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Methane recovery from anaerobic digestion of urea-pretreated wheat straw

Yiqing Yao [a, *], Andre David Bergeron [a], Maryam Davaritouchaee [b]

[a] Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164, USA
[b] The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

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ABSTRACT

Pretreatment is necessary to improve methane production from lignocellulosic biomass. Urea was adopted to pretreat wheat straw with the advantages of structure deconstruction, its nitrogen source, and prevention of pH drop in subsequent anaerobic digestion (AD). Scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FTIR) spectra measurements indicated that urea pretreatment is able to degrade the lignocellulosic structure, which was beneficial for the improvement of methane production. Urea pretreatment led to the satisfactory performance of AD with wheat straw as substrate. The maximum methane production of 305.5 L/kg volatile solids (VS) was obtained using 1% (w/w) urea loading, which was 45.2% higher than the untreatment. After 1%- and 3%-urea treatment, time used for achieving stable status (≥50%) was 2 days earlier compared to untreatment. Reductions of total solids (49.4%), VS (54.5%), cellulose (50.4%) and hemicelluloses (47.3%) on the optimal condition were the highest, which were 36.8%, 46.5%, 33.3% and 47.4% higher compared to untreatment. Higher levels of urea pretreatment (3% and 5%) were less efficient and resulted in the formation of pseudo-lignin according to FTIR. These results indicate that wheat straw can be used to produce methane significantly with urea pretreatment.

1. Introduction

The need for developing robust renewable energy platforms is imperative as a result of the short supply of fossil fuels and the negative environmental impacts which are caused by petroleum-based fuels burning [1]. According to the United Nations, the worldwide energy supply will be substituted by renewable energy up to 77% by the year of 2050 [2]. Sustainable methane production can effectively reduce the consumption of fossil fuels and the energy input of waste treatment industry, as well as the production of valuable organic fertilizers after anaerobic digestion (AD). The major components of biomass (carbohydrates, fats, and proteins) can be decomposed and converted into methane via AD. In contrast, only the carbohydrates part of biomass can be used for ethanol recovery rather than fats and proteins, more input energy is needed in various unit operation, the ethanol production is lower, so ethanol production from biomass is less economical [3,4].

Lignocellulosic materials can be used to produce methane. Wheat straw is one of the most abundant biomass in the world, there is 556.3 million metric tons of wheat straw produced worldwide with huge potential in methane production [5]. On the other hand, anaerobic co-digestion is a hot topic since it not only maintains the balance of nutrients in AD but also reduces the cost of treating various waste [5–8]. However, the bottleneck in this process is collecting appropriate materials for co-digestion, so AD of lignocellulosic biomass alone is necessary for the practical purpose [9].

For lignocellulosic biomass, the complex three-dimensional polysaccharide structures create recalcitrance to microbes in AD [10]. Therefore, pretreatment is necessary to break down these structures, enhance the access of hydrolytic enzymes and thereby improve the methane production.

There are many studies about chemical pretreatment of lignocellulosic materials. Chemicals used for pretreatment are usually acid such as sulfuric acid, and alkaline such as NaOH, $Ca(OH)_2$, KOH, LiOH, and ammonia; the lignocellulosic materials used for pretreatment are mainly agroforestry residues [11–14]. Alkaline pretreatment is currently the leading pretreatment method [15]. NaOH is used more than any other bases as an alkaline reagent for separating lignin and improving biogas production [16]. However,

* Corresponding author.
E-mail address: dzhtyao@126.com (Y. Yao).

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when the dose is high, large amounts of byproducts, including furfural, vanillin, and lignin polymers are generated which act as inhibitors to methanogens [17]. In addition, high levels of NaOH are toxic to methanogens [18].

Ammonia has some advantages to act as another liable alkaline candidate to pretreat lignocellulosic materials. Because first, it can swell lignocellulosic feedstocks excellently and lignin is much more influenced rather than cellulose and hemicellulose, this, in turn, leads to make the biodegradable components of biomass more accessible to microorganisms [19,20]; second, it can neutralize various acidic compounds produced in the acidogenesis stage and prevent pH drop [21].

Urea also has been used for pretreating softwood spruce, hardwood birch, bamboo and rice straw for bioethanol or biogas production [22–24]. However, pretreatment of wheat straw with urea is limited, the related mechanism of structure changes remains unclear [25,26]. The characteristics of lignin in different plant species are different, which influence the effectiveness of enzymatic hydrolysis [27]. For lignin, linkages, content and relative abundance of monolignols, and degree of crosslinking with polysaccharides vary with plant species [28,29]. In addition, as a nitrogen source, urea possesses considerable advantages over ammonia: lower cost for urea purchase, lower toxicity, and corrosivity, and easier handling [30,31]. Therefore, pretreatment of wheat straw with urea is more reasonable. Urea pretreatment was used for wheat straw in the present study with some considerations. First, mechanism of structure changes under urea pretreatment needs to be investigated. Second, nitrogen source addition can be realized simultaneously along with urea pretreatment, so there is no additional need to add nitrogen source. Third, the ratio of carbon to nitrogen (C/N) significantly affects microorganisms' activity, and accordingly methane production. We conducted urea pretreatment in a wider range of C/N ratio than the proposed range of 20–30 for some reasons: on one hand, the effective C/N ratio may be lower than the calculated C/N ratio, because volatile solids (VS) responsible for gas production after AD was not fully utilized, this phenomenon is common [32–34], so the calculated C/N ratio can be higher than the proposed 20–30 [35]. On the other hand, the effective C/N ratio may be higher than the low C/N ratio resulted by high urea loading, maybe there is ammonia produced from the process of fermentation, so the actual nitrogen source used for the growth and the breeding of microbes is less.

This research were built based on the aforementioned issue, and the objectives of this study were to: (1) characterize the structural changes of wheat straw during urea pretreatment via scanning electron microscopy (SEM), FT-IR spectra and X-ray diffraction analysis (XRD); (2) study the effect of urea pretreatment on the stability of AD; (3) investigate how urea pretreatment impress the daily and total methane production.

2. Materials and methods

2.1. Feedstock and inoculum

Wheat straw was obtained locally from farms near Pullman, Washington. The straw was dried and then sieved to obtain 6–12 mm particles by a hammer mill, and stored at 4 °C until further processing [36]. Effluent from a wastewater treatment plant located in Pullman, Washington was used as anaerobic inoculum. Table 1 displays the characteristics of wheat straw and inoculum.

Table 1
Characteristics of wheat straw and inoculum.

Parameter	Wheat straw	Inoculum
Total solid (%)	99.2 ± 0.1	9.9 ± 0.3
Volatile solid (%)	86.3 ± 0.2	5.0 ± 0.1
Total carbon (%)	35.3 ± 0.7	28.4 ± 0.8
Total nitrogen (%)	0.53 ± 0.2	1.6 ± 0.1
pH value	–	7.5 ± 0.0
Cellulose (%)	49.5 ± 0.2	41.3 ± 0.0
Hemicelluloses (%)	27.4 ± 0.0	28.6 ± 0.2
Lignin (%)	14.2 ± 0.1	ND

ND: not determinded.
The % content of Total carbon, total nitrogen, cellulose, hemicellulose and Lignin were calculated based on dry mass.

2.2. Pretreatment

Urea was mixed with ground wheat straw to three concentrations = 1.0%, 3.0% and 5.0% (w/w), sample containing no urea (untreatment) was considered as a control, C/N ratio for untreatment, 1%-, 3%- and 5%-urea pretreated samples were 60, 25, 18 and 13, respectively. Distilled water was added to samples in order to get 88% moisture content (MC) [37]. The resulted samples were stored at 20 ± 1 °C for 6 days [38]. After that, a portion of the pretreated samples was dried at 60 °C for 48 h and then stored at 4 °C until composition and structure analysis [37].

2.3. Digestion design

Urea-pretreated samples and untreatment were digested in 2 L anaerobic digesters. The amount of untreatment, 1.0 %-, 3.0 %- and 5.0 %-urea pretreated samples (w/w) placed into each digester was 20 g/L; Inoculum from a mesophilic wastewater treatment plant located in Pullman, Washington was simultaneously inoculated into digester [39], the amount per digester was 15 g/L [40]. Later, each digester was diluted with deionized water to reach 1.5 L of working volume. Total solids (TS) for each digester was 35 g/L. To start the AD experiment quickly, a high ratio of inoculum (43%) in mixtures was used which additionally increased microbial activities and lessened digestion time [36]. The prepared digesters were incubated at 35 °C and shaken at a speed of 120 rpm. The digestions were performed in triplicate.

2.4. Analytical methods

2.4.1. Chemical composition analyses

TS, VS, and pH were determined according to the Standard procedure for analyzing Water and Wastewater [41]. For the pH measurement of wheat straw, dry sample powder after passing 200 mesh was suspended into distilled water at 1:10 of sample powder-to-distilled water ratio, based on weight, which was maintained at 28 ℃ for 48 hours, pH of leach liquor was then measured by pH meter. Elemental analyzer (varioEL cube, Elementar Analysensysteme GmbH) was used to measure total carbon, total nitrogen, and total hydrogen. Carbohydrate and lignin content were identified according to the NREL laboratory analytical procedure (LAP) [42].

2.4.2. Biogas analyses

Biogas production was monitored every two days by using the method of water displacement, the water was saturated with sodium chloride [43]. When AD was completed, total biogas volume was calculated. Gas chromatograph (GC) (Agilent Technologies, 7890 A, Wilmington, DE, USA) equipped with a 25 m × 530 μm × 20 μm chromatographic column and a thermal conductivity detector (TCD) was used to analyze methane content. Hydrogen was used as a carrier gas at a flow rate of 35 ml/min. The temperatures of injector port, detector, and column oven were