable to the waste management community. WARM's current value of 0 mL of CH₄/g PLA is based on the assumptions that (1) landfills exist at temperatures between 21 and 35 °C and (2) semicrystalline PLA will not anaerobically degrade at those temperatures. The first assumption WARM uses to justify 0 mL of CH₄/g PLA is not conservative and may not be valid even for landfills in temperate climates.^{21,23} As such, accurate evaluations of PLA's environmental impact cannot be assessed with the current assumptions in WARM.²⁷ Whereas PLA biodegradation may be limited by retention time in an AD, 100 years or more in a landfill should allow for at least partial degradation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ttown@ufl.edu. Phone: (352) 392-0846.

Notes

The authors declare no competing financial interest.

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