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Effect of pretreatment and total solid content on thermophilic dry anaerobic digestion of *Spartina alterniflora*

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HIGHLIGHTS

- Biogas production rate but not biogas yield for thermo-lime pretreated sample was improved.
- Hot-water pretreated sample has higher biogas yield and *k* value than thermo-lime.
- High TS content led to metabolite accumulation due to mass transfer limitations.
- A decrease in TS content from 20.8% to 17.9% increased 29.6% of biogas yield.

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ABSTRACT

The effect of pretreatment [thermo-lime with 0.09 g $Ca(OH)_2$/g total solid (TS) of biomass at 120 °C for 4 h and hot water at 120 °C for 4 h] and TS content on the thermophilic anaerobic digestion of *Spartina alterniflora* was assessed in six batch reactors and three leaching bed reactors. The componential change in solid biomass was analyzed to understand the changes in biogas production. The biogas production rate but not the biogas yield of the sample pretreated with thermo-lime was improved compared with that of raw and hot-water pretreated samples. The biogas yield (206.8 mL/g TS) and production rate constant (*k*; 0.052 d^{-1}) of the hot–water pretreated sample were obviously higher than those of the thermo-lime-pretreated sample (168.3 mL/g TS and 0.028 d^{-1}) because more biodegradable matter were preserved in the former sample. Dry anaerobic digestion at high TS content caused a high componential reduction. However, the digestion also led to organic metabolite accumulation because of mass transfer limitations, which decreased biogas yield and production rate. A decrease in TS content from 20.8% to 17.9% increased 29.6% of biogas yield and 67.9% of *k* values. Process stability was enhanced with decreasing TS content.

1. Introduction

The smooth cordgrass (SC) *Spartina alterniflora* was introduced in China for wetland restoration in 1979 [1]. SC is effective in protecting coastal banks, accelerating land reclamation, reducing greenhouse emissions, and decomposing pollutants [2]. SC covered an area of at least 1120 km^2 in China in 2000 because of its rapid growth velocity, which led to serious environmental and ecological problems [1,2]. Thus, the effective utilization of this enormous resource for bioenergy production has attracted increasing attention. SC can be converted to biogas through anaerobic digestion. Such process generates three products: biogas (a mixture of methane and carbon dioxide), liquid digestate, and fiber digestate. Biogas may be used as energy resource, the liquid digestate as a liquid fertilizer, and the fiber residues as a nutrient-rich soil conditioner [3]. Yang et al. [4] obtained a biogas yield of 358 L/kg volatile solids (VSs) with 45% biodegradation efficiency after 60 d of wet anaerobic digestion of SC. Liang et al. [5] obtained a biogas yield of 283.9 L/kg VS after 60 d of thermophilic dry anaerobic digestion. The methane yield of SC can be increased from 7.09% to 44.26% through anaerobic co-digestion with cow feces [6].

However, hydrolysis reaction is the rate-limiting step in the anaerobic digestion of lignocelluloses. This limitation is due to the complex structure and composition of lignocelluloses, which are affected by cellulose crystallinity, polymerization degree, available surface area, and lignin content [7]. Pretreatment prior to utilization is a simple and effective method of improving the hydrolysis rate and efficiency of lignocelluloses. Generally, pretreatment methods are classified into physical (i.e. milling, liquid

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hot water and steam), chemical (alkaline, acidic and oxidative) and biological (i.e. commercial enzymes or fungi) pretreatments [7,8]. Thermo-lime pretreatment is effective in improving the digestibility of lignocellulosic biomass [8,9]. Lime pretreatment completely removes acetyl groups and approximately 50% of lignin content, thereby improving carbohydrate degradation efficiency and rate [10]. Pretreatment with 0.1 g of $Ca(OH)_2$/g dry biomass for 2 h at 100 °C or 120 °C improves the 3 d total sugar yield of switchgrass by fourfold [9]. Lime pretreatment at 120 °C for 4 h without oxygen increases the 3 d digestibility of corn stover by nine times [11]. Liang et al. [12] found that lime pretreatment increases the methane yield of SC by 122–180%.

Compared with thermo-lime pretreatment, hot water pretreatment has lower operation costs because no chemicals are added [7]. Water under high pressure penetrates the biomass and removes most hemicellulose and part of lignin during hot water pretreatment. By contrast, acid-catalyzed hydrolysis and solubilization of hemicellulose occur at high temperatures because of the action of acid matter released from hemicellulose [13,14]. However, most of these studies aimed to improve the efficiency of ethanol production; only a few studies investigated biogas production in pretreated biomass [12,13,15]. In the present study, the biogas production of SC pretreated with hot water and thermo-lime was compared by dry anaerobic digestion.

Dry anaerobic digestion is characterized by total solid (TS) content higher than 15% [16]. This process has attracted increasing attention because of its lower construction and operation costs compared with wet digestion [17,18]. TS content significantly affects biogas production efficiency and rate. A previous study evaluated the effect of different TS contents (10–35%) on anaerobic digestion and revealed that methane yield and production rate decrease with increasing TS content [17]. Radwan et al. [18] reported that the optimum TS content for biogas production of cotton stalks is 21%. In the present study, the performance of anaerobic digestion for SC pretreated with thermo-lime was compared for TS contents of 17% and 20%.

The present work evaluated the effects of thermo-lime and hot water pretreatments on the anaerobic digestion of SC. Biogas production, pH change, total organic carbon (TOC) content, and volatile fatty acid (VFA) content were investigated to compare anaerobic digestion of SC under different conditions. The effect of 17% and 20% TS contents on the anaerobic digestion of SC pretreated by thermo-lime was also investigated. The change in chemical composition after pretreatment and anaerobic digestion was examined to clarify the effect of different conditions on biogas production.

2. Materials and methods

2.1. SC and anaerobic seed cultures

SC was collected from Dafeng county, Jiangsu province, China in September 2012. The sample was chopped into 3–4 cm pieces using paper shears after air drying, placed in a sealed bag, and stored in the dark at ambient temperature for less than a month. The initial content of cellulose was 33.14% of the TS, hemicellulose 35.37% of the TS and lignin 9.64% of the TS, in addition the masses concentration of the main elements were carbon (C) 42.08% of the TS, hydrogen (H) 6.06% of the TS, nitrogen (N) 0.35% of the TS, and oxygen (O) 51.53% of the TS. The TS content of SC was 89.3% and VS content was 93.8% of the TS.

Anaerobic culture was obtained from previous digestion liquor in the laboratory [5]. The thermophilic anaerobic cultures were firstly kept under endogenous anaerobic conditions at 55 °C for about a week to reduce non-specific biogas generation [15]. And then the culture was filtered through a screen with a mesh size of 2-mm and then concentrated by settling before being used as the inoculums. The characteristics of anaerobic cultures was 4.9 g TS/100 g and 47.2 gVS/100 g TS.

2.2. Pretreatment methods and digesting sample preparation

SC was pretreated prior to anaerobic digestion. For thermo-lime pretreatment, SC, lime (0.09 g $Ca(OH)_2$/g TS of SC), and water (loading = 9.0 mL/g TS of SC) was first mixed in a stainless steel bucket, and then this bucket containing mixture was placed in an autoclave (Jiangyin Binjiang LS-75HD; maximum pressure = 0.22 MPa) at 120 °C for 4 h. Pretreatment conditions such as water loading, time, temperature and lime loading were selected according to previous reports [9,11]. For hot-water pretreatment, the same method as thermo-lime pretreatment was used except that no lime was added.

When the pretreatment time had elapsed, the stainless steel bucket containing pretreated liquid and solid samples was taken out from the autoclave after pressure decrease. Pretreated solid sample was prepared for anaerobic digestion for biogas production and whereas pretreated liquid sample was not subjected to anaerobic digestion. Pretreated solid biomass was first washed cleanly with tap water, and then dried at 45 °C for 72 h and a low dry temperature was selected for reducing volatile matter loss, and cooled to room temperature, and finally placed into a sealed bag, and stored in the dark at ambient temperature for a week before anaerobic digestion.

2.3. Experimental design of dry anaerobic digestion

Anaerobic digestion experiments were conducted in three identical leaching bed reactors (LBRs) and six batch reactors (1×10^{-3} m^3 volume of jar). The reactor temperature was set at 55 ± 1 °C because thermophilic anaerobic digestion has high gas production efficiency and rate, thereby needing short retention time for waste stabilization [19,20]. The biogas production for untreated SC and pretreated solid samples was compared in batch reactors. In order to investigate the effect of leachate recycle and TS contents on process stability and biogas production, three LBRs were used to anaerobic digestion of thermo-lime and hot-water pretreated solid samples. The LBR used has a height of 590 mm, an inner diameter of 140 mm, and a working volume of 6.0 L. A more detailed description of the LBR components is provided elsewhere [5]. The experimental design for the LBRs and batch reactors is shown in Table 1.

For the LBR experiments, solid sample of pretreated SC, distilled water, and seed cultures were placed in plastic buckets. The feedstock mixture was then placed in the LBRs after thorough mixing. Finally, dry digestion was performed at 55 ± 1 °C for 74 d. Anaerobic digestion of hot water- and thermo-lime-pretreated solid samples was conducted with the same TS content in LBR1 and LBR2, respectively. LBR3 was used to investigate the effect of reduced TS content in the reactor on biogas production. The predetermined TS contents of LBR1, LBR2, and LBR3 were 19.9%, 19.9%, and 15.4%, respectively. The actual TS contents of LBR1, LBR2, and LBR3 were 21.5%, 20.8%, and 17.9%, respectively, after 1 d of leachate production. According to literature [21], 450 mL of leachate was recycled to the top to spray the bed twice daily at a recycle rate of 900 mL/d during dry digestion. Approximately 10 mL of leachate sample was taken twice a week before leachate recirculation. The leachate was added with distilled water until the 450 mL capacity of leachate recirculation was reached. Biogas production was recorded daily by a wet tip gas meter and reported in L/d at 0 °C and 1.013×10^5 Pa. At the end of dry anaerobic digestion, all digested solid biomass was first taken out from LBR, and then washed the