



Hydrolysis and acidification of agricultural waste in a non-airtight system: Effect of solid content, temperature, and mixing mode



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ABSTRACT

A two-phase digestion system for treating agricultural waste is beneficial for methane production. This study explored the effect of solid content, temperature, and mixing mode on the process of hydrolysis and acidification using rice straw and cow dung launched in non-airtight acidogenic system. The results showed that the substrate could be hydrolyzed efficiently in the initial stage, the hydrolysis coefficient (k) of maximum cellulose and hemicellulose can be increased by 217.9% and 290.5%, respectively, compared with those of middle and last stages. High solid content played a leading role in promoting hydrolysis, resulted in hydrolysate content (sCOD) that was significantly higher than in treatments with low solid content ($P < 0.01$), and led to organic acids accumulation up to 5.8 and 6.7 g/L at mesophilic and thermophilic temperatures. Thermophilic temperature stimulated the hydrolysis and acidification of low solid content ($P < 0.05$), and improved organic acid accumulation of high solid content only during the middle stage ($P < 0.01$). Mixing mode was not a major factor, but increasing the mixing time was necessary for organic acid accumulation during the last stage ($P < 0.05$). In addition, the study comprehensively analyzed a series of corresponding relationships among each operating parameter during the whole treatment process using canonical correspondence analysis.

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1. Introduction

Agricultural waste is becoming a troubling pollution in China. It is composed primarily of straw and livestock manure. These substrates are rich in lignocellulose, which is resistant to biodegradation by microbial enzymes due to the combination of cellulose, hemicellulose, and lignin (Ward et al., 2008). If these wastes are used for anaerobic digestion (AD), $4.23 \times 10^{11} \text{ m}^3$ of biogas will be produced. Unfortunately, the amount of straw consumed is 0.5% of the total resources for biogas production (Li et al., 2016), and livestock manure is a challenging substrate with which to achieve efficient biogas production (Ye et al., 2013). Co-digestion is a traditional technology that could make up the nutrient balance to overcome the low efficiency of mono-feedstock and instability of AD (Yue et al., 2013; Ye et al., 2013). The average volume of biogas routinely produced from straw-manure substrate in China is $0.8\text{--}1.0 \text{ m}^3/\text{m}^3 \text{ d}$, which is 33–50% of that produced in developed countries of the EU. Therefore, methane production from agricul-

ture waste has a great capacity for improvement, which could be achieved by optimizing hydrolysis and acidification under different operating conditions.

Pretreatment of agricultural waste using hydrolysis and acidification primarily achieves substrate degradation and organic acid production using natural microbes in feedstock. The ultimate aim is to provide favorable feedstock for methanogens. Hydrolysis and acidification pretreatment is often performed in a separate reactor by creating favorable conditions for acid-producing bacteria. Previous studies reported that hydrolysis and acidification increased the methane yield by 7–15.8% when the organic loading rate of fruit, vegetable, and food wastes was $>2 \text{ g volatile solid (VS)/L}\cdot\text{d}$ (Shen et al., 2013). Chen et al. (2015) studied the effect and control of organic acid composition on methane production by acidification with rice straw and food wastes; the maximum acidification efficiency and methane yield reached 36% and $535 \text{ mL}\cdot\text{CH}_4/\text{g}\cdot\text{VS}$, respectively. During two-phase anaerobic digestion, the methane yield usually increased by 20–60% under conditions that produced more organic acids (Schievano et al., 2014). Accumulation of greater organic acid contents was considered as the most important measure to stimulate efficient methane production (Demirel and Yenigün, 2002). The feedstocks in these

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studies were based primarily on rich soluble substrates, whereas the process of hydrolysis and acidification of agricultural wastes that are enriched in lignocellulose has not been completely elucidated. Other studies reported that homogenization was necessary for pretreatment of lignocellulosic substrates using a separate reactor of hydrolysis and acidification before transfer to the methanogenic phase (Lindmark et al., 2014; Yuan et al., 2011a).

The traditional method of a closed-system anaerobic reaction is often used for the acidogenic phase to treat food wastes, municipal wastes, and wastewater, which contain >75% easily biodegradable organic matter and have a good fluidity (Ward et al., 2008; Wang et al., 2016). Treatment of agricultural waste was limited due to the recalcitrance of lignocellulose, which can also cause engineering issues such as pipe blockages during feeding. To solve these problems, a new trend has emerged using a non-airtight system for the hydrolysis and acidification, which allows air to enter the chamber during the reaction. This new strategy is applied in the acidogenic phase for two-stage methane production, which has the advantages of low cost, convenient feeding by a loader, and easy mixing. Many studies indicated that introducing a small amount of air into the reactor promotes lignocellulose hydrolysis, improves VS removal rate, and increases lignocellulose stability due to aerobic respiration of facultative anaerobes, and it also increased methane production efficiency by accumulating more organic acids (Xu et al., 2014; Lim and Wang, 2013; Yu et al., 2016). This is another substantial benefit of lignocellulose pretreatment compared with anaerobic hydrolysis and acidification. The approach is applied currently in some straw-fed biogas plants of Hebei, Shandong, Henan, and Jiangsu Provinces in China. However, ideal methane production requires effective hydrolysis of the substrate and the accumulation of sufficient organic acid as a pre-condition. Neither of these parameters of hydrolysis and acidification reactions has been investigated in this non-airtight system, especially under the influence of different factors.

Solid content, temperature, and mixing are important control parameters in AD. The traditional process in China uses a low solid content (TS < 15%) of AD because it rarely causes product inhibition and can be applied to almost all substrate types, but the biogas yield and efficiency from this process is not satisfied. The high solid content [total solids (TS) ≥ 15%] of AD is currently popular, because it tends to promote an increased biogas production rate and reduce the difficulty of post treatment. However, high concentration of organic acid is an unstable factor that affects the AD efficiency in the single-phase reactor, whereas the separate acidogenic phase (two-phase) appropriately regulates the organic acid content and transfer to the methanogenesis phase, and reduces the direct stimulation of AD (Yang et al., 2015; Lim and Wang, 2013). Temperature can affect biochemical reactions by altering the reaction rate, reaction pathway, and microbial yield. Most Chinese biogas plants fed with straw and livestock manure run normally under mesophilic (35 °C) or thermophilic (55 °C) conditions (Sheets et al., 2015). Mixing achieves a homogeneous distribution of the input material of substrates and microbes, which can increase the efficiency of mass and heat transfer of AD (Danesh and Oleszkiewicz, 1997). However, a study of the effects of solid content, temperature, and mixing on the acidogenic phase has not been reported previously.

The objective of this study was to investigate and compare the characteristics of hydrolysis and acidification using a mixture of rice straw and cow dung under different operating conditions of solid content, temperature, and mixing modes in the non-airtight acidogenic system. We also evaluated the relationships among environmental factors on substrate degradation and organic acid production, and optimized these parameters for a non-airtight hydrolysis and acidification system to improve efficient methane production from agricultural waste.

2. Materials and methods

2.1. Feedstock and inoculum

Rice straw (RS) was obtained from the Shangzhuang Experimental Station, China Agricultural University (Haidian District, Beijing City, China), and cow dung (CD) was obtained from the Doudian biogas plant (Fangshan District, Beijing City, China). The RS was processed before use by crushing to 1–2 mm particles, which were stored under ventilation conditions at 15–20 °C. The CD was further processed by filtering through a 2-mm sieve to remove coarse material, and was frozen at –20 °C to prevent further decomposition. The frozen CD was thawed at 4 °C and transferred to room temperature (25 °C) before use. Feedstock characteristics are presented in Table 1. The microbes responsible for hydrolysis and acidification in this study were derived from CS and CD; no extra microbes were added for the experiments.

2.2. Experimental design

The investigated factors of the hydrolysis and acidification process were solid content, temperature, and mixing modes. RS and CD were mixed at a ratio of 6:4. High solid content was set to 15% ± 1% TS (H), and low solid content was 5% ± 1% TS (L). Two temperature levels corresponded with thermophilic 55 °C (T) and mesophilic 35 °C (M) reactions. The mixing modes included unmixed (U), intermittent mixing (I), and continuous mixing (C). Combinations of the three factors (solid content, temperature, and mixing mode) were evaluated in a series of 12 batch tests, which were designated as THU, THI, THC, MHU, MHI, MHC, THU, TLI, TLC, MLU, MLI, and MLC. Each test was performed using three replicates, and the pretreatment time was 15 days.

The non-airtight acidogenic system was a continuous stirred tank reactor (CSTR) that was not completely sealed to simulate a microaerobic environment. The reactor was allowed gas exchange with the surrounding environment. The dissolved oxygen (DO) concentration ranged from 0.1–1 mg/L in the system (Cui et al., 2002), and the effective volume was 3 L. Mechanical agitation was responsible for homogenization, and the stirring blade was located at the bottom center of the reactor. The frequency of mixing was 15 rpm, and the intermittent mixing tests provided 15 min of mixing 2 times per hour. The water bath thermostat was used to adjust the reaction temperature. The tests were exposed to different hydrolysis and acidification times; samples were collected for the initial stage (0, 1, 2, and 3 d), the middle stage (5, 7, and 9 d), and the last stage (11 and 15 d). The sample volumes collected from each reactor were 12 mL. All samples were stored at –20 °C before analysis.

Table 1
Characteristics of feedstock.

Parameter	Rice straw	Cow dung
TS (%)	93.31 ± 0.06	59.89 ± 0.07
VS (%)	79.93 ± 0.13	48.93 ± 0.25
Cellulose (%)	37.90 ± 2.93	22.91 ± 0.28
Hemicellulose (%)	30.44 ± 0.40	22.85 ± 0.11
Soluble materials (%)	18.68 ± 3.98	39.83 ± 0.43
Lignin (%)	7.32 ± 0.18	8.09 ± 0.08
Ash (%)	5.66 ± 0.46	6.32 ± 0.17
TC (%)	44.53 ± 0.29	34.29 ± 0.13
TN (%)	0.69 ± 0.01	2.36 ± 0.14
Alkalinity (CaCO ₃ mg/L)	700 ± 26	880 ± 45

Values are means ± standard deviations (n = 3).

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