Potential of Black Liquor of Potassium Hydroxide to Pretreat Corn Stover for Biomethane Production

Muhammad Abdul Hanan Siddhu,[a] Jianghao Li,[a] Ruihong Zhang,[c] Jinmiao Liu,[a]
Jinli Ji,[a] Yanfeng He,[a] Chang Chen,[a,b,]* and Guangqing Liu [a,]*

Reducing the pretreatment cost of lignocellulosic biomass by utilizing alkali to alter its recalcitrant nature is an effective method for biofuel production. In this experiment, 1.5% KOH solution and its black liquor (spent liquor of KOH) (BL) were applied to pretreat corn stover (CS) at a temperature of 20 °C to enhance the digestibility for anaerobic digestion (AD). Results showed no significant difference in weighted average methane content on the basis of experimental methane and biogas yields between BL-treated and original KOH-treated CS after AD. The BL process significantly increased the overall methane yield by 52.4% compared with untreated CS (135.2 mL/g_{VS}), whereas no significant difference between the overall methane yields of 1.5% KOH-treated and BL-treated CS was observed. In addition, the BL process significantly saved water and KOH consumption, by 56.2% and 57.4%, respectively, compared with the 1.5% KOH pretreatment. Overall methane production was well explained by the modified Gompertz model. The physiochemical changes to CS after BL pretreatment were confirmed by SEM, FTIR, and XRD analyses. Our findings collectively suggest that recycling and reuse of KOH black liquor might be an efficient method for lignocellulosic biomass treatment and have the capability to reduce input costs in future AD processes.

Keywords: Black liquor; Corn stover; Potassium hydroxide; Recycling; Methane production

*Contact information: a: Biomass Energy and Environmental Engineering Research Center, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China; b: College of Life Science and Technology, Beijing University of Chemical Technology, Beijing 100029, China; c: Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616, United States; *Corresponding authors: chenchang@mail.buct.edu.cn; gqliu@mail.buct.edu.cn*

INTRODUCTION

China is the second largest maize producer in the world, with an annual increase in production of 5% for the last 20 years. It produced 0.4 billion tons of corn stover (CS) in 2012 (Jiang *et al*. 2012; National Bureau of Statistics of China 2013). Approximately 70% of produced CS is burnt in the field because of the high costs of collection and its low value. Burning of CS not only causes serious environmental problems, but also depletes natural resources (Zheng *et al*. 2009). Therefore, it is a necessity to find solutions to use this resource, while reducing the negative environmental effects of its incineration in the field (Feng *et al*. 2013).

Biogas is an environmental friendly bioenergy source that can be generated by microorganisms *via* anaerobic digestion (AD) of organic matter (carbohydrates, proteins, lipids, etc.) contained in municipal waste, agricultural waste, and dedicated energy crops (Srirangan *et al*. 2012). The characteristics and recalcitrant nature of the structure of lignocellulosic substrates greatly influence the biogas production, yield, and kinetics of the AD process. Therefore, various physiochemical and biological pretreatment methods have been applied for the destruction of the complex structural bonding of lignocellulosic biomass to enhance its digestibility (Triolo *et al*. 2011).

Alkaline pretreatment technologies are commonly applied to accelerate the biodegradation of lignocellulosic materials, although the alkali cost for pretreatment of biomass is high. In the alkaline pretreatment method, lignocellulosic biomass is soaked in an alkali solution (alkali + water). Alkaline pretreatment causes biomass to significantly swell, increases the surface area available for micro-organisms, converts the polymers into monomers, solubilizes some part of biomass, and breaks down and disintegrates the lignin structure. In other words, alkali solution pretreatment of lignocellulosic causes the saponification phenomenon, which in particular involves the disruption of the cross-linkage of ester bonds between xylan (hemicellulose) and lignin (Zhang *et al.* 2011). Among the alkaline pretreatments, sodium and potassium hydroxide (NaOH and KOH) pretreatment have been often studied by researchers in the past few years (Chandra *et al*. 2012; Geng *et al*. 2014). A combination of NaOH with CaO was used to pretreat CS for improving the sugar production yield and reducing treatment costs previously (Zhang *et al.* 2011). Effluents resulting from a high loading of NaOH may cause water pollution and soil salination, which are toxic to flora and fauna, and overall have negative impacts on the environment (Pang *et al*. 2008; Pienkos and Zhang 2009).

KOH has many advantages over NaOH. For example, potassium (K) is an essential nutrient for plant growth, and the effluent of KOH pretreatment can therefore be used as a soil amendment and fertilizer in the agriculture sector. These advantages make KOH more environmentally friendly than NaOH (Zhao *et al*. 2014; Zheng *et al*. 2014). Even with these advantages, high loading of alkali, fresh water for soaking, and input of downstream residues treatment make alkali pretreatment technology expensive (Xu *et al*. 2012). The kraft recovery system is widely applied for recovery of pulping chemicals and NaOH for abatement of negative environmental impact. However, the kraft recovery system needs high energy input and also causes some smelly products (Ragnar *et al.* 2002). Therefore, recycling of KOH black liquor (BL) after the first round of lignocellulosic biomass pretreatment may make the process cheaper and more environmentally friendly (Xu *et al*. 2012)

This study was planned to pretreat CS with KOH and subsequently explore the potential and performance of BL. The aims of this experiment study were as follows: (1) to evaluate the potential performance of KOH black liquor in pretreating CS to improve methane production; (2) to investigate the possibility of recycling utilization of black liquor; and (3) to determine the structural changes in BL-treated CS by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analysis.

EXPERIMENTAL

Substrate and Inoculum

Corn stover was acquired from a farm belonging to Deqingyuan Company, Beijing, China. A 9SC-360 mill kneading machine (Shuncheng, China) was used to crush the CS, and was then air-dried for three days. After this, the particle size of CS length was reduced to 15 to 20 mm by scissors and packed in plastic bags, and then stored at 4 °C until it was used in the experiment. The inoculum used for this AD experimental study was effluent from an anaerobic digester of Donghuashan biogas plant, located near to Beijing, China.

Inoculum was incubated at 37 ^{o}C for three weeks to remove background methane yield (Feng *et al*. 2013).

Potassium Hydroxide Pretreatment and Black Liquor Recycling

Initially, 40 g of raw CS was mixed with 336 mL of water to adjust the moisture content to 90% using Eq. 1. The KOH was then added to reach a concentration of 1.5% (W/V). The pretreatment was carried out at a temperature of 20 ^{o}C; and the solution was manually stirred for 1 min at 4 h intervals (Zheng *et al*. 2009). After 12 h, the treated CS was squeezed and the black liquor (BL) was collected. Then, BL was filtered using a metal sieve (Public Road Equipment Company, China) (Xu *et al*. 2012). Water was added to BL to reach a volume of 336 mL. Then, KOH was added to BL to adjust the pH up to the original level (pH of 13.35). The pH-adjusted BL was used to pretreat another batch (40 g) of CS. After 12 h, CS was squeezed and BL was collected. The BL was recycled 10 times using the same procedure mentioned above. Pretreated CS was packed in airtight bags and kept at 4 °C until it was used in the experiments.

$$\mathrm{MC}(\%)=\left(1-\frac{\text{dry matter weight of corn stover}}{\text{weight of corn stover}+\text{water added}}\right)\times 100\% \tag{1}$$

Anaerobic Digestion Test

The biomethane potentials (BMPs) of untreated, 1.5% KOH-treated, and BL-treated CS were evaluated in 1-L serum bottles. The ratio of feeding substrate to degassed inoculum (S/I) in all digesters was 1:1 (based on VS) (Owen *et al*. 1979). The digester working volume was 500 mL, and this volume was maintained by the addition of deionized water (Xiao *et al*. 2013). Pure argon gas was used to purge the headspace of the digesters for 4 min to ensure anaerobic conditions. Then, a rubber stopper and special cap were fixed on each digester to sustain anaerobic condition. These digesters were incubated at 37 °C for 30 days (Song *et al.* 2012). Blank digesters containing the same amount of inoculum were run for calculation of exact biogas yield of CS. The biogas volume produced in the digesters was measured every day. All digesters were manually shaken after the gas volume measurement.

Energy Content

Untreated and treated CS samples were dried in an oven at 105 °C for 24 h. Then, the gross heating values (GHV) of the dried samples were determined using an automatic calorimeter (DY-ZDHW-6, Hebi Daewoo Instrument, China).

Analytical Methods

Total solids (TS), volatile solids (VS), and fixed solids (FS) of CS and inoculum were measured according to the standard methods of APHA (APHA 1998). Chemical oxygen demand (COD) in BL was determined using a spectrophotometer DR 2800 (HACH, Germany) according to the HACH method 8000 of water analysis (Liu *et al.* 2015b). Most common elements (C, H, N, and S) in the CS and inoculum were determined using a Vario (Germany) El cube elemental analyzer. On a VS basis, the oxygen content was assessed by considering C + H + O + N = 99.5% (Rincón *et al*. 2012). The value of pH was measured using a le438 pH electrode (Mettler Toledo, USA) (Li *et al*. 2015a). The Van Soest method was applied to determine the fiber (cellulose, hemicellulose, and lignin) contents of CS using an A2000 fiber analyzer (ANKOM, USA) (Van Soest *et al*. 1991).

Daily atmospheric pressure and each digester headspace pressure were measured using a digital pressure gauge (3151 WAL-BMP-Test system, WAL Mess-und Regelsysteme GmbH, Germany) with an accuracy of 0.1% (based on the gauge range) (Li *et al*. 2015a). Equation 2 was used to calculate the daily biogas production volume for each digester (El-Mashad and Zhang 2010),

$$V_{\text{biogas}} = \Delta P * V_{\text{head}} * C/(R * T) \tag{2}$$

where V_{biogas} is the daily biogas volume (L), ΔP is the absolute pressure difference (MPa), V_{head} is the volume of the headspace (L), C is the gas molar volume under standard condition (22.4 L/mol), T is the absolute temperature (K), and R is the universal gas constant (8.314 J/K/mol).

A gas chromatograph (Agilent 7890A, USA) was used to determine the biogas composition (H_2, CH_4, and CO_2) (Li *et al*. 2015a). Comparison of topography among untreated, KOH-treated, 5th round of BL-treated, and 10th round of BL-treated CS was determined using a scanning electron microscopy (SEM) (Hitachi S-4700, Japan) at a magnification of 500×. The pretreatment effect on chemical features was investigated using the Fourier transform infrared (FTIR) spectra recorded by a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific, Waltham, MA) equipped with a DLaTGS detector in the range of 4000 to 400 cm^{-1}. Two milligrams of fine powder of untreated, KOH-treated, 5th round of BL-treated, and 10th round of BL-treated CS was mixed with KBr (100 mg) and formed into pellets for analysis. Comparison of the effect of pretreatment on the crystallinity of CS was performed using the X-ray diffraction (XRD) patterns. A Bruker D8-Advance (Germany) with Cu Kα1 radiation was used to examine the crystallinity of CS. Scans were obtained from 2θ of 5° to 60° at a rate of 5°/min (Li *et al*. 2014). The crystallinity index (CrI) was determined by the following equation (Eq. 3) (Buswell and Mueller 1952),

$$\text{CrI}(\%) = \left(\frac{I_{002} - I_{\text{AM}}}{I_{002}}\right) \times 100\% \tag{3}$$

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

Theoretical Methane Yield (TMY)

The elemental composition of CS was used to calculate the theoretical methane yield (TMY) using the Buswell formula with the following equations (Eqs. 4 and 5) (El-Mashad 2013),

$$\begin{aligned} &\text{C}_n\text{H}_a\text{O}_b\text{N}_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right)\text{H}_2\text{O} \\ &\rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)\text{CH}_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right)\text{CO}_2 + c\text{NH}_3 \end{aligned} \tag{4}$$

$$\text{TMY}\left(\frac{\text{mL CH}_4}{\text{g VS}}\right) = \frac{22.4 \times 1000 \times \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)}{12n + a + 16b + 14c} \tag{5}$$

where the molecular formula subscripts, n, a, b, and c, represent the molar proportion of elements carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) in the organic fraction of biomass; TMY stands for theoretical methane yield (mL); VS is for volatile solids.

Kinetics Model

The kinetics of methane production of untreated, 1.5% KOH-treated, and BL-treated CS were studied using the modified Gompertz model (Eq. 6) (Zhang *et al*. 2007),

$$B = B_0 \exp\left\{-\exp\left[\frac{\mu_m e}{B_0}\left(\lambda - t\right) + 1\right]\right\} \tag{6}$$

where B is the cumulative methane yield (mL/g_{vs}); B_0 is the ultimate methane yield (mL/g_{vs}); μ_m is the maximum methane output rate (mL/g_{vs}/d); λ is the lag phase time (d); e is 2.72; and t is the anaerobic digestion time (d).

Statistical Analysis

The experimental data were statistically analyzed using a paired t-test and one-way analysis of variance (ANOVA) at significance levels (α) of 0.01 and 0.05 (Kryvoruchko *et al*. 2009).

RESULTS AND DISCUSSION

Composition of CS and Inoculum

The compositions of CS and inoculum are shown in Table 1. The TS, VS, and FS accounted for 93.20%, 89.33%, and 3.87% of CS, respectively (on total weight basis).

Table 1. Characteristics of CS and Inoculum

Parameters	CS	Inoculum
TS (%)^a	93.20	8.46
VS (%)^a	89.33	4.12
FS (%)^a	3.87	4.35
VS/TS (%)	95.85	48.66
pH	ND	7.80
C (%)^b	45.41	28.08
H (%)^b	6.06	3.70
O (%)^b	42.83	ND
N (%)^b	1.07	2.89
C/N (%)	42.44	9.72
Cellulose (%)^b	40.87	ND
Hemicellulose (%)^b	34.26	ND
Lignin (%)^b	8.64	ND

ND, not detectable; CS, corn stover.

^{a} As total weight of sample; ^{b} As TS of sample.

The lignocellulose of CS consisted of 40.87% cellulose, 34.26% hemicellulose, and 8.64% lignin. Based on the elemental composition of CS, the composition formula ($C_{49.51}H_{79.29}O_{35.02}N$) was deduced. The TMY of CS was calculated by Eq. 3 to be 458.4 mL CH_4/g_{VS}.

Biogas and Methane Yield

The performances of untreated, 1.5% KOH-treated, and BL-treated CS were evaluated by AD in 1-L digesters for 30 days at mesophilic temperature (37 °C). Figure 1 represents the daily and cumulative biogas and methane yields. The average gas yields of first five rounds (1st to 5th) of BL-treated CS were taken and named as BL-1. The average gas yields from the next five rounds (6th to 10th) BL-treated CS were also taken and named as BL-2. The daily average biogas yield of untreated CS was 11.0 ± 0.7 mL, whereas the biogas yields of 1.5% KOH-, BL-1-, and BL-2-treated CS were 19.3 ± 0.2, 14.4 ± 1.1, and 15.2 ± 1.3 mL, respectively. The cumulative methane productions of untreated, 1.5% KOH-treated, BL-1-treated, and BL-2-treated CS were 135.2 ± 9.6, 276.7 ± 3.2, 201.2 ± 16.4, and 211.1 ± 21.4 mL/g_{VS}, respectively. The cumulative methane yields of 1.5% KOH-treated and BL-treated CS significantly increased from that of untreated CS. No significant difference in the cumulative methane yields of BL-1 and BL-2 was observed. Therefore, BL pretreatment effectively improved the digestibility of CS for the AD process.

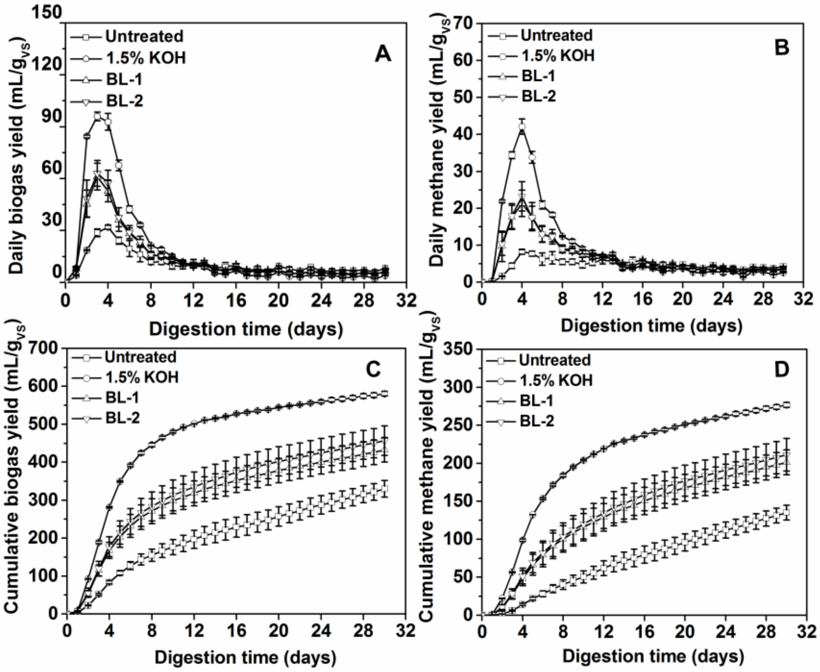

Fig. 1. Biogas and methane yields of untreated, 1.5% KOH-treated, and BL-treated CS

Methane Content

Figure 2 reveals that the methane content in biogas sharply increased in the first week of AD, and the trends were similar for 1.5% KOH-treated and BL-treated CS, whereas no difference between BL-1 and BL-2 was observed. The weighted average methane content (WAMC) was calculated on the basis of experimental methane yield (EMY) and experimental biogas yield (EBY). The WAMCs of untreated, 1.5% KOH-treated, BL-1-treated, and BL-2-treated CS were 41.0%, 47.7%, 46.5%, and 46.2%, respectively. The WAMCs of BL-treated and 1.5% KOH-treated CS were almost similar.

Therefore, BL pretreatment effectively pretreated CS and enhanced methane content as much as 1.5% KOH did.

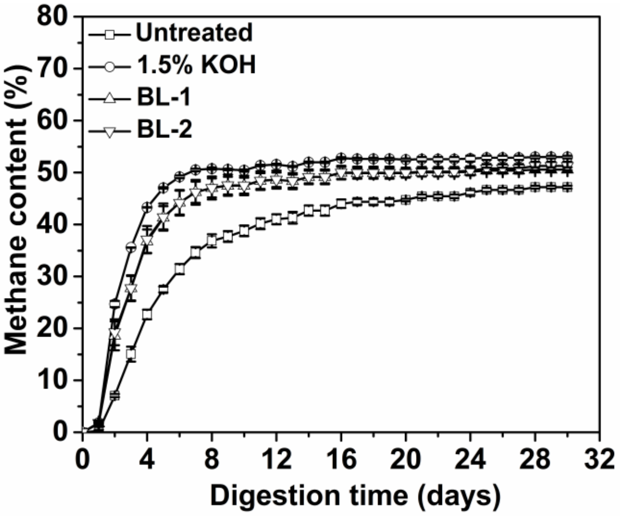

Fig. 2. Methane contents of untreated, 1.5% KOH-treated, and BL-treated CS

Solids Recovery after Pretreatment and Digestion Performance

The solids recovery, gross heating value (GHV), and chemical oxygen demand (COD) of BL and pH of different reactors are presented in Table 2. The GHV of 1.5% KOH-treated CS was 14,674 J/g, which was 14.18% less than that of the untreated CS (17,098 J/g), while the GHVs of BL-1- and BL-2-treated CS were 15,208 and 15,301 J/g, respectively. Increase of GHVs of BL-treated CS compared with 1.5% KOH treated was due to the accumulation of fine solids in BL. The VS recoveries of treated CS were measured after the pretreatment. The VS recovery rate of 1.5% KOH-treated CS was 73.26%, which was less than that of BL-1-treated CS (88.30%). On the other hand, the VS recovery rate of BL-2-treated CS was 97.57%, which was higher than that of BL-1-treated CS and much higher than that of 1.5% KOH-treated CS. The VS recovery rate of BL-2-treated CS was increased due to five times recycling (6 to 10) more than BL-1. Xu also pretreated the CS at room temperature with NaOH BL at 12 h residence time and found the TS recovery only reached 67.4% in the first round (Xu *et al*. 2012). The highest COD was measured in the liquor after 1.5% KOH treatment, while the lowest COD was observed for BL-1; it increased in BL-2 because of the accumulation of soluble components of CS. Therefore, the lower recovery rate indicated the loss of solids, which was caused by solubilization of hemicellulose and lignin of CS during 1.5% KOH pretreatment; moreover, because of the BL recycling process, the concentration of soluble components and some fine particles of CS increased, and some sticky leachates consequently formed, which then attached to the surface of pretreated CS.

The initial pH in the AD reactors was measured from the start and found to be in the permissible range from 8.14 to 8.40. After completion of the AD, the final pH in AD reactors decreased and was found to be in the range of 6.56 to 6.63, also in the permissible range. It has been reported that most methanogenic bacteria can perform well within this pH range, whereas the growth rate will start to decline below pH 6.60 (Li *et al*. 2015b). Therefore, pretreatment improved the digestion process performance stability during AD.

Table 2. Solids Recovery, GHV, and COD of BL after Pretreatment, and pH in Digesters for Untreated, 1.5% KOH-Treated, and BL-Treated CS

Samples	VS recovery (%)	Initial pH	Final pH	COD (mg/L)	GHV (J/g)
Untreated CS	-	8.14	6.56	-	17098
1.5% KOH treated	73.26	8.36	6.60	41750	14674
BL-1 treated	88.30	8.28	6.62	4470	15208
BL-2 treated	97.57	8.40	6.63	6880	15301

Evaluation of Overall Production Performance

The gas production performances of untreated, 1.5% KOH-treated, and BL-treated CS are presented in Table 3. Because of the solids loss, overall gas production was calculated from the experimental yields and solids recovery after pretreatment of CS. The overall methane yield of 1.5% KOH-treated CS was significantly lower than its EMY. This decrease may have occurred because of the high solids loss during the pretreatment (Liu *et al*. 2015b). No significant variation between overall methane yield and EMY of BL-treated CS was observed.

The overall methane yields of 1.5% KOH-treated and BL-treated CS were compared, and no significant difference was observed, whereas the BL process significantly increased the overall methane yield by 52.4% compared with the untreated CS (135.2 mL/g_{VS}). Therefore, the BL process pretreatment was very effective for enhancing the production performance.

Table 3. Gas Production Performances of Untreated, 1.5% KOH-Treated, and BL-Treated CS

Samples	EBY (mL/g_{VS})	EMY (mL/g_{VS})	Overall biogas yield (mL/g_{VS})	Overall methane yield (mL/g_{VS})
Untreated CS	329.7 ± 21.6	135.2 ± 9.6	329.7 ± 21.6	135.2 ± 9.6
1.5% KOH	580.4 ± 6.1	276.7 ± 3.2	425.2 ± 4.9	202.7 ± 2.6
BL-1treated	432.6 ± 32.4	201.2 ± 16.4	382.0 ± 32.5	177.7 ± 16.4
BL-2 treated	456.7 ± 38.7	211.1 ± 21.4	445.6 ± 39.7	206.0 ± 21.9

Changes to Chemical Structures

Physicochemical changes to untreated, 1.5% KOH-treated, and BL-treated CS were compared and evaluated by SEM, FTIR, and XRD.

SEM analysis

Changes in morphology after the pretreatments can be seen in the SEM images and presented in Fig. 3. The structure of untreated CS in image Fig. 3A was smooth and compact, as compared with Fig. 3B, C, and D, showing treated CS. On the other hand, Fig. 3B, for 1.5% KOH-treated CS, showed a patchy and uneven surface, which reflected the increase in surface area. During the pretreatment process, most of the hemicellulose and lignin was broken down or solubilized, and Fig. 3B appears similar to Fig. 3C and D of 5th round of BL-treated, and 10th round of BL-treated CS, respectively. Thus, the severity of the BL process was similar to that of 1.5% KOH treatment.

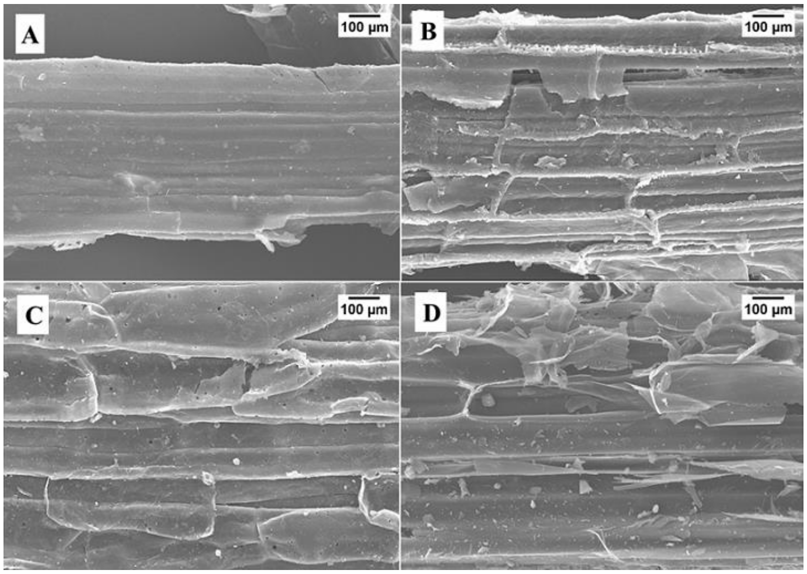

Fig. 3. SEM images (500×) of (A) untreated, (B) 1.5% KOH-treated, (C) BL-5th round treated, and (D) BL-10th round treated CS

FTIR analysis

FTIR spectra were acquired to describe and compare structural changes in the untreated and treated CS, as shown in Fig. 4. Reduction of the carbonyl band at 1734 cm^{-1} demonstrated that the ester bond of hemicellulose was effectively destroyed and that the hemicellulose was reduced after 1.5% KOH, the 5th round of BL-treated, and the 10th round of BL-treated pretreatments. Additionally, the strength of the band at 1605 cm^{-1} for 1.5% KOH-treated CS was similar to that of the 5th round of BL-treated, and the 10th round of BL-treated CS, which indicated that no significant difference was present concerning the delignification of KOH and BL pretreatments.

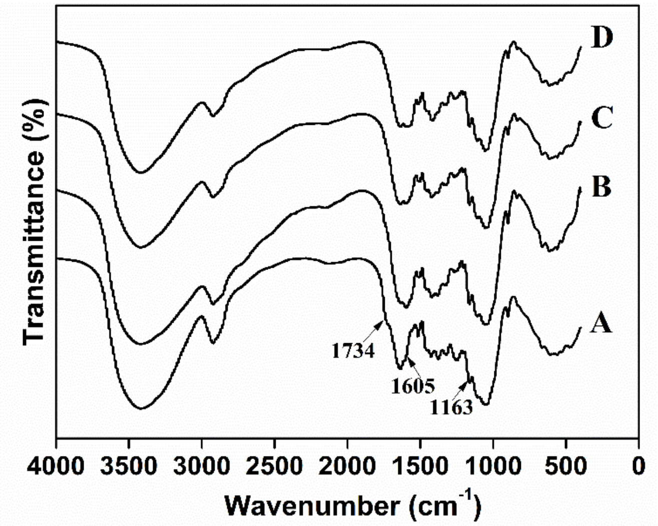

Fig. 4. FTIR spectra of (A) untreated, (B) 1.5% KOH-treated, (C) BL-5th round treated, and (D) BL-10th round treated CS

The strength of the cellulose peak at 1163 cm^{-1} in 1.5% KOH-treated CS increased compared with untreated CS because of the removal of hemicellulose and lignin. The comparability of the peaks among 1.5% KOH, the 5th round of BL-treated, and the 10th round of BL-treated CS was alike, indicating that all pretreatment effects were similar.

XRD analysis

XRD was used to describe the changes in crystalline structures in untreated and treated CS, and the patterns are shown in Fig. 5. Two peaks appeared at 2θ of 22° and 16°, which represented the crystal style of cellulose I. The CrI value of untreated CS was 37.7%, which was calculated using Eq. 2. It increased to 51.8%, 50.2%, and 50.5%, respectively, after 1.5% KOH treatment, the 5th round of BL treatment, and the 10th round of BL treatment. There was no significant difference in CrI between 1.5% KOH-treated and the 5th round of BL-treated, and the 10th round of BL-treated CS. This result revealed that 1.5% KOH and BL pretreatments significantly removed the non-crystalline hemicellulose and lignin. Therefore, BL pretreatment strength was very similar to that of KOH.

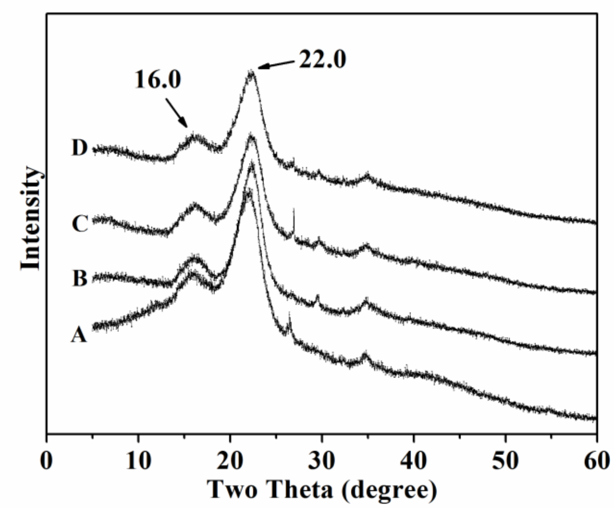

Fig. 5. XRD patterns of (A) untreated, (B) 1.5% KOH-treated, (C) BL-5th round treated, and (D) BL-10th round treated CS

Kinetic Model of Overall Methane Production

The modified Gompertz model was applied to the overall methane yields of untreated and treated CS for validation and comparison of pretreatment performance, as illustrated in Fig. 6. The responses of specific parameters are presented in Table 4. It can be concluded from the high R^2 values (0.981 to 0.991), which were near to 1, that the modified Gompertz model accurately simulated and explained the overall methane yields.

The kinetics of the modified Gompertz model indicated that the lag phase time (λ) decreased from untreated to BL-2-treated CS (1.9 to 0.2). Hence, with BL pretreatment of CS, the AD process started faster compared with the case with untreated CS. Decrease in λ value from untreated to BL-treated indicated the fast start digestion process. An increase in μ_m value was observed from untreated to BL-treated, and a higher value of μ_m meant higher methane production rate. Additionally, the B_o values demonstrated that the methane production potential of BL-treated CS was higher than that of untreated CS, and was also similar to that of KOH-treated CS. Therefore, pretreatment with BL can effectively improve methane production in the AD process.

Table 4. Parameters of the Modified Gompertz Model from Different Anaerobic Digestions of Untreated, 1.5% KOH-Treated, and BL-Treated CS

Samples	B_0 (mL/g_{VS})	μ_m (mL/g_{VS}/d)	λ (d)	R^2
Untreated	148 ± 5	5.8 ± 0.2	1.9 ± 0.4	0.991
1.5% KOH	190 ± 2	19.1 ± 1.2	0.7 ± 0.3	0.981
BL-1	170 ± 4	10.3 ± 0.6	0.2 ± 0.5	0.981
BL-2	198 ± 4	11.9 ± 0.7	0.2 ± 0.4	0.983

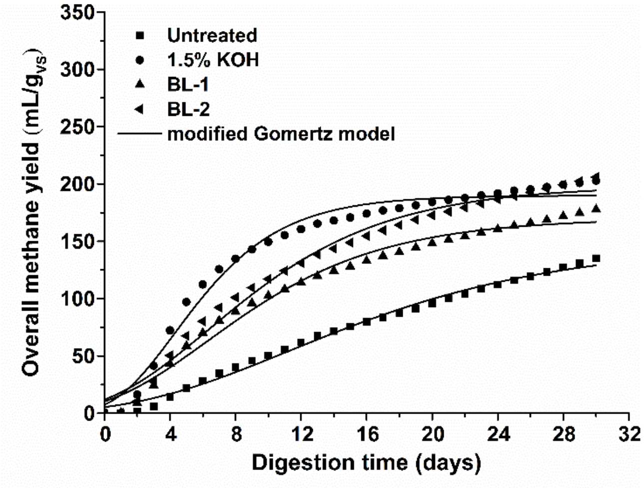

Fig. 6. Kinetics of modified Gompertz plots of overall methane yield from untreated, KOH-treated, and BL-treated CS

Water and KOH Consumption in Black Liquor Process

The change in pH after the pretreatment was an indicator of KOH consumption. The initial pH (13.35) of 1.5% KOH solution (336 mL) changed to 13.0 after the pretreatment of CS (Liu *et al*. 2015a). In the BL pretreatment process of CS, the pH also changed from the initial pH to 11.4 ± 0.4. The average fresh water quantity added to maintain the BL solution level was 147 ± 12 mL, whereas the average fresh quantity of KOH added to maintain BL solution pH was 2.4 ± 0.5 g.

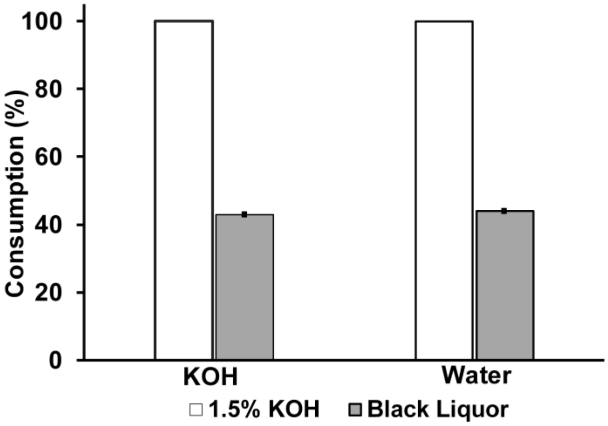

Fig. 7. Average consumption of water and KOH in ten rounds of BL treatment processes

During the comparison of the BL pretreatment process with 1.5% KOH, only 43.8% fresh quantity of water and 42.6% fresh quantity of KOH were consumed to maintain the solution level up to 336 mL and to raise the pH equal to 13.35, as shown in Fig. 7. A total of 56.2% water and 57.4% KOH were saved by the BL process of pretreatment of CS compared with pretreatment of 1.5% KOH. Therefore, the BL process effectively pretreated CS and also reduced water and KOH consumption during pretreatment.

CONCLUSIONS

1. The black liquor (BL) significantly destroyed the recalcitrance structure of corn stover (CS) during the pretreatment as well as reduced the pretreatment cost.
2. No significant differences in the overall methane yields and WAMCs of BL-treated and original KOH-treated CS were observed after anaerobic digestion (AD).
3. The BL process significantly increased the overall methane yield, by 52.4%, compared with untreated CS (135.2 mL/g_{VS}).
4. In addition, the BL process significantly saved water and KOH consumption, by 56.2% and 57.4%, respectively.

ACKNOWLEDGMENTS

The authors appreciate the financial support of the National Hi-tech R&D Program of China (863 Program, 2012AA101803), the National Key Technology Support Program of China (2012BAC25B06), and the Fundamental Research Funds for the Central Universities (YS1407).

REFERENCES CITED

APHA (1998). *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC.

Buswell, A. M., and Mueller, H. F. (1952). “Mechanism of methane fermentation,” *Industrial & Engineering Chemistry* 44(3), 550-552. DOI: 10.1021/ie50507a033

Chandra, R., Takeuchi, H., Hasegawa, T., and Kumar, R. (2012). “Improving biodegradability and biogas production of wheat straw substrates using sodium hydroxide and hydrothermal pretreatments,” *Energy* 43(1), 273-282. DOI: 10.1016/j.energy.2012.04.029

El-Mashad, H. M. (2013). “Kinetics of methane production from the codigestion of switchgrass and *Spirulina platensis* algae,” *Bioresource Technology* 132, 305-312. DOI: 10.1016/j.biortech.2012.12.183

El-Mashad, H. M., and Zhang, R. (2010). “Biogas production from co-digestion of dairy manure and food waste,” *Bioresource Technology* 101(11), 4021-4028. DOI: 10.1016/j.biortech.2010.01.027

Feng, L., Li, Y. Q., Chen, C., Liu, X. Y., Xiao, X., Ma, X. X., Zhang, R., He, Y., and Liu, G. (2013). “Biochemical methane potential (BMP) of vinegar residue and the influence of feed to inoculum ratios on biogas production," *BioResources* 8(2), 2487-2498. DOI: 10.15376/biores.8.2.2487-2498

Geng, W., Huang, T., Jin, Y., Song, J., Chang, H. M., and Jameel, H. (2014). "Comparison of sodium carbonate-oxygen and sodium hydroxide-oxygen pretreatments on the chemical composition and enzymatic saccharification of wheat straw," *Bioresource Technology* 161, 63-68. DOI: 10.1016/j.biortech.2014.03.024

Jiang, D., Zhuang, D., Fu, J., Huang, Y., and Wen, K. (2012). "Bioenergy potential from crop residues in China: Availability and distribution," *Renewable and Sustainable Energy Reviews* 16(3), 1377-1382. DOI: 10.1016/j.rser.2011.12.012

Kryvoruchko, V., Machmüller, A., Bodiroza, V., Amon, B., and Amon, T. (2009). "Anaerobic digestion of by-products of sugar beet and starch potato processing," *Biomass and Bioenergy* 33(4), 620-627. DOI: 10.1016/j.biombioe.2008.10.003

Li, J., Zhang, R., Siddhu, M. A. H., He, Y., Wang, W., Li, Y., Chen, C., and Liu, G. (2015a). "Enhancing methane production of corn stover through a novel way: Sequent pretreatment of potassium hydroxide and steam explosion," *Bioresource Technology* 181, 345-350. DOI: 10.1016/j.biortech.2015.01.050

Li, L., Feng, L., Zhang, R., He, Y., Wang, W., Chen, C., and Liu, G. (2015b). "Anaerobic digestion performance of vinegar residue in continuously stirred tank reactor," *Bioresource Technology* 186, 338-342. DOI: 10.1016/j.biortech.2015.03.086

Liu, X., Zicari, S. M., Liu, G., Li, Y., and Zhang, R. (2015b). "Improving the bioenergy production from wheat straw with alkaline pretreatment," *Biosystems Engineering* 140, 59-66. DOI: 10.1016/j.biosystemseng.2015.09.006

Liu, X., Zicari, S. M., Liu, G., Li, Y., and Zhang, R. (2015a). "Pretreatment of wheat straw with potassium hydroxide for increasing enzymatic and microbial degradability," *Bioresource Technology* 185, 150-157. DOI: 10.1016/j.biortech.2015.02.047

National Bureau of Statistics of China (2013). *China Statistical Yearbook,* National Bureau of Statistics of China, Beijing, China.

Owen, W. F., Stuckey, D. C., Healy, J. B., Young, L. Y., and McCarty, P. L. (1979). "Bioassay for monitoring biochemical methane potential and anaerobic toxicity," *Water Research* 13(6), 485-492. DOI: 10.1016/0043-1354(79)90043-5

Pang, Y. Z., Liu, Y. P., Li, X. J., Wang, K. S., and Yuan, H. R. (2008). "Improving biodegradability and biogas production of corn stover through sodium hydroxide solid state pretreatment," *Energy and Fuels* 22(4), 2761-2766. DOI: 10.1021/ef800001n

Pienkos, P. T., and Zhang, M. (2009). "Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates," *Cellulose* 16(4), 743-762. DOI: 10.1007/s10570-009-9309-x

Ragnar, M., Henriksson, G., Lindström, M. E., Wimby, M., Blechschmidt, J., and Heinemann, S. (2002). "Paper and pulp," in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co DOI:10.1002/14356007.a18_545.pub4

Rincón, B., Heaven, S., Banks, C. J., and Zhang, Y. (2012). "Anaerobic digestion of whole-crop winter wheat silage for renewable energy production," *Energy and Fuels* 26(4), 2357-2364. DOI: 10.1021/ef201985x

Song, Z. L., Yang, G. H., Guo, Y., and Zhang, T. (2012). "Comparison of two chemical pretreatments of rice straw for biogas production by anaerobic digestion," *BioResources* 7(3), 3223-3236. DOI: 10.15376/biores.7.3.3223-3236

Srirangan, K., Akawi, L., Moo-Young, M., and Chou, C. P. (2012). “Towards sustainable production of clean energy carriers from biomass resources,” *Applied Energy* 10, 172-186. DOI: 10.1016/j.apenergy.2012.05.012

Triolo, J. M., Sommer, S. G., Moller, H. B., Weisbjerg, M. R., and Jiang, X. Y. (2011). “A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential,” *Bioresource Technology* 102(20), 9395-9402. DOI: 10.1016/j.biortech.2011.07.026

Van Soest, P. J., Robertson, J. B., and Lewis, B. A. (1991). “Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition,” *Journal of Dairy Science* 74(10), 3583-3597. DOI: 10.3168/jds.S0022-0302(91)78551-2

Xiao, X., Zhang, R. H., He, Y. F., Li, Y. Q., Feng, L., Chen, C., and Liu, G.Q. (2013). “Influence of particle size and alkaline pretreatment on the anaerobic digestion of corn stover,” *BioResources* 8(4), 5850-5860. DOI: 10.15376/biores.8.4.5850-5860

Xu, J., Zhang, X., and Cheng, J. J. (2012). “Pretreatment of corn stover for sugar production with switchgrass-derived black liquor,” *Bioresource Technology* 111, 255-260. DOI: 10.1016/j.biortech.2012.02.006

Zhang, R., El-Mashad, H. M., Hartman, K., Wang, F., Liu, G., Choate, C., and Gamble, P. (2007). “Characterization of food waste as feedstock for anaerobic digestion,” *Bioresource Technology* 98(4), 929-935. DOI: 10.1016/j.biortech.2006.02.039

Zhang, X., Xu, J., and Cheng, J. J. (2011). “Pretreatment of corn stover for sugar production with combined alkaline reagents,” *Energy and Fuels* 25(10), 4796-4802. DOI: 10.1021/ef201130d

Zhao, S., He, P., Qiu, S., Jia, L., Liu, M., Jin, J., and Johnston, A. M. (2014). “Long-term effects of potassium fertilization and straw return on soil potassium levels and crop yields in north-central China,” *Field Crops Research* 169, 116-122. DOI: 10.1016/j.fcr.2014.09.017

Zheng, M., Li, X., Li, L., Yang, X., and He, Y. (2009). “Enhancing anaerobic biogasification of corn stover through wet state NaOH pretreatment,” *Bioresource Technology* 100(21), 5140-5145. DOI: 10.1016/j.biortech.2009.05.045

Zheng, Y., Zhao, J., Xu, F., and Li, Y. (2014). “Pretreatment of lignocellulosic biomass for enhanced biogas production,” *Progress in Energy and Combustion Science* 42, 35-53. DOI: 10.1016/j.pecs.2014.01.001

Article submitted: December 28, 2015; Peer review completed: February 27, 2016; Revised version received: March 22, 2016; Accepted: March 29, 2016; Published: April 6, 2016.
DOI: 10.15376/biores.11.2.4550-4563