Thermophilic Solid-State Anaerobic Digestion of Alkaline-Pretreated Corn Stover

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Thermophilic Solid-State Anaerobic Digestion of Alkaline-Pretreated Corn Stover

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ABSTRACT: Solid-state anaerobic digestion (SS-AD) of corn stover (CS) was conducted at mesophilic (37 °C) and thermophilic (50 °C) conditions with/without solid-state NaOH pretreatment. Fourier transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were employed to help with the understanding of the changes of the physicochemical structure of pretreated CS. Additionally, thermophilic SS-AD of pretreated CS and chicken manure (CM) was investigated. First-order, Cone, and modified Gompertz models were used to evaluate the methane production. Results showed that solid-state NaOH pretreatment could partly dissolve lignin and hemicelluloses and significantly increase the internal surface area of CS, which could make it more readily biodegradable. At a substrate/inoculum (S/I) ratio of 3, mesophilic SS-AD of CS failed because of the accumulation of organic acids. However, under thermophilic SS-AD conditions, biogas and methane yields of pretreated CS were found to be 386.3 and 194.8 mL g^{-1} of VS_{added}, respectively, which were 29.4 and 40.1% higher than those of untreated CS. Thermophilic solid-state co-digestion of pretreated CS with CM showed no beneficial effects for enhancing the biogas and methane yields, because of the accumulation of volatile fatty acids and ammonia. Methane production could well be explained by the Cone and modified Gompertz models compared to the first-order model, because higher R^2 values were obtained. On the basis of the results of the Cone model, the first-order rate constant (k) of thermophilic SS-AD of CS and CM decreased from 0.132 to 0.039 day^{-1} with the increasing portion of CM. Through the modified Gompertz model, a higher lag phase time (λ) and lower maximal methane production rate (μ_m) were found, with the content of CM increasing under thermophilic solid-state co-digestion conditions. These results collectively suggested that thermophilic SS-AD of pretreated CS could be a promising way to produce biogas in the future.

■ INTRODUCTION

As a commonly used renewable energy generation method, anaerobic digestion (AD) can perform at psychrophilic (10−20 °C), mesophilic (30−40 °C), and thermophilic (50−60 °C) reaction temperatures to produce methane/biogas.[1,2] The majority of commercial AD systems in China and in the U.S. are operated at mesophilic temperatures, with optima at 35−37 °C. Thermophilic AD has several advantages compared to mesophilic AD, including a higher methane yield, lower retention time, and higher rate of pathogen destruction.[3] However, thermophilic AD has a higher risk of system failure in response to a change of environmental conditions or the accumulation of inhibition factors.[4]

Solid-state anaerobic digestion (SS-AD) has been developed for digesting high solid content substrates (total solids ≥ 15%).[5] Typical SS-AD, such as Biocel, Biopercolat, Dranco, Kompogas, and Valorga process systems, have been reported to convert the organic fraction of municipal solid waste (OFMSW) into biogas and fertilizer.[6] Lignocellolosic biomass, with a high total solid content, also has the potential to produce biogas via SS-AD.[7−9]

Corn stover (CS), a major source of lignocellulosic biomass, has a tremendous annual yield.[9] Pretreatments have been widely applied to increase its biodegradability before being fed into a anaerobic digester.[5] Alkaline pretreatment is a simple and efficient way with several positive effects, including delignification, increase in accessible surface area, and decrease in polymerization degree (DP) and crystallinity of biomass.[10,11] Sodium hydroxide (NaOH) pretreatment has proven to be an effective method to improve digestibility and enhance methane yield of CS.[12] In comparison to "wet-state" pretreatment, solid-state NaOH pretreatment was simpler and more environmentally friendly, because of lower water consumption and no liquid waste generation.[12−15] However, most of the pretreatment time was time-consuming (usually varied from 3 to 21 days).[15] Thus far, there is less information about the effects of short-term (less than 24 h) solid-state NaOH pretreatment on structural changes of CS and its biogas production.[16,17]

In addition to the low biodegradability, inherent deficiency of nitrogen and lack of balanced nutrients also limit the use of CS.[18] Previous studies found that co-digestion of CS and chicken manure (CM) at mesophilic conditions could increase the specific biogas and methane yields.[9,19] The performance of solid-state co-digestion of NaOH-pretreated CS and CM at thermophilic conditions has not been studied.

The objectives of this study were (1) to compare the biogas and methane production of untreated and short-term solid-state NaOH-pretreated CS at mesophilic and thermophilic conditions via SS-AD, (2) to evaluate the changes of CS after 1 day of solid-state NaOH pretreatment using Fourier transform

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infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) analyses, and (3) to investigate the feasibility of co-digestion of pretreated CS and CM under thermophilic SS-AD conditions.

■ MATERIALS AND METHODS

Substrates and Inocula. CS was obtained from a local farm in Yanqing county of Beijing, China. CS was rubbed with a 9SC-360 kneading machine (Shuncheng, China), ground by a mill (KINGSLH, China) to go through a 18-mesh sieve (1 mm), and stored in airtight containers. CM was collected from a hennery (DQY Company, Beijing, China) and was kept at −20 °C. Mesophilic inoculum was digested sludge from a biogas plant treating municipal wastewater (Xiaohongmen, Beijing, China). The total solids (TS) and volatile solids (VS) were determined to be 88.8 and 83.6% for CS, 24.9 and 19.4% for CM, and 4.6 and 2.7% for mesophilic inoculum. Cellulose, hemicelluloses, lignin, nitrogen, and ash of CS were measured to be 42.3, 29.8, 9.4, 0.7, and 5.9%, respectively, on a TS basis.[9] Before use, mesophilic inoculum was degassed and acclimated (pre-incubation) in a 37 °C incubator for about 3 weeks to minimize the background biogas production.[20] Thermophilic inoculum was acclimated by cultivating the mesophilic inoculum from 37 to 50 °C with a heating rate of 1−2 °C day^{-1} in 1 L reactors using 1 g of VS L^{-1} of food waste as feedstock. After approximately 5 weeks of incubation, thermophilic inoculum was fully degassed and domesticated. Mesophilic and thermophilic inocula were condensed to increase their TS contents by centrifugation (Legend RT+ centrifuge, Thermo Fisher Scientific, Waltham, MA) to meet the need of SS-AD.

Solid-State Sodium Hydroxide Pretreatment. A total of 300 g of CS (moisture content of 11.2%) was mixed evenly with NaOH (5%, on the basis of dry matter of CS), followed by adding water to adjust the TS content to 50%. Then, the NaOH-soaked CS was sealed and kept at room temperature for 1 day.[13] During the pretreatment, no liquid waste solution was generated. After pretreatment, a portion of sample was dried at 60 °C for 48 h and then taken for physical and chemical analyses.[12] The rest was used for AD tests. For analysis of characteristics of substrate and incoulum and the structural changes of CS before and after pretreatment, triplicate samples were used.

Solid-State AD. The untreated and pretreated CS were separately mixed with concentrated inocula to a substrate/inoculum (S/I) ratio of 3, and the initial TS content was adjusted to 20% by water.[7,9] Feedstocks were loaded in 1 L glass bottles and incubated in incubators (YIHENG, China) maintained at 37 and 50 °C, respectively. Different mixtures of pretreated CS and CM (CS/CM) of 1:0, 3:1, 1:1, 1:3, and 0:1 (on a VS basis) were used in thermophilic co-digestion tests (namely, R1−R5). The corresponding TS contents ranged from approximately 20 to 23%. Duplicate reactors were applied, and inoculum blanks were used to correct the biogas yield in mesophilic and thermophilic AD. Reactors were manually shaken twice a day for about 1 min.

Analytical Methods. TS, VS, and alkalinity were determined according to the standard methods.[21] Biogas was measured using a manometric system. The pressure in the headspace of reactors was detected using a 3151 WAL-BMP-Test system pressure gauge (WAL Mess-and Regelsysteme GmbH, Germany).[9] Cellulose, hemicelluloses, and lignin contents were analyzed using an AMKOM 2000 fiber analyzer (AMKOM, Macedon, NY).[22] Other measurements, including ammonia, pH, methane, and volatile fatty acids (VFA) determination, were conducted according to previously reported methods.[9,19] Fourier transform infrared (FTIR) spectra was obtained by a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific, Waltham, MA) equipped with a DLaTGS detector. The solid samples were mixed with KBr, ground to a fine powder, and pressed into pellets for infrared (IR) transmission studies. A total of 30 scans were taken, with a resolution of 4 cm^{-1}.[16] A S-4700 scanning electron microscope (Hitachi, Japan) was used to visualize untreated and pretreated CS at a magnification of 500×. XRD was performed with a D8 ADVANCE diffractometer equipped with a sealed tube Cu Kα source. Scans were obtained from 2θ of 5−60° with a step size of 0.03° at 4 s per step. Crystallinity index (CrI) of cellulose was calculated according to the method by Segal (eq 1)[23]

$$\mathrm{CrI}\ (\%) = [(I_{002} - I_{\mathrm{AM}})/I_{002}] \times 100 \quad (1)$$

where CrI represents the crystallinity index (%), I_{002} means the maximal diffraction intensity on the [002] lattice plane and I_{AM} stands for the amorphous zone diffraction intensity at 2θ of 18°.

Kinetics Models. In this study, first-order, Cone, and modified Gompertz models were used to fit the measured methane yields.[20,24] Model equations are shown in Table 1.

Table 1. Summary of Models Used To Describe Methane Production from Different Reactors under Mesophilic and Thermophilic Conditions

model	equation[a]	reference
first-order	$B = B_0[1 - \exp(-kt)]$	20
Cone	$B = \dfrac{B_0}{1 + (kt)^{-n}}$	24
modified Gompertz	$B = B_0 \exp\left\{-\exp\left[\dfrac{\mu_{\mathrm{m}} e}{B_0}(\lambda - t) + 1\right]\right\}$	20

[a] B represents the cumulative methane yield (mL g^{-1} of VS); B_0 means the maximal methane yield (mL g^{-1} of VS); k is the rate constant (day^{-1}); λ refers to the lag phase time (day); μ_{m} stands for the maximal methane production rate (mL g^{-1} of VS day^{-1}); t represents the incubation time (day); e is equal to 2.721828; n means the shape factor (dimensionless).

Statistical Analysis. The significance of biogas and methane yields and other measured parameters were obtained using analysis of variance (ANOVA) at α = 0.05. PASW Statistics 18 (IBM, Armonk, NY) was used for data analysis, and Origin 8.0 (OriginLab, Northampton, MA) was used for graphing and modeling.

■ RESULTS AND DISCUSSION

Changes in the Physicochemical Structure of Pretreated CS. Alkaline pretreatment has been reported to increase the internal surface area of the feedstock because of swelling, decrease the crystallinity of cellulose, remove lignin, and alter the lignin structure, which are useful to improve the digestibility of the lignocellulosic biomass.[11] Among them, delignification is a remarkable advantage. Kim and Holtzapple[25] reported that the delignification mechanism of lignocellulosic biomass can be described in three stages: initial, bulk, and residual stages. First, phenolic α-O-4 linkages and some phenolic β-O-4 linkages are cleaved. Then, non-phenolic β-O-4 linkages are cleaved. Finally, carbon−carbon linkages in lignin are cleaved, and carbohydrates are released. In this work, FTIR, XRD, and SEM were used to investigate the changes in the physicochemical structure of short-term solid-state NaOH-pretreated CS.

The FTIR spectra of untreated and pretreated CS are shown in Figure 1. As presented in this figure, the carbonyl band at approximately 1733 cm^{-1}, which has been ascribed to hemicelluloses, was reduced in the pretreated CS. This was expected because the NaOH pretreatment could remove a portion of the hemicelluloses.[11] Additionally, lignin bands at approximately 1598 cm^{-1} (aromatic ring stretch) were reduced in the pretreated CS, suggesting that lignin was partly removed and altered.[26] The broadening of the C−H stretch absorbance near 1374 cm^{-1} for pretreated CS indicated that the structure of lignocelluloses was partially destroyed.[16]

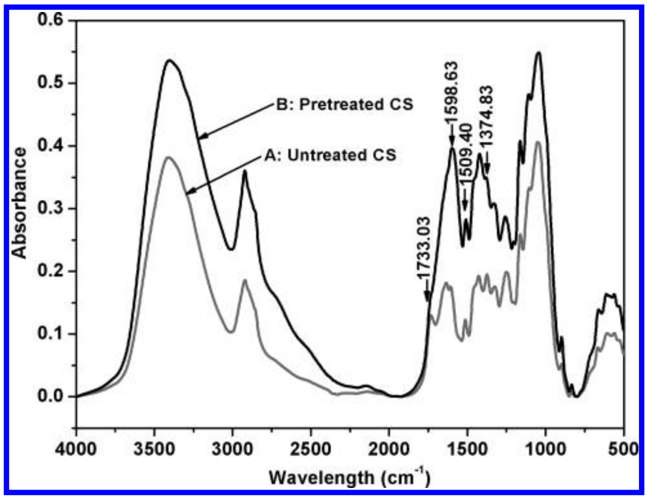

Figure 1. FTIR images of untreated (spectrum A) and 5% NaOH solid-state pretreated (spectrum B) CS.

As seen in Figure 2 (XRD spectra), two peaks at 2θ of 21.7° and 16.0°, representing the crystal style of cellulose I,[27] both appeared in pretreated and untreated CS, indicating that NaOH pretreatment did not change the cellulosic crystal style of CS. The crystallinity index (CrI) for untreated and pretreated CS was found to be 41.1 and 39.0%, respectively. Considering the heterogeneity of samples during characterization, there was no significant difference on CrI of untreated and pretreated CS.

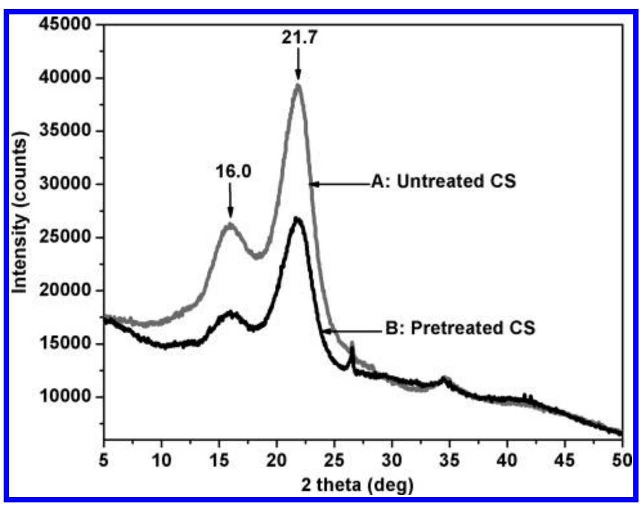

Figure 2. XRD images of untreated (spectrum A) and 5% NaOH solid-state pretreated (spectrum B) CS.

According to the SEM images shown in Figure 3, the untreated CS exhibited a relatively compact and smooth texture, while the pretreated CS showed a rough and partially broken surface, indicating that lignin in the cell wall and waxes surrounded the surface of CS might be broken down or dissolved, and degradable carbohydrates were likely to be more exposed.

Fiber analyzer was used to measure the degradation of CS. After NaOH pretreatment for 1 day, the dry matter of cellulose, hemicelluloses, lignin, and total lignocelluloses (cellulose, hemicelluloses, and lignin) was reduced by 0.3, 6.4, 1.7, and 8.4 g based on initial dry CS of 100 g, indicating decreases of 0.7, 24.3, 21.1, and 10.8% by weight, respectively. Generally, the results were in agreement with the qualitative findings.

The above results collectively showed that 5% NaOH solid-state pretreatment (on TS basis) for 1 day at room temperature could partly dissolve lignin and hemicelluloses and significantly increase the internal surface area of CS, which might make it easier for microorganisms to digest.

Solid-State AD of CS under Mesophilic and Thermophilic Conditions. For SS-AD, one of the most important disadvantage is that it needs a lot of inoculum to achieve a fast start-up and efficient biogas production.[5,28] To reduce the use of inoculum, a higher S/I ratio was desired. However, usually, a higher S/I ratio could result in organic overloading. Liew et al.[29] found that, at S/I of 3, SS-AD of CS showed higher methane yields of 80.0 L kg^{-1} of VS. Whereas, at S/I ratios of 4 and 5, methane yields of CS were only approximately 50.0 and 5.0 L kg^{-1} of VS, respectively. A S/I ratio higher than 3 will result in a low methane yield. Thus, in this study, to reduce the usage of inoculum and obtain a higher methane yield, a S/I of 3 was used.

Cumulative biogas yields and methane contents of untreated and pretreated CS are shown in Figure 4. After digestion for 30 days, under mesophilic conditions, both untreated and pretreated CS showed low biogas yields of 26.4 ± 0.9 and 53.5 ± 0.9 mL g^{-1} of VS_{added}, respectively (Figure 4A). As seen from Figure 4B, methane contents in the biogas increased slowly during the mesophilic digestion. At the end of digestion, the methane contents in biogas were lower than 20%, indicating that these mesophilic digesters failed.[9] Thermophilic SS-AD showed significantly higher ($p < 0.01$) biogas yields compared to mesophilic SS-AD. Under thermophilic conditions, biogas

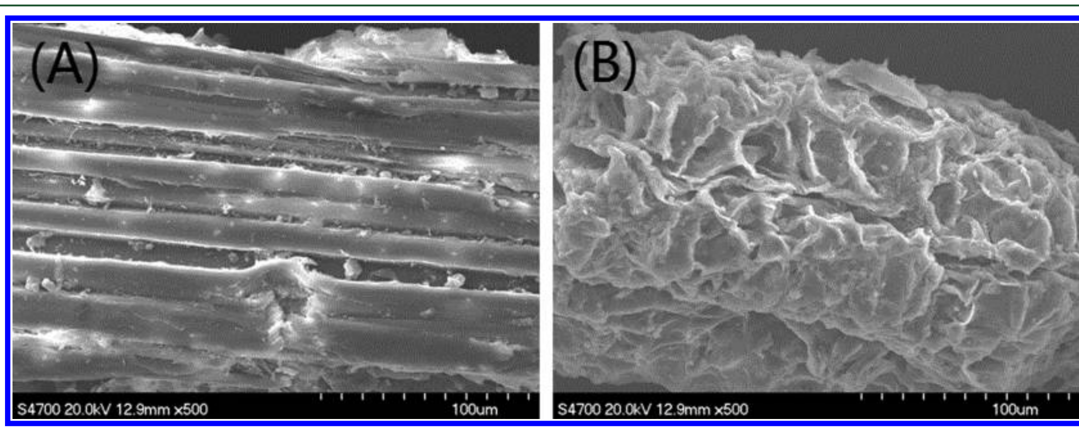

Figure 3. SEM images of CS (500×): (A) untreated CS and (B) CS pretreated with 5% NaOH, on the basis of dry matter of CS.

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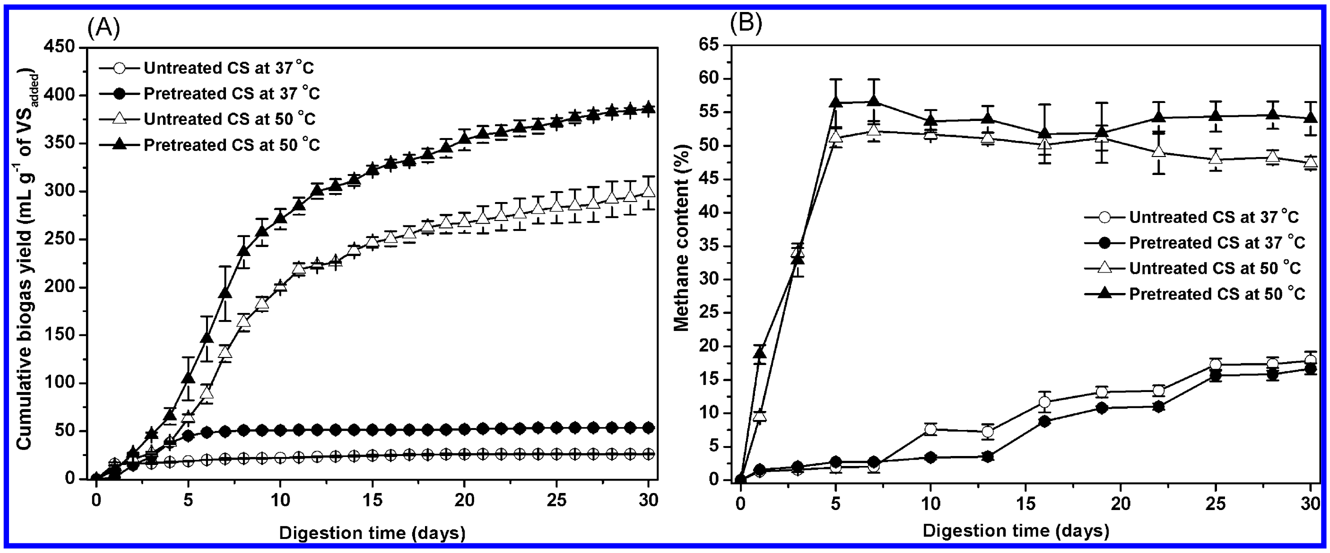

Figure 4. Cumulative biogas yields and methane contents of untreated and NaOH-treated CS at mesophilic and thermophilic conditions.

Table 2. Parameters of Different Reactors under Mesophilic and Thermophilic Conditions[a]

sample	initial pH	final pH	final TAN (g kg^{-1})	final FA (mg kg^{-1})	final TVFA (g kg^{-1})	TVFA/TA
			Mesophilic			
untreated CS[9]	7.8 ± 0.3	5.2 ± 0.1	0.8 ± 0.1	0.2 ± 0.1	6.8 ± 0.6	0.63 ± 0.01
pretreated CS	8.8 ± 0.1	5.5 ± 0.1	0.9 ± 0.1	0.4 ± 0.2	24.6 ± 0.4	2.39 ± 0.07
			Thermophilic			
untreated CS	8.8 ± 0.0	7.0 ± 0.3	1.1 ± 0.1	15.8 ± 11.2	0.8 ± 0.1	0.06 ± 0.01
pretreated CS/CM = 1:0	8.7 ± 0.0	7.4 ± 0.1	1.1 ± 0.1	35.5 ± 15.2	0.6 ± 0.1	0.07 ± 0.01
pretreated CS/CM = 3:1	8.9 ± 0.0	7.8 ± 0.0	2.0 ± 0.2	148.3 ± 15.7	2.8 ± 0.3	0.11 ± 0.01
pretreated CS/CM = 1:1	8.9 ± 0.1	8.1 ± 0.0	3.0 ± 0.3	427.2 ± 39.0	4.1 ± 0.3	0.12 ± 0.01
pretreated CS/CM = 1:3	8.8 ± 0.0	8.3 ± 0.1	3.9 ± 0.2	813.9 ± 250.9	8.0 ± 0.5	0.20 ± 0.01
pretreated CS/CM = 0:1	9.1 ± 0.1	7.7 ± 0.1	4.7 ± 0.2	289.5 ± 99.8	26.0 ± 0.9	1.40 ± 0.02

[a]CS, corn stover; CM, chicken manure; TAN, total ammonia nitrogen; FA, free ammonia; TVFA, total volatile fatty acids; and TA, total alkalinity.

yields of untreated and pretreated CS were determined to be 298.6 ± 5.4 and 386.3 ± 2.5 mL g^{-1} of VS_{added}, respectively. Pretreated CS achieved 29.4% more biogas yield compared to the untreated group. Figure 4B shows that methane contents in pretreated CS digesters increased immediately in the first 5 days and then stabilized at around 55%. The methane content of the untreated CS group in the steady stage was approximately 50%. The methane yield of pretreated CS was found to be 194.8 ± 3.1 mL g^{-1} of VS_{added}, which was 40.1% higher than the untreated CS. Results indicated that NaOH pretreatment could significantly improve the biogas and methane yields of CS via thermophilic SS-AD.

Stability parameters of SS-AD of CS are shown in Table 2. Under mesophilic SS-AD, a higher final total volatile fatty acids (TVFA) concentration of 6.8 and 24.6 g kg^{-1} was found for untreated and pretreated CS. According to Li et al.,[9] the TVFA concentration above 6 g kg^{-1} could result in severe inhibition. Besides, the accumulation of TVFA could cause the decline of the pH value. After digestion for 30 days, the final pH values for mesophilic SS-AD of untreated and pretreated CS were measured to be 5.2 and 5.5, respectively. The preferred pH values for AD ranged from 7.0 to 7.8.[9] A low pH could inhibit methanogenesis and disrupt the performance of the digester. Furthermore, the TVFA/total alkalinity (TA) ratios in mesophilic SS-AD of untreated and pretreated CS were 0.63 and 2.39, respectively, whereas a TVFA/TA value below 0.4 is regarded as optimal for AD.[9] For the thermophilic SS-AD system, all of the stability parameters were in a normal range. According to Li et al.,[5] operating SS-AD systems at thermophilic conditions can accelerate the AD process and the biogas yield of organic samples at thermophilic conditions is much higher than that in mesophilic conditions. Besides, on the basis of the results by Shi et al.,[4] thermophilic digestion could lead to greater populations of acetoclastic methanogens, which could endure a high VFA concentration and convert VFA into biogas. Thus, in this study, no accumulation of VFA was found and higher methane yields were obtained under thermophilic SS-AD. More experiments about microbial community dynamics and reactor performance are needed.

Interestingly, although NaOH pretreatment did not increase the biogas and methane yields at a S/I ratio of 3 under mesophilic conditions, the final TVFA in the pretreated CS reactor was very significantly higher ($p < 0.01$) than that of untreated CS (Table 2 and Figure 5), which implied that NaOH pretreatment could increase the acidification rate of CS. The TVFA productivity in pretreated CS reactor was 24.6 ± 0.4 g kg^{-1}, and the acetic acid and butyric acid contributed 63.1 and 29.5% to the TVFA (Figure 5), respectively, indicating that CS might be a potential feedstock to produce valuable carboxylic acids.[30]

Different trials of AD of untreated and NaOH-pretreated CS were summarized and compared in Table 3. Optimum doses of sodium hydroxide reported in the literature ranged from 2 to 6%, on the basis of dry matter of CS, and the pretreatment time

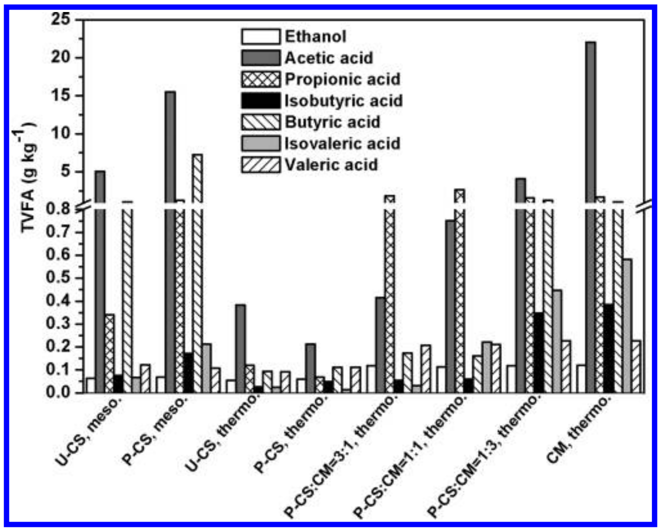

Figure 5. Total VFA concentrations after 30 days of digestion. U-CS, untreated corn stover; P-CS, pretreated corn stover; CM, chicken manure; meso, mesophilic; and thermo, thermophilic.

varied one by one.[12−15] Generally, NaOH pretreatment could increase the methane yield from 15.3 to 73.4%.[14,15] In the current work, the methane yield of pretreated CS was 194.8 mL g^{-1} of VS_{added}, which was 40.1% higher than those of untreated CS under thermophilic SS-AD conditions. Considering that the pretreatment time is only 1 day, the improvement could be acceptable. Volumetric methane productivities of untreated and pretreated CS under thermophilic SS-AD conditions were found to be 13.4 and 18.7 $L_{methane}\ L_{reactor\ volume}^{-1}$, respectively. High volumetric methane productivity was considered to be helpful in reducing the volume of reactor.[5,9] However, among all reported data, methane yields of CS were found to be lower than 300 mL g^{-1} of VS_{added}. According to Li et al.,[31] the theoretical methane yield of CS was approximately 450 mL g^{-1} of VS_{added}, indicating that there was still room to increase the biodegradability of CS. More work is worth being done to improve the pretreatment efficiency.

Co-digestion of Pretreated CS and CM under Thermophilic Conditions. Cumulative biogas and methane yields of thermophilic solid-state co-digestion of NaOH-treated CS and CM are shown in Figure 6. A negative relationship was found in both biogas and methane yields, with the content of CM in mixtures increasing from 0 to 100% (on the basis of VS). The methane yields of R1, R2, R3, R4, and R5 were determined to be 194.8 ± 3.1, 160.9 ± 9.6, 115.1 ± 15.4, 79.1 ± 18.2, and 3.1 ± 0.9 mL g^{-1} of VS_{added}, respectively. Statistical analysis showed that methane yields from co-digestion of CS and CM were very significantly lower ($p < 0.01$) than that of mono-digestion of CS.

At CS/CM ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 (R1−R5), the C/N ratios were calculated to be 63.2, 27.3, 17.4, 12.8, and 10.1, respectively. The optimum C/N ratio was reported to be 15−30.[9] Although C/N ratios of R2 and R3 were located in the preferred range, no synergistic effects were obtained in thermophilic solid-state co-digestion systems. This might be due to the inhibition of ammonia and TVFA. As seen in Table 2, with the chicken manure portion in the feedstock growing, the concentration of free ammonia (FA) increased. The FA values were all above 150 mg kg^{-1} (R2−R5), which implied that instability occurred in the AD system.[9,32] We can also clearly find from Table 2 and Figure 5 that the TVFA

Table 3. Summary of the Integrated Process of NaOH Pretreatment and AD of CS[a]

pretreatment					batch AD								
NaOH dose[b] (wt %)	MC (%)	T (°C)	time (day)	size (mm)	mixing type	T (°C)	time (day)	concentration	S/I	C/N adjustment	EBY/EMY (mL g^{-1} of VS)	increase[h] (%)	reference
2	88.0	20	3	5−10	continuous	35	75	65[c]	5.0[d]	NH_4Cl	366.0[d]/211.0	72.9/73.4	15
5	47.5[d]	20	1	<5	not given	37	40	22[e]	2.3[d]	no	372.4/not given	37.0/not given	13
5	50	20	1	<1	batch	37	30	20[e]	3	no	53.6/1.4	not given	this study
5	50	20	1	<1	batch	50	30	20[e]	3	no	386.3/194.8	29.4/40.1	this study
6	80.0	20	21	5−10	continuous	35	75	65[c]	4.1[g]	NH_4Cl	466.0/246.0[d]	48.5/not given	12
6	90	20	3	5−20	batch	37	20	6[f]	1	no	not given/272.6	not given/48.4[d]	14
6	90	20	3	0.25−1	batch	37	20	6[f]	1	no	not given/287.0	not given/15.3[d]	14

[a]MC, moisture content; T, temperature; S/I, substrate/inoculum ratio, on the basis of VS; EBY, experimental biogas yield; and EMY, experimental methane yield. [b]On the basis of dry CS weight. [c]In units of g of TS L^{-1}. [d]Calculated on the basis of data in references. [e]TS concentration, %. [f]In units of g of VS L^{-1}. [g]On the basis of TS. [h]As compared to untreated CS.

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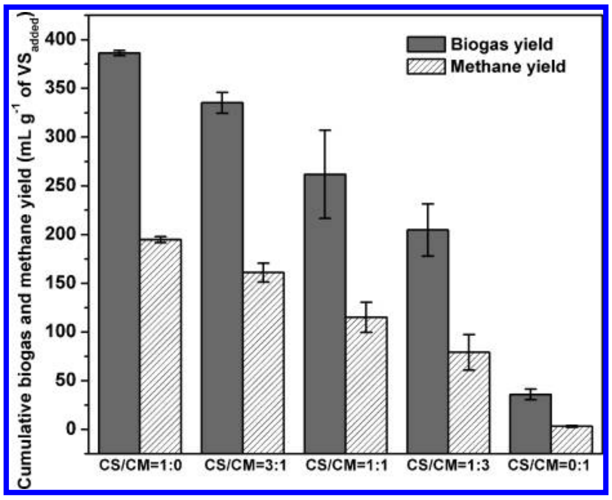

Figure 6. Cumulative biogas and methane yields of thermophilic solid-state co-digestion of NaOH-treated CS and CM.

concentrations of R4 (CS/CM = 1:3) and R5 (CM alone) were 8.0 and 26.0, respectively. The concentration above 6 g kg^{-1} of TVFA and 3 g kg^{-1} of propionic acid could result in severe inhibition.[9,33] Thus, in this study, increasing the CM portion in the mixtures was found to have a negative effect.

Modeling Analysis. The estimated parameters of the studied models of different reactors under mesophilic and thermophilic conditions are shown in Table 4. For the first-order model, the determination coefficient (R^2) ranged from 0.897 to 0.945, except for the thermophilic SS-AD reactors of R4 (CS/CM = 1:3; R^2 = 0.462) and R5 (CM alone; R^2 = 0.751). This indicated that the assumption of the first-order model might not suit well for all SS-AD tests. Similar results were found by Brown et al.,[7] where a low R^2 of 0.771 was obtained in SS-AD of pine. For the modified Gompertz and Cone models, the R^2 ranged from 0.909 to 0.998 and from 0.934 to 0.999, respectively, indicating that methane production could well be explained by these two models. On the basis of the results of the Cone model, for the mesophilic SS-AD of CS, NaOH pretreatment could significantly increase k compared to untreated CS (0.275 day^{-1} of pretreated CS versus 0.025 day^{-1} of untreated CS). A higher k value means a higher hydrolysis rate, which is helpful for improving the efficiency of AD. For the thermophilic SS-AD of CS and CM, the k values ranged from 0.039 to 0.132 day^{-1}. Generally, with the portion of CM increasing, lower k values were found. According to the results of the modified Gompertz model, thermophilic SS-AD of CM showed the highest lag phase time (λ) of 26.16 days, while thermophilic SS-AD of pretreated CS showed a lower λ of 2.45 days. With the addition of CM, a higher λ and lower μ_m were found. A higher λ means a slow startup, and a lower μ_m indicates a lower digestion efficiency. Consistently, in the thermophilic solid-state co-digestion system, with the content of CM in mixtures increasing from 0 to 100%, higher TVFA and ammonia concentrations were obtained and lower biogas and methane yields were found (Table 2 and Figure 6).

CONCLUSION

Solid-state NaOH pretreatment with a dose of 5% at room temperature for 1 day could significantly enhance the fermentation efficiency of CS via thermophilic SS-AD. The biogas and methane yields of pretreated CS were found to be 386.3 ± 2.5 and 194.8 ± 3.1 mL g^{-1} of VS$_{added}$, respectively, which were 29.4 and 40.1% higher than the untreated CS. At a S/I ratio of 3, thermophilic solid-state co-digestion of CS and CM showed no beneficial effects on enhancing the methane yield. On the other hand, thermophilic SS-AD of CS alone showed a better methane yield compared to mesophilic SS-AD. The volumetric methane productivity of pretreated CS reached 18.7 L$_{methane}$ L$_{reactor\ volume}$$^{-1}$. Thermophilic SS-AD of pretreated CS could be an alternative way to produce biogas and is a worthwhile topic for further research.

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Notes

The authors declare no competing financial interest.

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Table 4. Parameters of the Studied Models of Different Reactors under Mesophilic and Thermophilic Conditions[a]

	first-order model		Cone model			modified Gompertz model		
sample	k (day^{-1})	R^2	k (day^{-1})	n	R^2	μ_m (mL g^{-1} of VS day^{-1})	λ (day)	R^2
				Mesophilic				
U-CS	0.055 ± 0.008	0.941	0.025 ± 0.029	0.89 ± 0.21	0.934	0.02 ± 0.00	1.37 ± 0.67	0.937
P-CS	0.193 ± 0.018	0.909	0.275 ± 0.019	1.90 ± 0.26	0.935	0.07 ± 0.01	0.81 ± 0.44	0.909
				Thermophilic				
U-CS	0.066 ± 0.010	0.935	0.123 ± 0.002	2.94 ± 0.14	0.995	4.25 ± 0.21	3.09 ± 0.25	0.991
P-CS/CM = 1:0	0.076 ± 0.009	0.945	0.132 ± 0.003	2.64 ± 0.14	0.993	5.77 ± 0.32	2.45 ± 0.29	0.987
P-CS/CM = 3:1	0.065 ± 0.004	0.897	0.090 ± 0.001	3.24 ± 0.08	0.999	4.00 ± 0.09	4.69 ± 0.14	0.998
P-CS/CM = 1:1	0.054 ± 0.003	0.914	0.061 ± 0.002	2.02 ± 0.07	0.998	2.21 ± 0.06	3.55 ± 0.22	0.997
P-CS/CM = 1:3	0.015 ± 0.003	0.462	0.039 ± 0.001	11.39 ± 0.76	0.978	2.87 ± 0.26	21.05 ± 0.40	0.963
P-CS/CM = 0:1	0.033 ± 0.003	0.751	0.049 ± 0.001	3.82 ± 0.35	0.938	0.12 ± 0.05	26.16 ± 6.94	0.993

[a]U-CS, untreated corn stover; P-CS, pretreated corn stover; and CM, chicken manure.

NOMENCLATURE

AD = anaerobic digestion
C/N ratio = carbon/nitrogen ratio
CM = chicken manure
CrI = crystallinity index
CS = corn stover
FA = free ammonia
FTIR = Fourier transform infrared
SEM = scanning electron microscopy
S/I ratio = substrate/inoculum ratio
SS-AD = solid-state anaerobic digestion
TAN = total ammonia nitrogen
TS = total solids
TVFA/TA ratio = total volatile fatty acids/total alkalinity ratio
VS = volatile solids
XRD = X-ray diffraction

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