Research Article

Anaerobic Codigestion of Food Waste and Polylactic Acid: Effect of Pretreatment on Methane Yield and Solid Reduction

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Food waste and biopolymers, plastics derived from plants, are unexploited sources of energy when discarded in landfills without energy recovery. In addition, polylactic acid (PLA) and food waste have complimentary characteristics for anaerobic digestion; both are organic and degrade under anaerobic conditions. Lab-scale reactors were set up to quantify the solubilization of pretreated amorphous and crystalline PLA. Biochemical methane potential (BMP) assays were performed to quantify CH4 production from both treated and untreated PLA in the presence of food waste and anaerobic digested sludge. Amorphous and crystalline PLA reached near-complete solubilization at 97% and 99%, respectively, when alkaline treatment was applied. The PLA that received alkaline treatment produced the most of CH4 throughout the run time of 70 days. The PLA without treatment resulted in 54% weight reduction after anaerobic digestion. Results from this study show that alkaline pretreatment has the greatest solid reduction of PLA and maximum production of CH4 when combined with food waste and anaerobic digested sludge.

1. Introduction

Biopolymers such as polylactic acid (PLA) are made from biobased feedstocks, many of which are biodegradable [1]. Akin to petroleum plastics, there are two types of biopolymers: crystalline (rigid and molecular chains adhered with other molecular chains) and amorphous (flexible and molecular chains move when pushed or pulled). PLA, possibly the most prolific biopolymer to date, has reached production of approximately 140,000 metric tons per year [2]. Most PLA on the market is used in medical applications, 3D printing, or as single-use disposable food packaging and related products, such as utensils [3–5].

Organic waste streams often include PLA and food waste that have negative environmental impact when disposed of in landfills and compost facilities. PLA in food applications has the distinct advantage that it can be composted alongside food waste; however, compost facility managers and studies report that the PLA biopolymer does not fully degrade in industrial composting facilities [4, 6, 7]. Despite PLA being the most readily available biopolymer on the market for industrial and consumer use, only 7% degrades in 90 days [8]. Although small amounts of PLA are disposed of, a significant percentage of PLA is discarded in the environment with a degradation time of six months to two years [9].

The GHGs that are emitted from food waste have led to many states in the US and European countries to limit the amount of food waste that can go to landfills [10, 11]. Over 100 organizations, a part of the Saria Group [12], acknowledge food waste as a problem that needs sustainable solutions and should be viewed as valuable resources. Using food waste as a renewable energy source, via anaerobic digestion (AD), reduces environmental impacts compared
to other waste management technologies [13]. Food waste has a high energy potential and an estimated decay rate of 0.14 yr⁻¹ which makes it a perfect candidate for waste to energy technologies such as AD [14].

Previous studies have already successfully codigested food waste with anaerobic digested sludge (ADS) inoculum: e.g., municipal wastewater [15], brewery effluent [16], grass silage, and farm waste [17]. Elbeshbishy et al. [18] demonstrated the benefits of successful digestion of food waste with anaerobically digested inoculum from municipalities. Hobbs et al. [19] demonstrated realistic AD outcomes of food waste to inoculum without pH adjustments and showed favorable results for ratio 1.42 g chemical oxygen demand (COD)/g volatile solids (VS). Ratio 1.42 resulted in most advantageous performance, such as decreased lag time for CH₄ production and high CH₄-COD recovery, compared to ratios 0.42 and 3.0 [19].

Recent studies have demonstrated the ability to digest biopolymers with municipal sludge in mesophilic conditions and yield CH₄ that can be used for combined heat and power (CHP) [20]. Also, Iätavaara et al. [21] and Yagi et al. [22] were able to reach 60% mineralization of PLA, in the powder form, within 40 days in thermophilic conditions. Although these studies confirm that PLA can be anaerobically digested, it is still unknown if complete degradation of PLA products such as cups and thin films is possible. It is also not well studied if these products can be degraded under mesophilic conditions at the same rate of food waste.

PLA is a particulate solid, and hence, its availability for microbial hydrolysis is often rate limiting [23]. Therefore, pretreatment of PLA is necessary to enhance degradation [24]. There are very few studies that assess the pretreatment of PLA. Hottle et al. [25] performed compost experiments using alkaline amendment (a finely ground calcium silicate feedstock at 2% concentration) to enhance the degradation of clear PLA in an aerobic environment and reported that up to 18.75% of initial mass was reduced within 22 days. Benn and Zitomer [26] chemically pretreated PLA with sodium hydroxide (NaOH), codigested the pretreated PLA with dog food, and recovered more COD as CH₄ from pretreated PLA as opposed to nontreated PLA. Although there are no studies that assess the ability to anaerobically digest PLA and food waste, the potential exists once the alkalinity and pH are under optimal conditions.

This study seeks to assess alkaline pretreatment for accelerating the solubilization of PLA and to quantify the CH₄ production from codigesting both treated and untreated PLA with food waste. Alkaline pretreatments of amorphous and crystalline PLA were performed with sodium hydroxide (NaOH) to analyze the solubilization of PLA. CH₄ production was assessed for food waste, PLA (untreated and treated), and anaerobic digested sludge (ADS) to determine conditions for enhanced methanogenic yield. Codigestion of food and PLA waste creates the potential to (1) redirect a significant fraction of waste entering the municipal waste stream, (2) reduce or offset GHG emissions from landfills, and (3) produce renewable energy.

2. Experimental Protocol

2.1. Food Waste Preparation. Food waste was collected from Clemson University’s catering service. The food waste was a mix of the following foods: string beans, lima beans, edamame, parsley leaves, potatoes, chickpeas, chicken, and pork. To form a heterogeneous mixture for this study, the food waste was prepared by mixing the whole food waste by hand, followed by chopping and grinding food waste with 500 mL of water in food processor (Black and Decker model FP1140BD, USA; 450 Watts) for 10 minutes on setting 2, which resulted in a paste. The food waste paste was blended (model Black and Decker BL1120SG, USA; 550 Watts) with 700 mL of water for 10 minutes on setting 4 to create a food waste slurry concentration of 107 g of food waste/L.

2.2. PLA Solubilization Tests. Thin-film amorphous PLA bags and crystalline PLA cups manufactured by NatureWorks LLC and produced by EarthFirst and Repurpose Compostables, respectively, were used in this study. Both PLA products report that they are 100% plant based and consist of the proprietary resin, Ingeo™, derived from PLA. The thin-film bags and cups were cut into 2 × 2 cm and weighed. Solubilization assessment of thin-film and crystalline PLA was performed in 250 mL serum bottles; the parameters of which are given in Table 1. Two bottles, one for amorphous PLA and the other for crystalline PLA, were prepared with deionized water. A 10 M NaOH solution was added to each bottle until a pH of 11.0 ± 0.5 was achieved. The control amorphous and crystalline PLA consisted of deionized water. The samples were incubated at 21 ± 1°C on a stationary bench. After 15 days, the pH of the alkaline solutions was adjusted to the range of 6.8 to 7.2 pH, which are ideal conditions for anaerobic digestion [27].

2.3. BMP Assays of Food Waste and PLA (Treated and Untreated). Lab-scale biochemical methane production (BMP) tests were used to determine the biodegradability and CH₄ production of cosubstrate (i.e., food waste, crystalline PLA, and ADS) (Figure 1). Anaerobic digested sludge (ADS) was collected from a local wastewater management plant and used as an inoculum. Negative controls (i.e., ADS in basal media without electron donor and food waste) were prepared, and the CH₄ produced by the control was subtracted from the total CH₄ on a proportional basis to compute the CH₄ formation from the food alone. Duplicate positive controls (i.e., ADS with 30 mM acetate as a readily biodegradable electron donor) were set up to ensure that the inoculum was active in methanogenesis.

Treated BMP tests were created by cutting crystalline PLA into 2 × 2 cm fragments and adding 100 mL of deionized water and 16 mL of NaOH. The treated PLA was incubated at 12.96 ± 0.005 pH for 15 days. Treated PLA was neutralized to 7.17 with 2.0 M hydrochloric acid (HCl); 0.2 L of solubilized PLA was added to treated serum bottles along with H₂O, food waste, and ADS.

The amount of PLA used for untreated experiments was determined based on the density of PLA at 1.24 g/mL and the
volumetric ratios of PLA, NaOH, water, and HCl used in treated experiments. Untreated crystalline PLA was cut into 2 × 2 cm and weighed. Each 200 mL serum bottle consisted of 0.18 L of ADS, food waste, and H2O, and 1.1 g of PLA was added to the untreated serum bottle.

Treated and untreated BMP tests were performed in triplicate; the experimental parameters are given in Table 2. The samples were stored in an incubated shaker table at 180 rpm and temperature of 37 ± 1°C and ran for 70 days.

2.4. Analyses. All analytic tests were performed in triplicate, and the following analyses were performed: total chemical oxygen demand (TCOD), semisoluble chemical oxygen demand (SSCOD), total solids (TS), volatile solids (VS), and pH. Biogas production was measured daily with a frictionless glass syringe (Perfektum, NY), and contents were analyzed using an Agilent 7890B gas chromatograph with thermal conductivity detection (GC-TCD) (Shanghai, China). Data were reported at 35°C at 1 atm. Initial and final values of BMPs, TCOD, and SSCOD were measured by filtering sample through 1.2 μm glass microfiber filter (Whatman 1822-047 GF/C) and using HACH HR COD kits (TNT 821, 1500 mg/L). HACH 2800 spectrophotometer was used to obtain colorimetric results. The standard method was used to measure TS and VS [28].

3. Results and Discussion

3.1. PLA Results. In the 15-day incubation period, both alkaline-treated amorphous and crystalline PLA reached near complete solubilization at 97% and 99%, respectively (Figure 2). In both cases, alkaline-treated amorphous and crystalline PLA had higher levels of SSCOD than untreated PLA. Pretreated crystalline PLA had a higher SSCOD of 52.6 ± 5.2 g/L than the pretreated amorphous PLA SSCOD of 10 ± 2.20 g/L. This indicates that in the solubilization process, crystalline PLA has a higher measure of electron donors than amorphous PLA. Therefore, pretreated crystalline PLA is likely to result in a higher CH4 yield than pretreated amorphous PLA, just based on the release of SSCOD.

PLA dissolving in high alkaline solution has been seen previously, and the results report that hydrolysis of aliphatic polyester cleaves the ester bonds [29, 30]. The hydrolytic degradation of crystalline PLA leads to an increased rate of mass loss in solution [31] and increased consumption of O2 due to higher PLA content [32]. The biotic degradation of PLA is desirable during disposal, and degradation can be enhanced through thermal treatment [33] making anaerobic digestion viable.

3.2. BMP Results for Chemical Characteristics of Food Waste and PLA. Codigestion of food waste and treated and untreated PLA demonstrated satisfactory results and is supported by biotransformation to CH4. The initial pH values for treated BMP test are within the ideal range of 6.8–7.2, while untreated was not. The untreated tests were performed without pH adjustments to show realistic expected outcomes at wastewater treatment plants. SSCOD was higher for treated compared to untreated, suggesting that treated test has more organic material readily available for conversion to CH4.

The final pH values for treated and untreated suggest that the digester was in good condition since organisms produce alkalinity as they consume protein-rich organic matter [34]. Final SSCOD was lower for treated (0.1 g/L) versus untreated (0.7 g/L), and treated PLA further solubilized during anaerobic digestion. There was reduction in TS (99%) and VS (99%) for treated PLA. The VS:TS and SSCOD of untreated and treated test show that stabilization was completed by day 70.

There were some limitations in measuring TS and VS of the untreated PLA. Due to the size of the PLA, the TS and VS measurement could not be performed accurately and yield a fair comparison between treated and untreated PLA after experimental runs (Table 3). Therefore, the initial and
final weights of the PLA were compared to assess the change in weight. Untreated crystalline PLA experienced 53% reduction of initial weight due to the conversion of long polymer chains into shorter chains (Figure 3). Reduction in molecular weight and loss in physical properties occur in the amorphous phase which leads to degradation [35]. Complete degradation was not observed due to crystalline PLA’s high molecular weight and resistance to bacterial growth [36]. Untreated PLA color and structure changed to opaque and unstable due to the anaerobic digestion and temperature of the BMP test, as observed by others [4].

The nutrient-rich digested solid from the treated BMP test could be potentially used for land application in the US if it meets the Environmental Protection Agency regulations for safe application [37]. It is imperative that the effects of adding solubilized alkaline-treated PLA be evaluated for land application. Since PLA is solubilized, there will be no PLA aggregates left in the digested solid. Another factor important for land-applied digestate is nutrient availability, which will be important to investigate in future work. If land application of digested solid is not an option, solubilizing PLA decreases volume and will reduce volume needed to process waste at landfills.

3.3. Cumulative CH₄ Generation during BMP Test. Figure 4 shows cumulative CH₄ production for treated and untreated BMP test. The BMP result for untreated had minimal lag time of 2 days, with rapid and highest CH₄ production until day 40, after which gas production plateaus. Between day 60 and day 70, there was a less than 1% change in CH₄ production, indicating the limitations of reducing PLA solids completely via anaerobic digestion (Figure 4). Yagi et al. [22, 38] also reported partial conversion of untreated PLA to CH₄ under mesophilic conditions.

The treated PLA BMP test produced the highest CH₄ production throughout the duration of the test (Figure 4). There was an 8% increase in CH₄ production between day 60 and day 70 for treated BMP tests. The treated PLA BMP test showed no lag phase and produced 1021 mL of cumulative CH₄ at day 70. Similarly, Benn and Zitomer [26] reported reduced lag time for pretreated PLA compared to untreated PLA. The little to no lag time was likely due to the inoculum and pretreatment [33]. The immediate gas production in the positive control confirmed active seed sludge (not shown). The treated PLA BMP test demonstrates three very distinct phases in Figure 4. When multiple substrates are present, degradation will not occur at the same rate for each substrate [39], hence showing variation in CH₄ production. Treated BMP experienced a biphasic CH₄ production process at days 0–17, 19–47, and 52–70. Untreated BMP also experienced biphasic CH₄ production process at days 0–4, 6–10, and 17–70 and produced 756 mL of CH₄ at day 70. Degradation of PLA occurs in multistep with different microbial mechanism throughout the process [40]. Result suggests that CH₄ yields are dependent on the type of microbes that are present during the reaction.

The remaining untreated solubilized PLA would be landfilled. Kolstad et al. [41] reported that microorganisms that live in anaerobic conditions are unable to degrade the high molecular weight of PLA. Therefore, it is assumed that the residual untreated PLA from anaerobic digestion process will not continue to emit biogas when landfilled and will offset emission via carbon sequestration [42].
4. Conclusions and Future Recommendations

The main objective of this study was to determine whether pretreating PLA could increase CH$_4$ production, enhance food waste anaerobic digestion, and enhance PLA destruction in batch BMP assays. The results of this study show that alkaline treatment solubilizes PLA. After a 15-day incubation period under alkaline pretreatment, near complete solubilization was achieved for both amorphous (97%) and crystalline (99%) PLA. This study also showed that crystalline PLA has more organic nutrients. Pretreated crystalline PLA had a high organic content and SSCOD, making it a likely candidate that could produce increased methanogenic yield during anaerobic digestion. In addition, untreated PLA experiences weight reduction of 54% after the BMP test. The structure of the PLA was unstable, indicating that degradation had occurred and that anaerobic digestion assists in solid destruction and CH$_4$ production. In addition, untreated crystalline PLA produced less than 1% of the total gas production on day 70, indicating that gas production is coming to an end and that anaerobic digestion is not capable of completely reducing PLA solids without pretreatment.

This study showed that alkaline-treated crystalline PLA produced the most CH$_4$, compared to untreated PLA. After day 48, treated BMP test began to produce more CH$_4$ than untreated BMP test. Treated PLA and untreated produced 1021 and 756 mL of CH$_4$, respectively, within 70 days and graphically displayed a biphasic curve, highlighting the complexity of multiple substrates in the test. Overall, alkaline pretreatment of PLA may enable it to be codigested with food waste in anaerobic digestion systems. In addition, alkaline pretreatment of PLA may enhance the ability of these AD systems to produce CH$_4$.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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