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Enhancing the solid-state anaerobic digestion of fallen leaves through simultaneous alkaline treatment

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A B S T R A C T

Previous studies have shown that alkali pretreatment prior to anaerobic digestion (AD) can increase the digestibility of lignocellulosic biomass and methane yield. In order to simplify the process and reduce the capital cost, simultaneous alkali treatment and anaerobic digestion was evaluated for methane production from fallen leaves. The highest methane yield of 82 L/kg volatile solids (VS) was obtained at NaOH loading of 3.5% and substrate-to-inoculum (S/I) ratio of 4.1. The greatest enhancement in methane yield was achieved at S/I ratio of 6.2 with NaOH loading of 3.5% which was 24-fold higher than that of the control (without NaOH addition). Reactors at S/I ratio of 8.2 resulted in failure of the AD process. In addition, increasing the total solid (TS) content from 20% to 26% reduced biogas yield by 35% at S/I ratio of 6.2 and NaOH loading of 3.5%. Cellulose and hemicellulose degradation and methane yields are highly related.

1. Introduction

Due to concerns about the sustainability of petroleum supplies, the research community is evaluating alternative resources for fuels and energy production. Lignocellulosic biomass, such as energy crops, agricultural residue and municipal solid waste, is a promising renewable resource because it is widely available and can be converted to various forms of fuel and energy. Biogas, which contains about 60–70% methane, can be obtained from the anaerobic digestion (AD) of organic materials. However, due to the recalcitrant structure and composition of lignocellulosic biomass, such as lignin that interlinks cellulose and hemicellulose layers, the conversion efficiency is limited (Noike et al., 1985). Hydrolysis of lignocellulosic biomass is rate-limiting because of the low cellulolytic activity and low specific growth rate of cellulolytic microbes in anaerobic digesters (Lu et al., 2007). Therefore, pretreatment is often required to overcome biomass recalcitrance in order to facilitate the access of hydrolytic enzymes to degradable carbohydrates to improve sugar release and biogas production.

AD efficiency of lignocellulosic biomass can be improved by applying several pretreatment methods including steam, acid, alkaline, and biological treatments (Penaud et al., 1999; Frigon et al., 2011). Alkaline pretreatment is often favored for anaerobic digestion and sodium hydroxide (NaOH) was found to be one of the most effective alkalis for improving biogas production (Taherzadeh and Karimi, 2008). Alkaline pretreatment greatly improves the digestibility of lignocellulosic biomass through lignin solubilization, removal of hemicellulose, disruption of interlinking ester bonds, and neutralization of structural carboxylic acids (Mosier et al., 2005). In addition, alkalis help to prevent a drop of pH during the subsequent acidogenesis process and increase the efficiency of methanogenesis (Hashimoto, 1986; Pavlostathis and Gossett, 1985). However, alkaline pretreatment performed at low moisture and ambient temperature is particularly attractive. In a study conducted by Pang et al. (2008), a 48.5% increase in biogas was achieved from corn stover pretreated with 6% NaOH at 80% moisture content for 3 weeks at ambient temperature. In a parallel study, a 72.9% increase in total biogas yield was achieved with lower NaOH loading (2%) and shorter pretreatment time (3 days), when pretreatment moisture content was increased to 88% (Zheng et al., 2009). Recently, Zhu et al. (2010) reported that anaerobic digestion of alkaline pretreated corn stover produced 37% more biogas compared with untreated corn stover. The pretreatment was carried out with 5% NaOH at 53% moisture content for 1 day at ambient temperature. These studies indicate that alkaline pretreatment of lignocellulosic biomass is feasible with lower moisture content. However, pretreatment effectiveness is greatly affected by moisture content, NaOH loading, and pretreatment time.

Solid-state anaerobic digestion (SS-AD) refers to an AD process operated at total solids (TS) content of 20–55%. It has been used to digest the organic fraction of municipal solid waste in Europe (Bolzonella et al., 2003). SS-AD is well suited to handle

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lignocellulosic biomass and problems encountered in liquid AD, such as floating and stratification of solids, can be avoided in SS-AD (Chanakya et al., 1993). Compared to liquid AD (TS less than 15%), SS-AD has advantages such as less energy needed for heating, finished materials with higher TS content (20%), and no moving parts in the digester (Li et al., 2011). However, it requires large amounts of inoculum, longer retention time, and nitrogen supplementation when lignocellulosic biomass is used (Jewell et al., 1993; Li et al., 2011). Furthermore, pretreatment is generally required for lignocellulosic biomass to improve the efficacy of SS-AD (Li et al., 2011). Pretreatment methods, such as alkaline treatment prior to the AD process, have previously been established to increase the digestibility of lignocellulosic biomass and methane yield in SS-AD systems (Zhu et al., 2010). However, to our knowledge, no successful results have been reported on the simultaneous alkaline treatment and SS-AD of lignocellulosic biomass.

Simultaneous alkaline treatment and digestion offers several benefits compared with alkaline pretreatment followed by digestion. It can simplify the operation by eliminating a separate reactor required for alkaline pretreatment and reducing material handling. Additionally, the increase in alkalinity may help prevent a drop in pH during acidogenesis, which can create a more stable environment for the methanogenic bacteria (Pavlostathis and Gossett, 1985). However, excessive NaOH loading may inhibit anaerobic digestion either due to high pH or sodium ion toxicity (Rinzema et al., 1988). A recent study by Zhu et al. (2010) tested simultaneous NaOH treatment and SS-AD of corn stover at a C/N ratio of 18 and NaOH loading of 5%. However, no significant improvement in biogas production was observed compared with untreated corn stover. Appropriate NaOH loading needs to be established such that it is sufficient for delignification while not inhibiting the AD process. Furthermore, as the amount and activity of inoculum greatly affect methane yield and retention time for SS-AD (Raposo et al., 2006; Li et al., 2010), NaOH loading needs to be adjusted with substrate-to-inoculum (S/I) ratio during simultaneous alkaline treatment and SS-AD. Fallen leaves (leaf litter) are potentially a low cost feedstock for SS-AD because a tipping fee is normally charged for collection and hauling of such wastes from residential or commercial areas. The objectives of this study were to determine the effect of NaOH loading and S/I ratio on daily and cumulative methane production during SS-AD of leaves. Changes in total volatile fatty acids (VFA), alkalinity, and pH were measured and correlated to methane yield. In addition, degradation of cellulose and hemicellulose during SS-AD was investigated and compared to methane yield to verify the effect of NaOH treatment.

2. Methods

2.1. Feedstock and inoculum

Fallen leaves were collected from the campus of the Ohio Agricultural Research and Development Center (OARDC) in Wooster, OH, USA (40°48′33″N, 81°56′14″W) in October 2009. Leaves were dried at 40 °C for 72 h in a convection oven (Shel Lab FX28-2, Sheldon Manufacturing, Cornelius, OR, USA) to achieve a moisture content of less than 10% before storing in an air tight container. Prior to use, oven-dried leaves were ground through a 9 mm sieve with a grinder (Mighty Mac, MacKissic Inc., Parker Ford, PA, USA). Effluent from a mesophilic liquid anaerobic digester, which was fed food processing waste and operated by *quasar energy group* (Wooster, OH, USA), was used as the inoculum for SS-AD. Due to the low TS content, the effluent was dewatered by centrifugation. TS content increased from 3.9% to 6.1% after dewatering. Characteristics of leaves and inoculum are shown in Table 1. Structural carbohydrate and lignin contents of leaves are based on dry matter, whereas the rest of the values are based on total weight.

Table 1
Characteristics of leaves and inoculum.

Parameter	Leaves	Inoculum
Total solids (%)	91.6 ± 0.0	6.2 ± 0.0
Volatile solids (%)	85.1 ± 0.0	4.0 ± 0.0
Total carbon (%)	45.4 ± 0.2	2.7 ± 0.0
Total nitrogen (%)	0.9 ± 0.0	0.5 ± 0.0
Carbon to nitrogen (C/N) ratio	51.9 ± 1.8	5.5 ± 0.2
pH	6.8 ± 0.1	8.0 ± 0.0
Alkalinity (g $CaCO_3$/kg)	3.5 ± 0.0	8.9 ± 0.1
Total volatile fatty acid (g/kg)	1.5 ± 0.1	3.3 ± 0.1
Water soluble extractives (%)	25.7 ± 0.4	N/D
Ethanol soluble extractives (%)	7.3 ± 0.3	N/D
Cellulose (%)	11.1 ± 0.4	N/D
Hemicellulose (%)	11.5 ± 0.1	N/D
Lignin (%)	22.7 ± 0.6	N/D

ND, not determined.

2.2. Solid-state anaerobic digestion with simultaneous NaOH treatment

Oven-dried and ground leaves were mixed thoroughly with an appropriate amount of inoculum effluent and NaOH pellets (predissolved in effluent) to achieve three S/I ratios (on VS basis) at 4.1, 6.2, and 8.2, with NaOH concentrations of 2%, 3.5%, and 5%(on basis of dried leaves) for each S/I ratio (a total of 9 conditions). Reactors without any NaOH addition were run in parallel at each S/I ratio as controls. The C/N ratios were 18, 22, and 25, at S/I ratios of 4.1, 6.2, and 8.2, respectively. Deionized water was then added, when necessary, to obtain a TS content of 20%. Mixed materials were loaded into 1-L glass reactors. Reactors were sealed with a rubber stopper, and placed in a walk-in incubator for 30 days at a constant temperature of 37 °C and without agitation. Biogas generated was collected using a 5-L gas bag attached to the outlet of the reactor (CEL Scientific Tedlar gas bag, Santa Fe Springs, CA, USA) and biogas composition and volume were measured daily for the first 15 days and every 2 days afterwards. Duplicate reactors were run at each condition.

2.3. Analytical methods

The extractive content of leaves and materials taken from the reactor at the beginning and end of the AD process was measured according to the NREL Laboratory Analytical Procedure (Sluiter et al., 2008). Extractive-free solid fractions were further fractionated using a two-step acid hydrolysis method based on NREL Laboratory Analytical Procedure (Sluiter et al., 2010). Monomeric sugars (cellobiose, glucose, xylose, galactose, arabinose, and mannose) in the acid hydrolysate were measured by HPLC (Shimadzu LC-20AB, Columbia, MD, USA) equipped with a Biorad Aminex HPX-87P column and a refractive index detector (RID). Deionized water at a flow rate of 0.6 ml/min was used as the mobile phase. The temperatures of the column and detector were maintained at 80 °C and 55 °C, respectively.

The TS and VS contents of leaves, inoculum, and digestate were measured at the beginning and end of the AD process according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). Total carbon and nitrogen contents were determined by an elemental analyzer (Elementar Vario Max CNS, Elementar Americas, Mt. Laurel, NJ, USA). Total volatile fatty acids (VFA) and alkalinity were measured using a 2-step titration method (McGhee, 1968). Samples for pH, total VFA, and alkalinity measurement were prepared by diluting a 5-g sample with 50 ml of deionized water and subsequently filtering it using cheese cloth. The filtrate was then analyzed using an auto-titrator (Mettler Toledo, DL22 Food & Beverage Analyzer, Columbus, OH, USA).