Energy Conversion and Management 164 (2018) 36–41

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Improved methane production of corn straw by the stimulation of calcium peroxide

Shan-Fei Fu[a,b,c], Kai-Qiang Chen[a,b], Wen-Xin Sun[a,b], Rong Zhu[a,b,c], Yi Zheng[d], Hua Zou[a,b,c,*]

[a] School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China
[b] Jiangsu Key Laboratory of Anaerobic Biotechnology, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China
[c] Jiangsu Collaborative Innovation Center of Technology and Material of Water Treatment, Suzhou 215009, PR China
[d] Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA

ARTICLE INFO

Keywords:
Anaerobic digestion
Calcium peroxide
Hydrolysis
Micro-aeration
Microbial community structure

ABSTRACT

This research focused on the effect of calcium peroxide (CaO_2) addition on anaerobic digestion (AD) of corn straw. It was found that the CaO_2 dose of 0.032–0.256 $g \cdot g^{-1}$ TVS (total VS of substrate and inoculum) had positive effect on the AD of corn straw by improving methane yield and content in biogas. Maximum methane yield was achieved at the CaO_2 dose of 0.032 $g \cdot g^{-1}$ TVS, which was 241.6 $mL \cdot g^{-1}$ VS_S (VS of substrate) and 11% higher than that of the control. Methane content in biogas also increased according to the in situ immobilization of CO_2 by $Ca(OH)_2$ that produced via the reaction of CaO_2 with water (XRD analysis results). Microbial community structure was significantly affected by CaO_2 addition. The variation of bacterial community structure led to higher hydrolysis rate, and the variation of archaea community structure ensured the proceeding of methanogenesis process. The use of CaO_2 could be a cost-effective method to improve methane production of corn straw because it avoids harsh condition and high cost (e.g., chemical and energy inputs) associated with conventional chemical treatment techniques. The digestate from the AD with the addition of CaO_2 can contain high $CaCO_3$ content, making it a potential soil amendment for acidic soil.

1. Introduction

Using cellulosic biomass as renewable resource to produce bioenergy has attracted global interests during the past decades [1,2]. Anaerobic digestion (AD) technology has been widely used for organic waste disposal and energy production [3]. In AD process, the cellulosic biomass can be converted into biogas, a mixture of methane, carbon dioxide and small amounts of other gases [4,5]. Biogas typically has a calorific value of 22,000–25,000 $kJ \cdot m^{-3}$ [6], therefore it is considered as one of the major renewable energy source. In general, AD process can be divided into four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [7]. Cellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, and they bind with each other tightly by non-covalent forces and covalent cross-linkage [8]. Due to the complex components and strong structure of cellulosic biomass, the hydrolysis was demonstrated to be the rate-limiting step of AD [9,10], resulting in some common issues such as long retention time and low efficiency. Substrate pretreatment is the most studied method to improve the hydrolysis rate [7,10], including chemical, thermal, mechanical, and biological pretreatment as well as their combination. During pretreatment, the structure of substrate is partly destroyed. Which makes the substrate more accessible to microorganisms and extracellular hydrolytic enzymes present in AD. However, the pretreatment process is usually conducted in a separate reactor with the input of additional energy and/or chemicals, which leads to increased cost. Especially, the chemical pretreatment might also cause environmental problems. As a result, an economically feasible and environmentally friendly method should be developed to improve the hydrolysis rate and the overall AD efficiency of cellulosic substrate.

Recent research has shown the hydrolysis stage of AD could be accelerated under microaerobic condition [11,12]. In addition, microaerobic treatment (microaerobic pretreatment or introduction of limited oxygen into the AD system) has been successfully applied to improve the methane yield in several studies [13–16]. The microaerobic condition was considered to support the growth of aerobic and/or facultative microorganisms, which stimulated the secretion of extracellular hydrolytic enzymes (e.g., cellulose and protease) [14]. The production of more such enzymes could improve the hydrolysis of cellulosic substrate and finally increase the AD efficiency. Compared with other methods, the micro-aeration in AD by using oxygen only needs limited amount of oxygen or air, which is simpler, cheaper and more attractive [15].

* Corresponding author at: School of Environment and Civil Engineering, Jiangnan University, Wuxi, Jiangsu Province 214122, PR China.
E-mail addresses: fusf@jiangnan.edu.cn (S.-F. Fu), zouhua@jiangnan.edu.cn (H. Zou).

https://doi.org/10.1016/j.enconman.2018.02.070
Received 10 January 2018; Received in revised form 17 February 2018; Accepted 17 February 2018

Calcium peroxide (CaO_2), a commonly used oxidant has been extensively applied in agriculture, aquiculture, environmental restoration, and pharmaceuticals [17]. It can react with water to produce calcium hydroxide [$Ca(OH)_2$] and oxygen [17]. Due to this property, CaO_2 could be used as an alternative additive to provide oxygen for AD process and create a microaerobic condition to enhance the hydrolysis of substrate. Previous studies have demonstrated CaO_2 was an efficient additive for contaminant (e.g., phenolic endocrine disrupting compounds and polychlorinated biphenyls-containing electrical insulating oil) removal with the action of reactive oxygen species (ROS) derived from CaO_2 [17,18]. In the AD of active sludge, CaO_2 was used as an efficient additive to improve the activities of both hydrolytic enzymes and acid-forming enzymes, and therefore enhance the hydrolysis and acidification of active sludge [19]. In addition, $Ca(OH)_2$ produced via the reaction of CaO_2 with water could immobilize CO_2 in situ ($Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$), and therefore improve the methane content in biogas. Also, the produced $Ca(OH)_2$ or $CaCO_3$ could contribute additional alkalinity to the AD system, and therefore benefit the production of soluble chemical oxygen demand (SCOD) and volatile fatty acids (VFs) [20]. However, the $^{\cdot}OH$ generation from CaO_2 was found to have significant inhibition on methanogens [21]. In the study of Li et al. [19], the production of methane was inhibited with the CaO_2 dose in the range of 0.05–0.3 $g{\cdot}g^{-1}$ VSS (volatile suspended solid). Therefore, the dose of CaO_2 needs to be well controlled when it is used as an additive to enhance the AD efficiency. A critical dose should be determined between the stimulation effect on hydrolysis (due to O_2 and H_2O_2 generation from CaO_2) and the inhibition effect (arising from $^{\cdot}OH$ generation from CaO_2) on methanogenesis. In addition, the critical dose may vary between cellulosic feedstocks.

As a result, this study explored the possibility of using CaO_2 as an additive to increase the AD efficiency of corn straw. The effect of CaO_2 addition on the methane yield, methane concentration and SCOD (soluble chemical oxygen demand) production were analyzed. The dynamics of microbial community structure during the AD process were also investigated. The implementation of this study would provide a cost-effective solution to improve the AD performance on cellulosic feedstocks.

2. Materials and methods

2.1. Substrate and inoculum

Corn straw was collected from the field of PingDu, Qingdao, Shandong province, China. Before AD, the corn straw was air-dried to moisture content of 8% and chopped to particle size of about 0.5 cm. The inoculum used in this study was obtained from a mesophilic AD (at 35 °C) plant which uses cow dung and corn straw as substrates with hydraulic retention time of 35 days. Before used, the inoculum was filtered through a sieve with the opening of ten mesh. The characteristics of substrate and inoculum were shown in Table 1.

Table 1
Characteristics of substrate and inoculum.

Characteristics	Substrate (corn straw)	Inoculum
Moisture content (%)	8.5 ± 0.3	97.9 ± 0.1
Total solid (TS, %)	91.5 ± 0.3	2.1 ± 0.1
Volatile solid (VS, % of TS)	79.4 ± 0.4	71.3 ± 0.3
C (% of TS)	36.7 ± 1.6	–
N (% of TS)	1.3 ± 0.4	–
H (% of TS)	4.9 ± 0.4	–
C/N (% of TS)	28.2 ± 1.2	–

Note: "–" means this parameter was not tested.

2.2. Batch AD test

Mesophilic (37 °C) batch AD of corn straw was conducted in quadruplicate for a total fermentation time of 43 days. To start AD, 5.33 g (TS) corn straw, 2.67 g (TS) inoculum and different amount of CaO_2 were mixed in 300-mL glass bottles. The doses of CaO_2 were 0 (control), 0.032, 0.064, 0.128, and 0.256 $g{\cdot}g^{-1}$ TVS (total VS of substrate and inoculum), respectively (coded as C0, C1, C2, C3, and C4). A blank group containing inoculum only (without substrate or CaO_2) was also carried out to test the biogas production from inoculum. The working volumes for all AD batches were adjusted to 200 mL by adding nutrient solution as described in Angelidaki et al. [22]. All the bottles were flushed with N_2 for 5 min to remove the oxygen. After sealed with rubber stoppers, all the bottles were incubated in a shaking water bath at 37 °C with the shaking speed of 120 rpm.

2.3. Analysis of the fermentation residue by X-ray diffraction (XRD)

After AD, the digestates were collected and dried at 105 °C for 8 h followed by milling. The digestate powders were then subjected to $CaCO_3$ analysis with a wide angle X-ray diffraction (Bruker D8 Advance, Germany) at 40 kV and 40 mA in the scanning angle of 5–80° (2θ) at a scanning speed of 1.0°/min.

2.4. Analysis of AD performance

Biogas production was monitored in volume with water displacement method, and the methane content in biogas was analyzed with a gas chromatograph (GC, SP 6890, Shandong Lunan Inc., China) using argon as carrier gas. The GC was equipped with a Porapak Q stainless steel analytical column (180 cm long and 3 mm OD) and a thermal conductivity detector. The analysis temperatures of the injector, detector and oven were set at 50, 100 and 80 °C, respectively. Spectrophotometric method was used for SCOD measurement [23]. Prior to the SCOD analysis, AD effluent samples were centrifuged for 5 min at 10,000 rpm and the supernatants were filtered through 0.45 μm glass microfiber paper [23]. TS and VS of the substrate and inoculum were measured by following the standard method [24]. The element contents of corn straw were quantified with an elemental analyzer (Vario EL III elemental analyzer).

2.5. Analysis of the microbial community structure

During AD process, aliquots of 8 mL effluent were collected from all the groups (C0-C4) at the 3rd, 12th and 40th day of AD. As C1 showed the highest methane production, it was selected as an example from the treatment groups (C1-C4) to compare with C0 for analyzing the effect of CaO_2 addition on the microbial community structure. The collected effluent samples were stored in a -80 °C freezer until used. In this study, genomic DNA was extracted using the E.Z.N.A.® DNA Kit (Omega Biotek, Norcross, GA, U.S.) according to manufacturer's instruction. One percent agarose gel electrophoresis and spectrophotometry (optical density at 260 nm/280 nm ratio) were used to check the quality of extracted DNA. The V3–V4 hypervariable regions of the 16S rRNA gene were subjected to high-throughput sequencing which was done by the Beijing Allwegene Tech, Ltd (Beijing, China) using the Illumina Miseq PE300 sequencing platform (Illumina, Inc., CA, USA). The V3–V4 regions of the bacterial 16S rRNA gene were amplified by using the universal forward primer 338F (5′-ACTCCTACGGGAGGCAGCAG-3) and reverse primer 806R (5′-GACTACHVGGGTWTCTAAT-3′).

These primers contained a set of 8-nucleotide barcodes sequence unique to each sample. The PCR program included steps of 95 °C for 5 min, 25 cycles at 95 °C for 30 s, 55 °C for 30 s, and 72 °C for 30 s as well as a final extension of 72 °C for 10 min. The PCR reactions were performed in triplicate in 25 μL mixtures containing 2.5 μL of 10X Pyrobest Buffer, 2 μL of 2.5 mM dNTPs, 1 μL of each primer (10 μM), 0.4