CO_2-assisted Hydrothermal Pretreatment of Corn Stover for Enhanced Biomethane Production

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Abstract

The hydrothermal pretreatment of lignocellulose biomass for anaerobic digestion applies high temperature and pressure conditions, which are high energy consumption. This study examined the pretreatment of corn stover using low-temperature hydrothermal pretreatment with CO_2, to achieve better anaerobic digestion efficiency. The solid, liquid fraction after pretreatment was exposed to anaerobic digestion to produce biogas. Over the range of pretreatment conditions (50, 70, 90°C and 3, 5 MPa of CO_2), the results showed that corn stover pretreated under 5 MPa CO_2 at 90°C caused the highest removal rate of 56.3 and 31.7% in hemicelluloses and cellulose respectively, which results in 5.8 g L^{-1} reducing sugar were released in the liquid fraction. The highest methane yield of 185.9 (solid fraction) and 242.7 mL (g-VS^{-1}) (liquid fraction) was obtained, which are 23.3 % and 61.1 % higher than that in untreated corn stover. The results showed that pre-treatments with CO_2 have the potential to reduce structural obstacles of lignocellulosic materials and enhance their anaerobic biodegradability.

Keywords: Lignocellulose biomass, Anaerobic digestion, Corn stover, Hydrothermal pretreatment, Biogas

1. Introduction

Global concerns about greenhouse gas emissions and global warming and the rapid decline of fossil fuels have prompted a worldwide search for sustainable energy sources to replace chemical fuels. Lignocellulosic biomass is a reliable and promising feedstock for renewable energy due to its ability to capture and store carbon.

Lignocellulosic biomass includes agricultural waste, dedicated energy crops, forest residues, and organic municipal solid waste. Studies show that 181.5 billion tons of lignocellulosic biomass is produced annually worldwide, and the vast majority are not being utilized. Maize (Maize), a crop that grows in a wide range of agroecological conditions around the world, is composed primarily of cellulose, hemicellulose, and lignin, a complex matrix of cellulose molecules wrapped in thick lignin and hemicellulose structures. For this reason, researchers around the world are investigating biorefinery concepts to convert corn stover into biofuels and other potential value-added products.

Anaerobic digestion (AD) is a mature technology that is widely used to convert biodegradable biomass residues into biogas. Among the many biofuels, biogas from AD is known to be the most cost-effective and environment-friendly and almost any organic material can be used as feedstock for the digestion process, adding value to non-valued lignocellulosic feedstock. AD systems using corn stover (CS) as feedstock have been widely studied by researchers. CS pretreatment technology is the most discussed topic due to the crystal structure of CS and the properties of AD.

Hydrothermal pretreatment is widely recognized as a clean and economical process due to the use of "water only" as the pretreatment medium. However, hydrothermal pretreatment for AD of lignocellulose biomass is highly energy-intensive due to the application of high temperature and pressure conditions. Against this background, we developed a CO2-assisted hydrothermal pretreatment to overcome this drawback.

2. Materials and Methods

2.1. Feedstock and inoculum

CS harvested from a farm owned by Hokkaido University was first pulverized to give pieces with about 10 mm. Then, crushed dry samples were further sieved to a size of 60 mesh. The inoculum was obtained from a biogas plant operated by the Hokkaido University farm at mesophilic conditions treating livestock manure.

2.2. CO_2-assisted hydrothermal pretreatment of CS

9 grams of milled, air-dried CS will mix with 90 g of distilled water solution placed in a temperature-controlled batch reactor with 190 mL volume. The reactor was connected to the liquid CO_2 tank and liquid CO_2 flowed into the reactor without a pump after passing through the heater, due to higher CO_2 cylinder pressure. After reaching the desired pressure (3 or 5 MPa), the reactor will be placed in a water bath for heating. CO_2 free conditions were obtained by supplying N_2 (0.5 MPa) to the reactor. The pretreatment temp was 50, 70 and 90℃ with or without CO_2, and the pretreatment time was held for 1 h.

2.3. AD setup and analytical methods

Solid, liquid fractions or whole slurry after pretreatment was exposed to AD under thermophilic conditions (53 ± 2°C) in a 200 mL triangular beaker to produce biogas under the inoculum to feedstock ratio of 2:1 (volatile solid based) for 30 days. Anaerobic conditions were maintained by supplying nitrogen gas to the reactor after feedstock was added.

For the analytical methods, the volatile solids (VS) and total solids (TS) were determined by drying wet samples at 105℃ for 24 h, followed by incineration at 600℃ for 3 h. The compositional analysis of solid fraction was conducted using a two-stage acid hydrolysis method using sulfuric acid. The content of total reducing sugar was determined by the 3,5-dinitrosalicy acid method.

3. Results and Discussion

3.1. Effects of pretreatment on CS characteristic

3.1.1.Changes in the solid fraction after pretreatment

Changes in total solid (TS) recovery after various pretreatment are shown in Figure 1. With increasing temperature and pressure, the TS recovery rates decreased and varied from 57.5 – 64.5 %. The recovery rates of TS were 64.5 – 61.9 %, 63.3 – 60.0 %, and 61.8 – 57.5 % at 50, 70, and 90°C under CO_2 free, 3 MPa and 5 MPa conditions. As expected, the highest total solid degradation was obtained in the most severe condition.

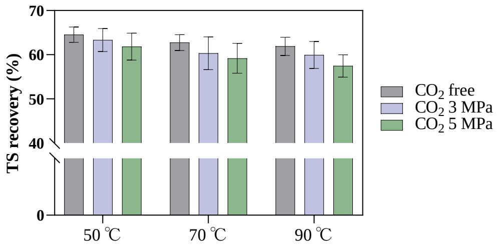

Figure 1. Changes of TS recovery rates after various pretreatments.

The chemical compositions of the untreated and pretreated CS after various pretreatment are shown in Figure 2. After the pretreatment, the hemicellulose content decreased from 32.7 to 24.4%, indicating the release and solubilization of hemicellulose after the pretreatment. The cellulose and lignin content increased from 35.6 – 41.6%, and 5.21 – 5.94%, respectively. The main reason for this is, the reduction amount of these components was less than the amount of TS reduction, which was reflected in the relative content increased in samples. The hemicellulose removal rate reached 56.3 % in the pretreatment at 90°C under CO_2 5 MPa, indicating that, CO2-assisted hydrothermal pretreatment could effectively remove hemicellulose Ma et al. (2022).

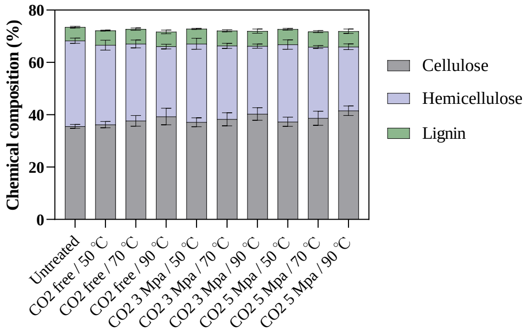

Figure 2. Chemical compositions of the CS after various pretreatments.

3.1.2. Changes in the liquid fraction after pretreatment

Changes of the reducing sugar yields after various pretreatments are shown in Figure 3. The concentration of reducing sugar increased with the pretreatment temperature and pressure, the highest yield was 5.8 g L^{-1}, achieved at 90°C at 5MPa. Which is 50.4% higher than that in CO_2 free conditions. These results indicated that CO2-assisted hydrothermal pretreatment can effectively extract reducing sugar from CS and may enhance corn stover digestibility and increase methane yields.

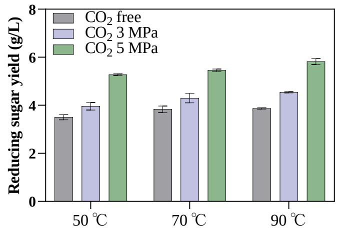

Figure 3. Changes of reducing sugar yields in liquid fraction after various pretreatments.

3.2. Biogas production

Figure 5 shows the cumulative CH_4 yield of untreated CS and solid and liquid fractions, after pretreatment. For the solid fraction, CH_4 production was varying from 150.7 to 185.9 mL (g-VS^{-1}), and the highest value was obtained in the condition of 90°C of 5 MPa, which was 23.3% higher than the untreated CS, indicating that pretreatment makes the solid fraction more susceptible to bacterial attack by altering its structural composition, thus the CH_4 yield has been improved. CH_4 production was varying from 213.1 to 242.7 mL (g-VS^{-1}) in liquid fraction, and the highest value was also obtained in the pretreated condition of 90°C of 5 MPa, which is 61.1% higher than the untreated CS. The liquid fraction yielded higher CH_4 yield compared to the solid fraction as most of the easily decomposed sugars are transferred to this phase during pretreatment.

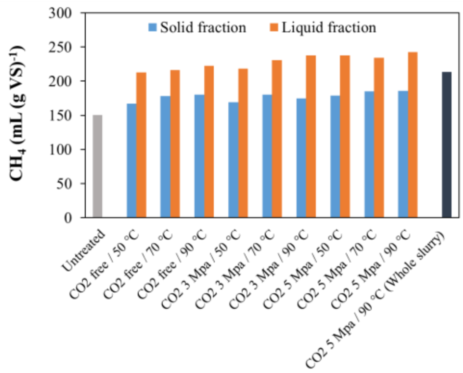

Figure 4. Cumulative methane yields of CS after various pretreatments.

4. Conclusions

CO_2-assisted hydrothermal pretreatment of CS was proposed to achieve enhanced CH_4 production. The results show that the proposed method can effectively remove hemicellulose from the solid fraction, making the solid fraction more susceptible to bacterial attack by changing its structural composition. Degradation products were transferred to the liquid fraction after pretreatment, thus yielding higher CH_4 yield compared to the solid fraction since most sugars were transferred to this phase during pretreatment and these sugars are easily decomposed during the AD process.

References

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