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Enhanced corn-stover fermentation for biogas production by NaOH pretreatment with CaO additive and ultrasound

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ABSTRACT

Corn stover provides a great potential of bioenergy and biomaterial production through biorefinery, rather than being discarded as solid wastes. Appropriate pretreatments can enhance the biodegradability and digestion efficiency of lignocellulosics, and NaOH pretreatment is considered as an effective method. However, most NaOH pretreatments are usually performed at high temperatures (>100 °C) and over a long reaction time (~days). In this study, we utilize both CaO-additive and ultrasound technique to improve the cost-effectiveness of NaOH pretreatment of corn stover at relatively low temperatures for a short treatment time. We first evaluate the effect of CaO/ultrasound-assisted NaOH pretreatment on the properties of corn stover, and then determine the performance of subsequent biogas production. We also estimate the costs and benefits of the entire biogas production processes. The results indicated that the developed CaO-and-ultrasound-assisted NaOH pretreatment could effectively improve the lignin conversion to 60% and promote the biogas production through anaerobic digestion to over 500 mL per gram of total solids. The benefit-cost ratio of the proposed pretreatment was estimated as 1.39–1.65, suggesting that the combination of ultrasound and CaO addition should result in a higher lignin conversion, and thus enhance the cost-effectiveness of biogas production.

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1. Introduction

Anaerobic digestion is considered an effective approach to dealing with organic wastes, such as lignocellulosic substrate, by converting the organic components into bioenergy. The digestate (a sludge-like by-product from anaerobic digestion) also can be utilized in agriculture as fertilizers or soil conditioners, if proper post-treatments are applied for ensuring the environmental sustainability. Therefore, wider application of anaerobic digestion technologies for organic matters could facilitate more rapid realization of circular bioeconomy.

Despite the high maturity of technology development, anaerobic digestion is still suffered by several challenges, such as flexibility of acceptable substrate (Masebinu et al., 2019) and process efficiency (Siddique and Wahid, 2018), especially for lignocellulosic substrates. Lignocellulosic substrates, such as corn stover (Gu et al., 2018; Li et al., 2018c), wheat straw (Yadav et al., 2019), vinasse (Liu et al., 2012), bagasse (Saratale et al., 2018), wood (Sun et al., 2011), switchgrass (Liu et al., 2015) and water clover such as Marsilea spp (Rajesh Banu et al., 2018), consist of high contents of cellulose, hemicellulose and lignin. However, these lignocellulosic components cannot be readily utilized to produce biogas through saccharification and fermentation because of their polymeric structures. In particular, lignin is poorly biodegradable and limits the access to fermentable sugars by microorganisms in bioreactors, thereby reducing biogas (or biomethane) production. To achieve the cost-competitive biogas production, several studies have critically illustrated the importance and significance of efficient biomass pretreatment and lignin separation (or conversion) due to its diverse structure and complex chemistry (Wang et al., 2019; Xu et al., 2018).

Pretreatment is an essential step to disrupt lignin in biomass and enhance the accessibility of lignocellulosic compounds (Li et al., 2018b; Pan et al., 2016). Appropriate pretreatments also could weaken the intra- and intermolecular hydrogen bonds in

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cellulose and enhance its hydrolysis to platform compounds, such as glucose and bio-alcohol (Gallezot, 2012; Kim et al., 2008). Conventional pretreatments for lignocellulosic biomass, such as mechanical milling (Pan et al., 2015a), dilute acid (Duan et al., 2019), alkaline (Li et al., 2018a) and hot water (Md Yunos et al., 2017) methods, have been extensively studied. In continuous fermentation, alkali is usually added to regularly adjust the pH value of fermentation fluid (Liu et al., 2012). It is noted that the lignocelluloses pretreated by alkali can continuously provide the weak basicity to counteract the acid present in fermented liquid, thereby potentially reduce the overall operating costs. The commonly-used alkaline source for alkaline pretreatment is NaOH. Liu et al. (2018) applied NaOH for acidogenic effluent to pretreat corn stover and found that the methane production was successfully improved by 37%, compared to only NaOH-pretreated corn stover. Kuhn et al. (2016) also conducted a pilot-scale batch alkaline pretreatment of corn stover, where the maximum lignin dissolution of ~54% could be obtained when 7% NaOH was applied at 140 °C. Like this case, most NaOH pretreatments have been performed at relatively high temperatures (above 100 °C) and over a long reaction time (up to a few days) to ensure effective dissolution of lignin.

Recently, several advanced techniques, such as ultrasound (Yuan et al., 2019a), microwave (Kavitha et al., 2016), electron beam (Leskinen et al., 2017), heavy ion beam (Xu et al., 2019), ionic liquid (Mahmood et al., 2017) and thermochemical dispersion disintegration (Rajesh Banu et al., 2018), have been increasingly applied for pretreatment of feedstock to anaerobic digesters. Ultrasonication as a process intensification technique has attracted great attention because of its relatively cost-effective and environment-friendly features. Ultrasound combined with proper solvents allows destruction of lignocellulosic structures and thus increases the product yields of thermochemical and/or biochemical reactions by up to 300% (Luo et al., 2014). For instance, Nakashima et al. (2016) combined ultrasound (20 kHz for 3 h) with sodium percarbonate (Na_2CO_3: 0.4 mol/L and H_2O_2: 0.6 mol/L), and successfully improved the saccharification of cellulose and hemicellulose in lignocellulosic substrates. Despite the recent progress in ultrasonic technologies, performance evaluation of ultrasound-assisted approach to different pretreatments for a variety of biomass feedstocks is rarely published.

Every year, a significant amount of corn stover as agricultural waste is produced around the world, e.g., the annual production of corn stover only in China is over 220 million tonnes (Ministry of Agriculture, 2016). If corn stover, which also mainly consists of cellulose, hemicellulose, and lignin, is properly pretreated and solubilized, it can be more efficiently converted to biofuels like biogas. In this study, we apply ultrasound and CaO for assisting NaOH pretreatment of corn stover as feedstock for anaerobic biogas production. Here, we keep the reaction temperature relatively low (e.g., 30–50 °C) and treatment time short to improve the cost-effectiveness of the NaOH pretreatment. We first evaluate the effect of CaO- and ultrasound-assisted NaOH pretreatment on the properties of corn stover. Then we determine the biodegradability and digestion efficiency of the pretreated substrate based on cumulative biogas production and technical digestion time. Lastly, we perform a preliminary economic analysis to estimate the costs and benefits of the entire processes from feedstock pretreatment to biogas production. To the best of our knowledge, no research has been done on the performance evaluation of ultrasound-assisted NaOH pretreatment at mild temperatures (e.g., 30–50 °C) for corn stover.

2. Materials and methods

2.1. Materials

Corn stover was harvested from the farms located at Liuhe District, Nanjing City (Jiangsu Province, China). Corn stover was dried, chopped and then ground to particle sizes of 250–380 μm (i.e., 40–60 mesh) by a disintegrator (FW100, Tianjin Taisite Instrument Co., China). The ground samples were, then, sealed in plastic bags with zippers and stored at room temperature until use.

Sludge used in this study was obtained from the wastewater treatment plant of the Nanjing General Brewery (Nanjing City, China), and acclimatized for 30 d to provide preferably microbial growth. Table 1 presents the physico-chemical properties of corn stover and sludge, such as the total solid (TS) and volatile solid (VS), used in this study and those reported in the literature. The TS and VS contents of corn stover used in this study were about 96.2% and 94.1%, respectively. The contents of cellulosic and hemicellulosic biopolymers and lignin were comparable with others.

2.2. Analytical methods

The fiber analysis for cellulose, hemicellulos, and lignin in corn stover was performed according to the van Soest method (van Soest et al., 1991). The ash content was measured by burning the residual samples at 575 °C for 6 h. Total nitrogen (TN) was determined using the analyzer (Digital Autoanalyzer III, Bran + Luebbe GmbH, Norderstedt, Germany). The amount of reducing sugars in hydrolysate was determined by the 3, 5–dinitrosalicylic acid method (Ghose, 1987; Miller, 1959). After pretreatment, the carbohydrates in corn stover would break down into various types of monosaccharides and/or polysaccharides. Lignin is usually fractionated into materials with different molecular weights and the amount of lignin conversion before and after the pretreatment was determined based on the fiber analysis.

2.3. Ultrasound/CaO intensified NaOH pretreatment

In pretreatment experiments without ultrasound, 9.1 g of dried corn stover was mixed with 91 mL of deionized water to form a slurry (a liquid-to-solid ratio of 10 w/w, according to the results mostly suggested in the literature (He et al., 2015; Hong et al., 2015; Li et al., 2012)). The designated amounts of CaO and NaOH (i.e., 0–6% and 0–6%, respectively) were introduced in the slurry at 30–50 °C for 6–12 h. In pretreatment experiments with ultrasound, 5 g of dried corn stover was mixed with 100 mL of deionized water to form a slurry (a liquid-to-solid ratio of 20 w/w, i.e., the optimal ratio based on our preliminary tests). The prepared slurry samples were pretreated by ultrasound with the power of 150 W and frequency of 40 kHz (KQ3200V, Kunshan Ultrasonic Instruments Co., Kunshan, China). The ultrasound tests were conducted at 50 °C for 0.5 h. In the course of the pretreatment, the pH values of slurry samples were measured. After the pretreatment, the lignin conversion of corn stover (η, %) was determined by Eq. (1) based on the solubilized amounts of corn stover lignin in the solution.

$$\eta\ (\%) = \frac{C_{L,o} - C_{L,p}}{C_{L,o}} \times 100 \tag{1}$$

where $C_{L,o}$ and $C_{L,p}$ are the content of lignin in corn stover before and after pretreatment, respectively. The pretreated corn stover slurry samples were supplied to the subsequent anaerobic fermentation for biogas production.

2.4. Anaerobic fermentation

The performance of anaerobic digestion of the pretreated corn stover was evaluated in a reactor with a total volume and a working volume of 250 mL and 170 mL, respectively. The corn

Table 1
Physico-chemical properties of raw corn stover and sludge used in this study and those reported in the literature.

Item	Composition	Unit	Corn stover						Sludge
			This study	Yuan et al. (2019b)	Wei et al. (2015)	Song et al. (2019)	Wen et al. (2019)	Yang et al. (2019)	This study
Proximate analysis	Moisture	%	3.9	–	–	–	–	–	75.2
	TS	%	96.2 [a]	94.6	93.4	95.3	94.9	94.1	24.8 [a]
	VS	%	94.1 [a]	88.1	84.5	86.9	96.3	89.0	13.1 [a]
	TN	%	0.84	1.01	1.12	0.75	0.69	0.78	–
	C/N ratio	%	53.0	44.8	39.0	53.0	64.1	49.5	–
	Ash	%	6.0	–	–	–	–	–	–
Fiber analysis	Cellulose	%	30.7	38.6	35.0	37.1	39.9	34.1	–
	Hemicellulose	%	27.4	30.3	31.4	27.6	31.5	28.4	–
	Lignin	%	14.1	8.7	14.5	5.4	4.4	5.57	–

[a] The TS content was determined at the conditions of 102 ± 2 °C for 3 h, while the VS content was determined at 550 °C for 2 h according to the standard methods. Acronyms: TS (total solid), VS (volatile solid), TN (total nitrogen), C/N (carbon-to-nitrogen).

stover loading of 65 g/L was applied in the batch anaerobic digestion. The digesters were seeded with mixed liquor suspended solids (MLSS) of 15 g/L. To meet the desired MLSS value, in the case of alkaline pretreatment without ultrasound, the loadings of treated corn stover and sludge were 51.0 and 11.8 g/L, respectively, and the total water content was about 175 mL. For pretreatment with ultrasound, the loadings of treated corn stover and sludge were 34.0 and 8.0 g/L, respectively, and the total water content was 147 mL. The carbon-to-nitrogen (C/N) ratio in the digester was adjusted to 30 by NH_4Cl, which is the rule-of-thumb good ratio for anaerobic bacterial growth (Siddique and Wahid, 2018). In the course of fermentation experiments, the batch bioreactors were placed in a thermostat water bath incubated at 37 ± 1 °C. The volume of biogas production was monitored twice every day by a water displacement method and the corresponding cumulative biogas volume was calculated. Oxygen in each digester was purged by flushing nitrogen gas, and then all bottles were capped and sealed.

2.5. Preliminary economic analysis

Cost-benefit analysis is a policy instrument for decision-making that assesses the costs and benefits of one or more specific activities or projects. In this study, we conduct a preliminary cost-benefit analysis for different operating conditions of alkaline pretreatment for corn stover. The total costs include reagents (chemicals), fresh water use, and electrical energy for heating and ultrasound, as indicated in Eq. (2), while the benefits include the profit of biogas sale and the avoidance of corn stover disposal. The details of the economic analysis, such as process energy consumption and material prices, were illustrated in the Supplementary Information (Table S1).

$$C = M \cdot (A_1 n_1 + A_2 \cdot n_2 + A_3 \cdot (T - T_0) \cdot n_3 + A_4 \cdot t \cdot n_3 + A_5 \cdot n_3) \tag{2}$$

where C is the total cost of ultrasound-assisted alkaline pretreatment (USD), M is the mass of raw corn stover (kg), A_1 is the unit cost of NaOH (USD/kg), A_2 is the unit cost of CaO (USD/kg), A_3 is the cost for heating the hydrolysate for 1 °C (USD per kg of hydrolysate), A_4 is the cost of ultrasonic processes for an hour (USD per kg of hydrolysate), A_5 is the cost of fresh water (USD per kg of hydrolysate), n_1 is the mass of NaOH to pretreat one kg of raw corn stover (kg), n_2 is the mass of CaO to pretreat one kg of raw corn stover (kg), n_3 is the mass ratio of corn stover to fresh water (kg), T is the designated pretreatment temperature (°C), T_0 is the initial temperature (i.e., 30 °C), and t is the pretreatment time (h). Table S1 (see the Supplementary Information) summarizes the unit price of raw materials and chemicals used in the economic analysis.

To evaluate the cost effectiveness of different operating conditions, the benefit-cost ratio (*BCR*) is often calculated by Eq. (3):

$$BCR = B/C \tag{3}$$

where B and C are the total benefits and costs, respectively. The *BCR* presents the amount of the revenue gained per unit cost spent.

3. Results and discussion

3.1. Effect of CaO and NaOH pretreatment for lignin conversion

To evaluate the conversion of lignin via CaO-intensified NaOH pretreatment, we first conduct several experiments on independent CaO or NaOH pretreatments. Fig. 1(a), (b), and (c) show the effect of alkaline concentration, temperature, and treatment time on the conversion of lignin in corn stover (as determined by Eq. (1)), respectively, for independent CaO and NaOH pretreatment. The details of experimental data for independent CaO and NaOH pretreatment can be found in Tables S2 and S3. The conversion of lignin in corn stover using NaOH pretreatment was only significantly higher than that using CaO pretreatment ($p < 0.05$). As shown in Fig. 1(a), the conversion of lignin generally increased as the alkali concentration increased from 1% to 10%. In the case of NaOH pretreatment, the conversion of lignin increased particularly when NaOH concentration increased from 8% to 10%. The highest conversion ratio of lignin was 63% using 10% NaOH at 30 °C for 6 h, and the contents of cellulose increased from 270 to 470 mg/g-TS, accordingly. In the case of pretreatment with CaO only, the conversion of lignin gradually increased as the alkali concentration increased from 2% to 10%. The highest conversion ratio of lignin was only 34% using 10% CaO at 30 °C for 6 h.

Temperature exhibits a remarkable effect on the conversion of lignin in corn stover, especially for NaOH pretreatment. For instance, as the temperature increased from 20 °C to 60 °C, the conversion of lignin using NaOH pretreatment significantly increased: 24% at 20 °C to 50% at 60 °C ($p < 0.05$). In the case of CaO pretreatment, the conversion of lignin increased from 18% to 30% with the increase of temperature from 20 °C to 50 °C. However, when the temperature further increased from 50 °C to 60 °C, the lignin conversion decreased to 27%. This lower conversion might be attributed to the following reasons: (i) the water solubility of CaO decreased as the temperature increased, e.g., ~1.65 g/L at 20 °C and ~1.16 g/L at 60 °C (NLA, 2019); (ii) the cross-linked calcium ions with lignin molecules would further decrease the solubilization of lignin during the alkaline pretreatment (Xu et al., 2016). Despite the low lignin conversion at higher temperatures, the high lignin contents in pretreated lignocellulosic substances did not exhibit

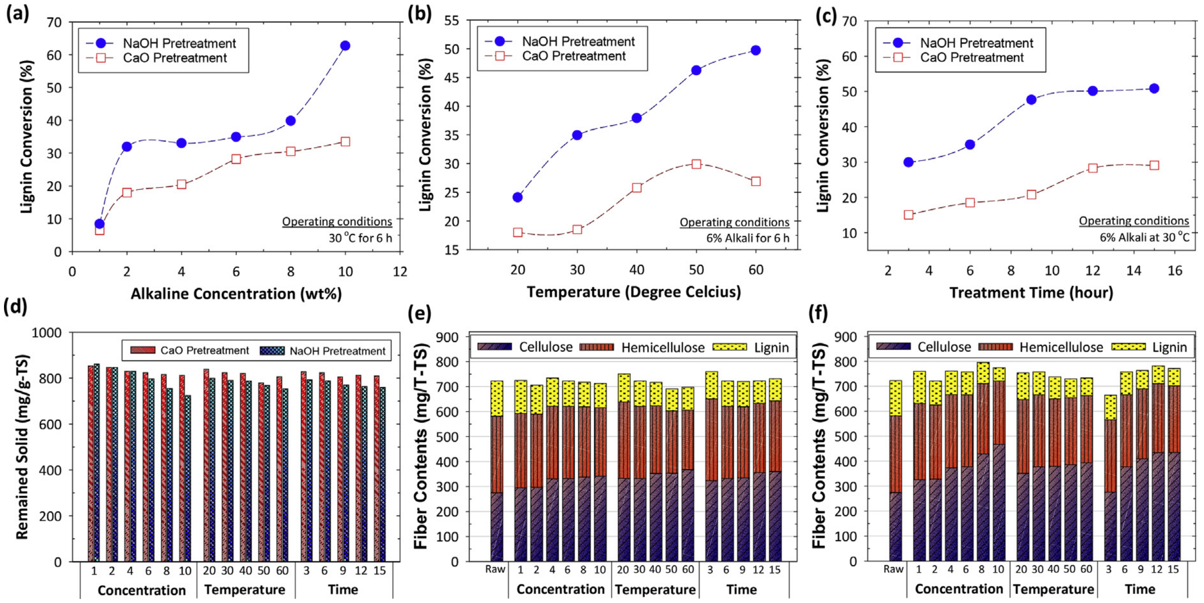

Fig. 1. Effect of (a) alkaline concentration, (b) temperature and (c) treatment time on lignin conversion for independent CaO or NaOH pretreatment. (d) effect of operating factors on remained solid content. Fiber analysis of corn stover before and after (e) CaO or (f) NaOH pretreatment.

harmful impacts on the subsequent hydrolysis and digestion processes (Xu et al., 2010).

Similarly, treatment time plays an important role in the conversion of lignin as well as the operating costs of pretreatment. It is also noted that a short time of alkaline pretreatment is beneficial to retaining the obtained cellulose from further reacting with OH- ions. In general, the conversion of lignin in corn stover increased as the pretreatment time increased. For corn stover pretreated with NaOH, the lignin conversion incrementally increased from 3 to 9 h. After 9-h pretreatment, however, the conversion of lignin was limited and slowly increased, which would result in a significant increase of the operating costs. Similar observations were made in the case of CaO pretreatment that the conversion of lignin increased from 3 to 12 h and remained almost unchanged afterward.

During alkaline pretreatment, solid loss would substantially compromise with the total amount of available sugar recovery in the subsequent enzymatic hydrolysis, which is of great concern especially when a strong base or severe pretreatment conditions are applied. As shown in Fig. 1(d), decreasing alkaline loading, temperature, and treatment time favored the reduction of solid loss during alkaline pretreatment. The amount of remaining solid after the CaO pretreatment was generally greater than that after the NaOH pretreatment. For instance, in the case of 6% alkali at 30 °C, approximately 0.78–0.84 g-solid/g-TS remained after the CaO pretreatment, while 0.75–0.80 g-solid/g-TS remained after the NaOH pretreatment. This was attributed to the fact that, compared to sodium ions, divalent calcium ions had a higher affinity for lignin and could provide more linkages within the corn stover that are negatively charged at alkaline conditions due to the ionization of functional groups (e.g., carboxyl, methoxy and hydroxyl). This could provide better resistance against solubilization and thus avoid serious solid loss during alkaline pretreatment. A similar observation was reported in the literature (Xu and Cheng, 2011).

Besides the lignin conversion, Figs. 1(e) and (f) compare the compositions of insoluble solids after CaO and NaOH pretreatments, respectively, at various alkaline loadings, temperatures and treatment times. The far-left column represents the composition of the raw corn stover prior to alkaline pretreatment. The results indicated that the content of cellulose generally increased after the pretreatment, which varied from 30 to 37% (for the CaO pretreatment) and 28–47% (for the NaOH pretreatment). In particular, the cellulose content significantly ($p < 0.05$) increased as the NaOH-pretreatment time was prolonged. The content of hemicellulose also exhibited a significant difference for various alkaline loadings and treatment times ($p < 0.05$). As the temperature increased from 20 °C to 60 °C, the content of hemicellulose in insoluble solids after pretreatment decreased. This might be attributed to the higher degradation rate of hemicellulose under the CaO or NaOH pretreatment at a higher temperature.

3.2. *Efficacy of CaO-intensified and ultrasound-assisted NaOH pretreatment*

According to the aforementioned results, we found that the performance of lignin conversion using NaOH pretreatment only was superior to that using CaO pretreatment only. However, CaO can be considered a supplementary reagent to NaOH for improving process economics of alkaline pretreatment, especially at an ambient temperature. The usage of both CaO and NaOH could be manipulated to achieve a cost-effective pretreatment as CaO is much cheaper than NaOH (You et al., 2019). Also, as the solubility of CaO is relatively low, a significant amount of CaO would exist in the form of insoluble solids and gradually dissolve to supplement the alkalinity consumed by the corn stover.

Here, we perform additional experiments for evaluating the effect of CaO addition (i.e., CaO-intensified) on the performance of NaOH pretreatment. Fig. 2(a) shows the conversion of lignin in corn stove via CaO-intensified NaOH pretreatment, with various alkali concentration from 2% to 6%. The details of experimental data can be found in Table S4. The results indicated that the CaO addition could significantly enhance the performance of the NaOH pretreatment for lignin conversion ($p < 0.05$). The conversion of lignin generally increased as CaO and/or NaOH doses increased. Under the conditions of 50 °C for 12 h, the maximum lignin conversion of 47% could be obtained by 6%-CaO and 6%-NaOH pretreatment. Fig. 2(a) also shows the amount of reducing sugar in the solution after the CaO-intensified NaOH pretreatment. Similar trends of the lignin

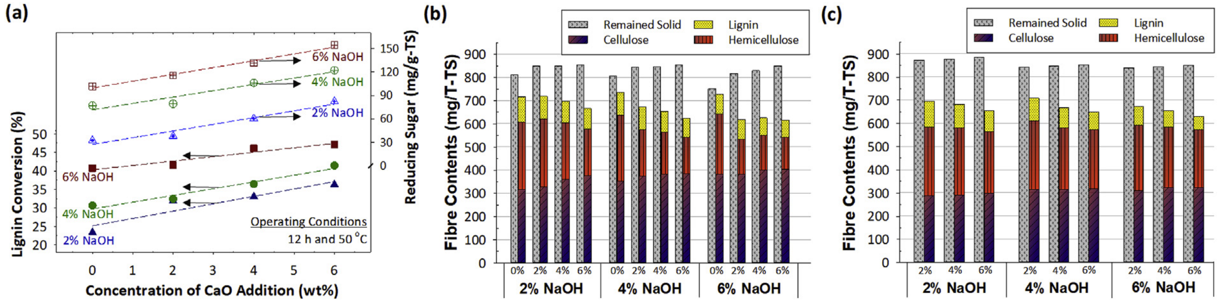

Fig. 2. (a) Conversion of lignin (solid symbols) in corn stove and content of reducing sugar (hollow symbols) in hydrolysate via CaO-intensified NaOH pretreatment. Changes in contents of remained solid, lignin, hemicellulose and cellulose (b) after CaO-intensified NaOH pretreatment operated at 50 °C for 12 h, and (c) after ultrasound-assisted and CaO-intensified NaOH pretreatment at 50 °C for 0.5 h.

conversion were observed for the amount of the reducing sugar in the solution. The maximum amount of reducing sugar in the solution was approximately 155 mg/g-TS in the case of 6%-CaO and 6%-NaOH pretreatment.

Fig. 2(b) shows the amount of remaining solid and the compositions of insoluble solids after the CaO-intensified NaOH pretreatment with different alkaline loadings at 50 °C for 12 h. In general, the amount of remaining solids increased as the CaO concentration increased. It is also noted that the amount of remaining solids may include the insoluble portions of CaO additive (as indicated in Table 2). Within the temperature range between 30 °C and 50 °C, the CaO additive was found to be completely dissolved only in the case where its content was 1%. With the increase of the CaO concentration, the amount of insoluble CaO increased. It would be beneficial to maintaining the pH at a higher level throughout the pretreatment, thereby enhancing the performance of lignin conversion. As shown in Fig. 2(b), compared to NaOH pretreatment, the amount of corn stover retained can be successfully improved by the CaO-intensified NaOH pretreatment, while the lignin conversion was further enhanced. Due to the enhanced lignin conversion, the content of cellulose was found to increase with the increase of both CaO and NaOH concentrations.

To further enhance the performance of CaO-intensified NaOH pretreatment, we modify the experimental setup by applying external ultrasound during pretreatment. Since we anticipate the treatment time could be significantly reduced by ultrasound, the pretreatment herein was conducted for only 30 min, in comparison to the aforementioned treatment time of 12 h. The details of experimental data can be found in Table S5. Fig. 2(c) shows the composition changes of corn stover after the ultrasound-assisted alkaline pretreatment. The results indicated that the amount of the remained solids ranged between 840 and 885 mg/g-TS, while the conversion of lignin was found to be 22–60%. The ultrasound can enhance the mixing and reactions between alkaline reagents and lignin, thereby decreasing the treatment time (Bussemaker and Zhang, 2013). Therefore, the ultrasound treatment can effectively prevent the loss of solid and hemicellulose because lignin is less exposed to NaOH. A shorter alkaline treatment is also beneficial to retaining the cellulose contents since the hydrolysis of cellulose is a slow reaction and generally requires a longer reaction time. In summary, the lignin conversion of corn stover using the alkaline pretreatment combined with ultrasound technique was comparable with that using the alkaline pretreatment only. However, the alkaline treatment time could be remarkably reduced from 6 to 12 h down to 0.5 h at a similar temperature, thereby avoiding the loss of other components such as cellulose and hemicellulose.

Table 2
Amount of insoluble CaO at different concentrations and temperatures.

No.	CaO (g/g-TS)	Equivalent-Ca(OH)$_2$ (g)	Amount of insoluble CaO (g/g-TS)		
			30 °C	40 °C	50 °C
1	0.010	0.013	0.000	0.000	0.000
2	0.020	0.026	0.011	0.012	0.013
3	0.040	0.053	0.038	0.039	0.039
4	0.060	0.079	0.064	0.065	0.065
5	0.080	0.106	0.090	0.092	0.092
6	0.100	0.132	0.117	0.118	0.118

3.3. Ultrasound-enhanced alkaline pretreatment of corn stover for biogas production

Fig. 3(a) and (b) show the cumulative biogas production of corn stover pretreated without and with ultrasound, respectively. In general, the cumulative biogas production within the first 10 d among various pretreatment scenarios was not significantly different. However, after the 10th day, the biogas production of several scenarios with CaO-additive pretreatment remarkably increased, especially for the case using 4% CaO and 6% NaOH. This might be due to that, with CaO additive, the corn stover has a larger buffer capacity to compensate the adverse effect of acidification during the anaerobic digestion. The cumulative biogas production from the anaerobic fermentation of corn stover with CaO-intensified NaOH pretreatment (but without ultrasound) was 48% higher than that of the control sets, i.e., from ~330 to ~490 mL per gram of TS, using 4% CaO and 6% NaOH at 50 °C. In contrast, in the cases using a high CaO concentration of 6%, the biogas production was significantly reduced ($p < 0.05$). This might be attributed to the higher calcium concentration that results in the formation of calcium precipitates, leading to the scaling of biomass and reactors (Cao et al., 2015). The available nutrients in digesters may also be consumed due to the formation of calcium precipitates, and thus reduce the biomass activity (Deng et al., 2008). Despite the fact that calcium is one of the most important elements for microbial growth and stability, it would, if present in excess, inhibit the activity of certain methanogens. In the case where CaO-intensified NaOH pretreatment was applied along with ultrasound, the cumulative biogas production from the anaerobic fermentation of corn stover was enhanced (i.e., from ~300 to ~510 mL/g-TS) than that without ultrasound. More details on the pH value and daily biogas production are summarized in Figs. S1 and S2. It thus suggests that the ultrasound pretreatment could enhance biogas production due to its higher conversion efficiency for lignin in corn stover.

Methane is mainly produced during the methanogenic phase, which often requires a longer period of reaction time and a larger reactor volume. Therefore, engineers put a lot of efforts to improve anaerobic digestion efficiency to the reactor volume for the sake of cost-effectiveness. Here, we use the concept of technical digestion

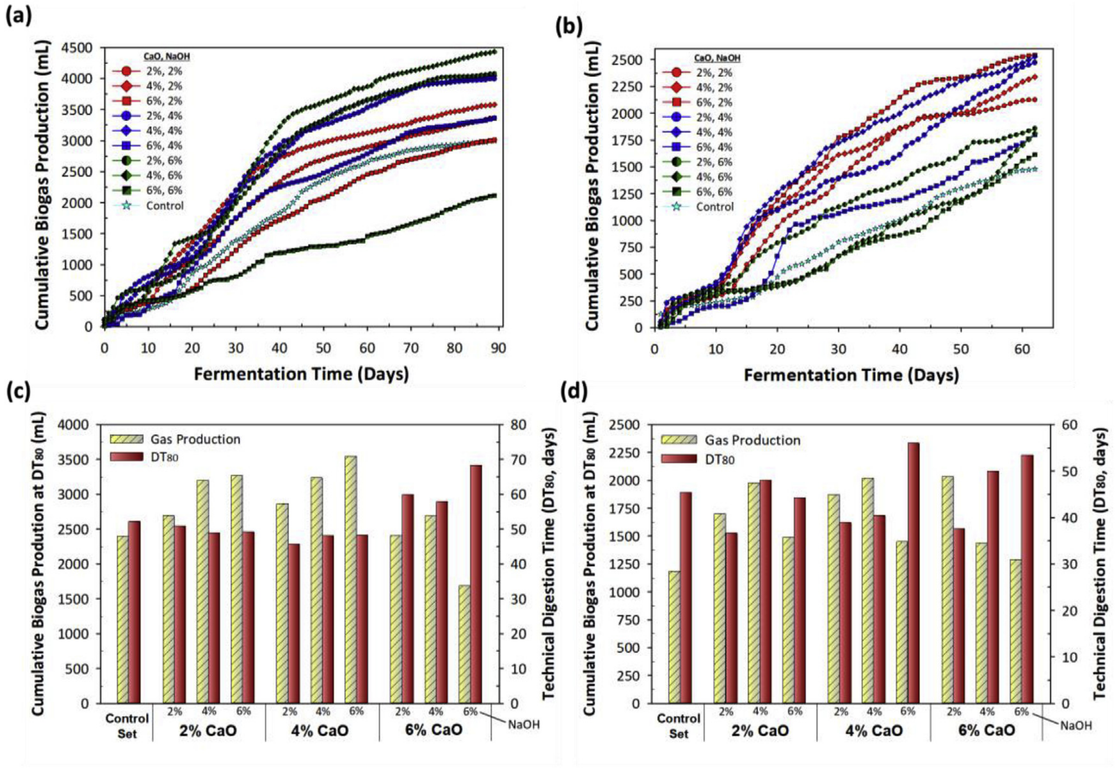

Fig. 3. Cumulative biogas production from anaerobic fermentation using (a) alkali pretreatment, and (b) alkali pretreatment intensified by ultrasonic pretreatment. The DT_{80} and its biogas production of fermentation using (c) alkali pretreatment, and (d) alkali pretreatment intensified by ultrasonic pretreatment.

time (DT_{80}) to evaluate the biodegradability (or digestion efficiency) of the pretreated substrate. The DT_{80} represents the time needed to reach 80% of the maximal biogas production. Fig. 3(c) and (d) show the DT_{80} and its associated cumulative biogas production using corn stover pretreated without and with ultrasound, respectively. For the pretreatment without ultrasound, the DT_{80} of the corn stover pretreated by 6% CaO additive was generally higher than that of the control, which would not be desirable. Pretreatment using 4% CaO additive exhibited a relatively shorter DT_{80} (~48 d) compared to the control, where, at the point of DT_{80}, a biogas production of 360—390 mL/g TS could be achieved. With the additional effects from ultrasound during the CaO and NaOH pretreatment, the DT_{80} could be reduced up to 31% if the same alkaline concentration was applied. The cumulative biogas production at DT_{80} for all cases with ultrasound applied was greater than that of the control, indicating that the ultrasound could positively affect the biogas production. By balancing the DT_{80} and its biogas production, the suitable DT_{80} value was determined to be around 37.5 d (in the case of 6% CaO and 2% NaOH) with the biogas production of ~405 mL/g-TS.

Fig. 4(a) and (b) show both the remaining VS content and the VS reduction after digestion of corn stover pretreated without and with ultrasound, respectively. In general, the more VS reduced as the higher alkaline concentration was applied. In the case where ultrasound was additionally applied, the maximum VS reduction of 35% could be achieved with the corn stover pretreated with 4% CaO and 6% NaOH. However, the patterns and trends of the VS content and reduction for the case with ultrasound were quite different compared to those without ultrasound. Since the ultrasound pretreatment would generally reduce DT_{80}, the VS reduction in some cases was lower. With the ultrasound pretreatment, the maximum VS reduction of 50% could be achieved in the case of using 6% CaO and 2%NaOH.

Table 3 compares the pretreatment conditions and their associated biogas and methane yields from anaerobic digestions with corn stover reported in the literature. Independent alkaline pretreatment is usually performed at a long time from several hours up to 3 days. As shown in this study, alkaline pretreatment intensified by other chemicals (e.g., CaO) or techniques (e.g., ultrasound) could effectively reduce the treatment time down to less than an hour, while achieving a similar lignin conversion efficiency. Moreover, Kuhn et al. (2016) developed the anthraquinone-intensified alkaline pretreatment, and the maximum lignin conversion of 54% could be achieved with a 7%-NaOH pretreatment at 140 °C. In this study, a similar lignin conversion of 46% could be achieved when the feedstock was pretreated using the mixture of 6% NaOH and 4% CaO at 50 °C. This indicated that the combined physico-chemical approaches could also lower the required temperature to achieve a similar level of lignin conversion. The interactions (significance) among alkaline concentrations, reaction temperatures and the use of additional physical pretreatment on the lignin conversion should be evaluated in our future study. For the subsequent biogas production, we found that a higher lignin conversion did not necessarily result in greater biogas production. In this study, a maximum biogas production of 510 mL/g-TS, corresponding to a lignin conversion of ~42% (which was not the highest), could be achieved with the ultrasound-assisted CaO-intensified NaOH pretreatment at 50 °C for 30 min. This might be attributed to the fact that, with the use of CaO in the pretreatment, the cross-linked calcium ions with lignin would decrease the solubilization of lignin (thus lignin conversion), while afterward providing a buffer capacity to compensate the adverse effect of acidification during the anaerobic digestion.

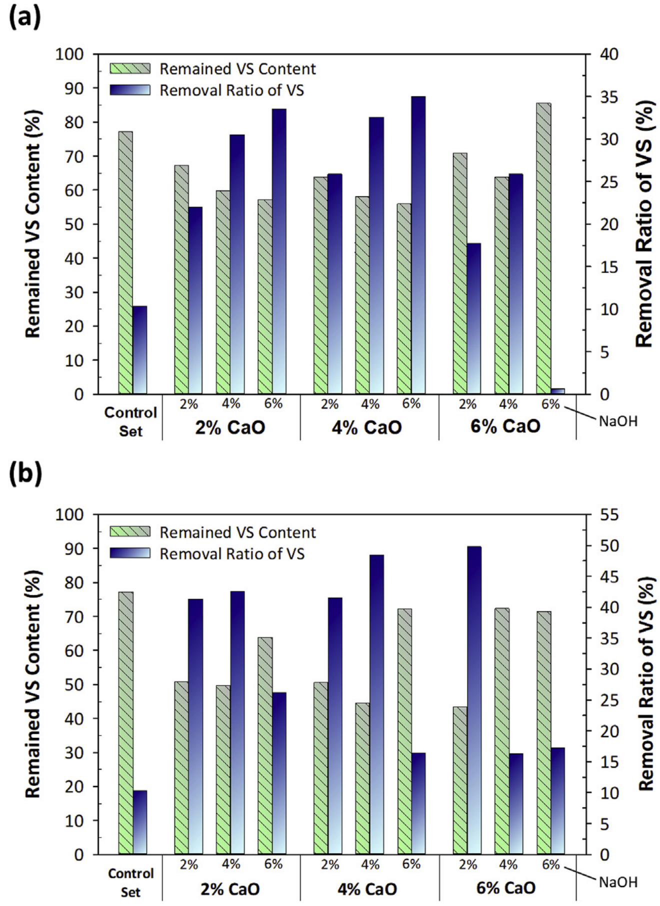

Fig. 4. The content and removal ratio of VS after fermentation in the case of using (a) alkali pretreatment, and (b) alkali pretreatment intensified by ultrasonic pretreatment.

3.4. Benefit-cost ratios for pretreatments with different operating conditions

The benefit-cost ratio (BCR), i.e., the relative net revenue per spent cost, is a useful indicator to evaluate the economic feasibility of different processes or operations. This suggests that the operating costs of pretreatment could be compensated by the profits from the biogas sales. Table 4 presents the costs and benefits of alkaline pretreatment with different operating conditions for corn stover. It was observed that the cost for NaOH generally shared a large portion of the total costs. Without the ultrasound assistance, NaOH pretreatment using a low alkaline concentration (i.e., 4% rather than 6%) exhibited a higher BCR, despites its lower biogas production. Similar observations were found in the case of CaO-enhanced NaOH pretreatment. For instance, in the case of 4% CaO additive, the pretreatment using 4% NaOH had a higher BCR (i.e., 1.49) than that using 6% NaOH (i.e., 1.25). In any case, the BCR of alkaline pretreatments without ultrasound ranged between 1.28 and 1.68. In contrast, the ultrasound-assisted CaO-enhanced NaOH pretreatment exhibited a great potential to achieve the cost effectiveness. At a similar operating temperature and alkaline concentration, the BCR of the alkaline pretreatment with ultrasound ranged between 1.39 and 1.65. The maximum BCR was found to be 1.65, where the ultrasound-assisted alkaline pretreatment was applied with 6% CaO and 2% NaOH at 50 °C for 0.5 h. The ultrasound can effectively reduce the pretreatment time, while increasing the amount of subsequent biogas production. A less pretreatment time will result in a higher treatment capacity per land footprint or a smaller reactor size per treatment capacity, thereby leading to a lower capital cost.

In this study, the uncertainty of the economic analysis includes the biogas sale price and electricity cost. The source and situation of biogas supply and demand are quite different among different countries (Scarlat et al., 2018). After purification and upgrading, biogas can be utilized in the form of electricity (biopower), heating (bioheat) and fuels (biochemicals), thereby resulting in a great variation of biogas prices. Typically, the prices of biogas rely on several factors, such as the feed-in tariff system and the ownership of biogas plants and power grids. In Europe, the financial valuations of biogas vary from 1 to 12 EuroCt/kWh, depending on the utilization paths (Herbes et al., 2018). In addition, the distance between the source of lignocellulosic substrate and biogas plants would influence the cost-effectiveness of the biogas production. Pan et al. (2015b) indicated that the concept of industrial symbiosis by sharing services, information, and industrial byproducts should be considered when designing a waste-to-energy and —resource supply center. Thus, the total costs to the business can be effectively reduced, while maximizing the overall utilization efficiency of energy and resource. Nonetheless, an uncertainty analysis on economic viability for pilot-scale operations should be performed in a future study. It also should be noted that the costs considered in this analysis include the fresh water use; however, we could use alternative water sources (e.g., processwater) for anaerobic digestion. In other words, the total costs for feedstock and materials could be reduced. Similarly, the digestrate could be further treated and utilized as a fertilizer, depending upon the chemical compositions of the digestrate. This could provide additional benefits for the anaerobic digestion of corn stover, thereby increasing the BCR.

Table 3
Yields of biogas and methane from anaerobic processes performed with corn stover at different regimes using NaOH pretreatment.

Pretreatment [a]	Feedstock property [b]			Pretreatment condition				Performance of anaerobic bioreactor			Reference
	TS (%)	VS (%)	C/N (−)	Temp (°C)	Time (hr)	NaOH (wt%)	Lignin conversion (%)	C/N (−)	Biogas yields	Methane yields	
Independent NaOH	93	90	59	20	72	2	23	–	420 mL/g-VS	230 mL/g-VS	Zheng et al. (2010)
Acidogenic effluent of NaOH	94	83	57	20	72	2	–	25	550 mL/g-VS	340 mL/g-VS	Liu et al. (2018)
Intensified by anthraquinone	93	–	–	140	0.5	7	54	–	–	–	Kuhn et al. (2016)
Intensified by methanol	–	–	–	80	1	10	55	–	–	–	Yuan et al. (2018)
Intensified by 5% CaO	–	–	56	25	6	7.5	45	25	–	320 mL/g-VS	You et al. (2019)
Independent NaOH	96	94	53	50	12	6	41	30	330 mL/g-TS	–	This study
Intensified by 4% CaO	96	94	53	50	12	6	46	30	490 mL/g-TS	–	This study
Intensified by 6% CaO and UTS	96	94	53	50	0.5	2	42	30	510 mL/g-TS	–	This study

[a] UTS: ultrasound.
[b] TS: total solid; VS: volatile solid; C/N: carbon-to-nitrogen ratio.

Table 4
Cost and benefit of batch alkaline pretreatment with different operating conditions for corn stover.[a]

ID	Operating condition[b]				Cost (USD)							Benefit (USD)			BCR (−)
	CaO (%)	NaOH (%)	Temp (°C)	Time (hr)	UTS	NaOH	CaO	HT	UTS	Water	Total	Biogas[b]	Disposal avoidance	Total	
1	–	4	30	12	No	13.1 (73%)	0.0 (0%)	0.0 (0%)	0.0 (0%)	4.9 (27%)	18.0 (100%)	26.4 (87%)	3.9 (13%)	30.3 (100%)	1.68
2	–	6	30	12	No	19.7 (80%)	0.0 (0%)	0.0 (0%)	0.0 (0%)	4.9 (20%)	24.6 (100%)	27.6 (88%)	3.9 (12%)	31.5 (100%)	1.28
3	–	6	50	12	No	19.7 (72%)	0.0 (0%)	2.7 (10%)	0.0 (0%)	4.9 (18%)	27.3 (100%)	32.6 (89%)	3.9 (11%)	36.5 (100%)	1.34
4	–	6	30	12	No	19.7 (80%)	0.0 (0%)	0.0 (0%)	0.0 (0%)	4.9 (20%)	24.6 (100%)	31.1 (89%)	3.9 (11%)	35 (100%)	1.42
5	4	4	50	12	No	13.1 (57%)	2.3 (10%)	2.7 (12%)	0.0 (0%)	4.9 (21%)	23.0 (100%)	30.3 (89%)	3.9 (11%)	34.2 (100%)	1.49
6	4	6	50	12	No	19.7 (67%)	2.3 (8%)	2.7 (9%)	0.0 (0%)	4.9 (17%)	29.6 (100%)	33.2 (89%)	3.9 (11%)	37.1 (100%)	1.25
7	6	2	50	0.5	Yes	6.6 (22%)	3.4 (12%)	5.4 (18%)	4.3 (15%)	9.7 (33%)	29.5 (100%)	44.9 (92%)	3.9 (8%)	48.8 (100%)	1.65
8	4	4	50	0.5	Yes	13.1 (38%)	2.3 (7%)	5.4 (16%)	4.3 (12%)	9.7 (28%)	34.9 (100%)	44.6 (92%)	3.9 (8%)	48.5 (100%)	1.39

[a] Assume that USD 1.000 equals to CNY 7.000.

[b] UTS: ultrasound; HT: heating.

3.5. Implications of ultrasound-alkaline pretreatment: challenges and opportunities

It has been well-known that alkaline pretreatment could provide an effective approach to disrupting the structural linkages between lignin and cellulose, and thus reducing the extent of crystallinity and polymerization (Baruah et al., 2018), while avoiding fragmentation of hemicellulose (Behera et al., 2014). In this study, the results of the economic analysis revealed that the combined approaches, i.e., ultrasound-alkaline pretreatment, should be more cost-effective, compared to that obtained by using the alkaline method alone. From the perspective of alkaline treatment, CaO could be used as a supplementary reagent to NaOH for improving process economics (CaO is more economical than NaOH), especially at mild temperatures. Despite the similar lignin conversion, the CaO-assisted NaOH pretreatment was found to further enhance the biogas yield (510 mL/g-TS) compared to NaOH pretreatment alone (330 mL/g-TS). However, a major challenge of this chemical pretreatment still remains the recovery of the added alkalis (i.e., CaO and NaOH). One potential solution is to use electrokinetic cells for selectively separating the alkaline compositions from the hydrolysate. Also, the effect of different operating factors, such as solid loading and their interactions, on the lignin conversion and the operational costs should be systematically evaluated from the statistic point of view, which should be our future research.

4. Conclusions

In this study, we apply both ultrasound-assisted and CaO-additive approaches for enhancing NaOH pretreatment for corn stover at mild conditions, thereby achieving cost-effective biogas production. In general, a prolonging pretreatment time and increased alkaline concentration and temperature exhibit positive effects on improving the biodegradability of corn stover; however, the losses of total solid portions and cellulose contents would increase accordingly. We found that the use of CaO for replacing a portion of NaOH in pretreatment could be beneficial due to the following advantages. (i) Operating cost can be saved since CaO is much cheaper than NaOH. (ii) As the solubility of CaO is low, a significant amount of CaO exists in the form of solid and would gradually dissolve to supplement the alkalinity consumed by the corn stover pretreatment. Furthermore, the combination of ultrasound technique with alkaline pretreatment can significantly enhance lignin conversion and subsequent biogas production ($p < 0.05$). The results indicated that a maximum biogas production of 510 mL/g-TS was achieved using corn stoverpretreated with alkali and ultrasound at 50 °C for 30 min, compared to that without ultrasound. Considering the pretreatment costs and biogas sale profits, a maximum BCR of 1.65 could be achieved according to the benefit cost analysis. Our future research would focus on (i) developing electrokinetic separation for the recovery of the residual alkalis (i.e., CaO and NaOH) from hydrolysates, and (ii) evaluating the effect and interactions of different operating factors, such as solid loading, on the lignin conversion and subsequent biogas production.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.117813.

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