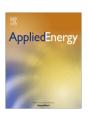
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A physicochemical method for increasing methane production from rice straw: Extrusion combined with alkali pretreatment



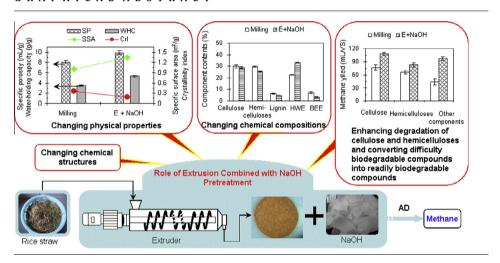
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HIGHLIGHTS

- The first report of using extrusion combined with NaOH pretreatment for methane production from LB.
- Pretreatment with an ALR of 3.0% at 35 °C for 48 h increased methane production from rice straw by 54%.
- The ER efficiency improved from 38.9% to 59.9% using extrusion combined with NaOH pretreatment.
- The changes in the physicochemical characterization of rice straw were investigated.

G R A P H I C A L A B S T R A C T



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ABSTRACT

Pretreatment is a crucial processing step in the conversion of lignocellulosic biomass (LB) into methane by anaerobic digestion. A physicochemical LB pretreatment method, i.e., using an extruder to reduce the biomass size prior to sodium hydroxide (NaOH) pretreatment, was reported. The optimal condition for economic feasibility and pretreatment efficiency was an alkaline loading rate of 3.0% at 35 °C for 48 h. Under this condition, the methane production from the rice straw that was processed by extrusion combined with NaOH pretreatment was 54.0% higher than that of a control sample. The energy recovery (ER) efficiency improved from 38.9% to 59.9% using the combination pretreatment. The mechanisms that caused the significant improvement in the methane production and ER efficiency in the extrusion–NaOH pretreatment were investigated. The pretreatment changed the physical properties (water-holding capacity, specific porosity, specific surface area and crystallinity index), the chemical composition (lignin, benzene–ethanol extractives and hot-water extractives) and the chemical structure, which increased degradation of holocelluloses and other difficulty biodegradable compounds.

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Abbreviations: AD, anaerobic digestion; ADF, acid detergent fiber; ADL, acid detergent lignin; AIA, acid insoluble ash; ALR, alkaline loading rate; BEE, benzene-ethanol extractives; BMP, biological methane potential; C/N, carbon-to-nitrogen ratio; Crl, crystallinity index; ER, energy recovery; FTIR, Fourier transform infrared; HHV, higher heating value; HWE, hot-water extractives; LB, lignocellulosic biomass; LHV, lower heat value; NaOH, sodium hydroxide; NDF, neutral detergent fiber; SEM, scanning electron microscope; SLR, solid-to-liquid ratio; SP, specific porosity; SPSS, statistic package for social science; SSA, specific surface area; STP, standard temperature and pressure; TS, total solids; VS, violate solids; WHC, water-holding capacity; XRD, X-ray diffraction.

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1. Introduction

In 2012, the world energy consumption was 12476.6 Mtoe, of which petroleum, coal and natural gas consumption were 4130.5, 3730.1 and 2987.1 Mtoe, respectively. Fossil fuel consumption accounted for 86.9% of the world energy consumption, whereas renewable energy accounted for a mere 1.9% [1]. The high demand for energy, the unstable and uncertain availability of fossil fuels, and concern over global climate warming have produced an increasing urgency for the development of new, sustainable and renewable energy that can displace traditional fossil energy [2]. Lignocellulosic biomass (LB), with a worldwide annual production of 200 billion tons, has become a primary candidate for biofuel production [3.4]. The development of new technologies for renewable energy production from LB, especially agricultural residues, is very promising for the following reasons: (1) LB is abundant and renewable; (2) the non-edible parts, i.e., the stalks and leaves, of agricultural residues are used for fuel production, which does not compete with food production; and (3) LB use affects both energy consumption and the environment because renewable energy is recovered from agricultural residues while treating waste biomass [4,5].

Anaerobic digestion (AD) offers the advantages of a low-cost, mature, and stable technology and in particular, produces a high energy recovery (ER) from LB [6,7]. AD produces a methane-rich biogas that can provide heating, for power generation or as a vehicle fuel to replace fossil fuels [8]. However, LB has a complex structure that results in poor hydrolysis and biodegradability during the AD process [3]. The primary chemical composition of LB is cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses can be converted into methane, whereas lignin cannot be degraded by anaerobic microbes [9]. Moreover, lignin is hydrophobic and resistant to microbial attack, which limits the accessibility of holocelluloses (cellulose and hemicelluloses) to anaerobic microbes, which lowers the substrate availability and methane production [4]. Pretreatment is a crucial processing step in which anaerobic microbes convert LB into methane. The physical properties, chemical composition and chemical structure of LB can be altered using several pretreatment methods that increase the accessibility of holocelluloses to enzymes, thereby enhancing the digestibility of LB and increasing methane production [3,10].

Alkaline pretreatment is one of the current leading pretreatment methods and offers several benefits such as the solubilization of lignin and hemicelluloses, the destruction of the ester bond of lignin-carbohydrate complexes and a decrease in the cellulose crystallinity; the residual alkali also provides alkalinity for the subsequent AD process [6,7,11]. A literature review shows that sodium hydroxide (NaOH) is a common alkali that is widely used in alkaline pretreatment [12,13]. Different LBs that are pretreated with NaOH for methane production are summarized in Table 1. The primary influence factors for the NaOH pretreatment are the temperature, the time, the solid-to-liquid ratio (SLR), and the alkaline loading rate (ALR). Most studies have focused on these operating factors over a wide range of temperatures (0-200 °C), times (10 min to 21 d), SLRs (1:0.8-1:19) and ALRs (1-152%) [14-19]. In general, pretreatment increases methane production (from 0% to 174.2%) from LB compared with untreated samples [13.20–25]. Biomass size reduction always occurs prior to NaOH pretreatment and affects the pretreatment. The extruder, which is more efficient than other physical pretreatment methods, has recently been used to enhance methane production from LB. The methane production increased significantly by 18-70% using extrusion as a pretreatment to test five agricultural residues [26]. A similar result was reported of an increase in methane production 72.2% by extrusion pretreated rice straw over that of the untreated rice straw [9].

However, to the best of our knowledge, there have been no previous reports of a pretreatment of extrusion combined with NaOH for improving methane production from LB.

Rice straw is the major component of agricultural residues. The annual yield of rice straw in the world is approximately 731 million tons [5]. Rice straw has a high silica content and is therefore unsuitable for use in animal feeding, pulping and papermaking [27]. Rice straw has a good potential for methane production. In this study, the effect of extrusion combined NaOH pretreatment on rice straw methane production was studied and the effect of other pretreatments such as milling and milling combined NaOH pretreatment also has been analyzed for comparison. The contributions of cellulose, hemicelluloses and other components to methane production from rice straw using different pretreatment methods were investigated. The changes in the physical properties, chemical composition and chemical structure of rice straw from pretreatment were also examined.

2. Materials

2.1. Feedstock and inoculum

Rice straw was obtained from a rice field in Yancheng city, Jiangsu province, China. Table 2 presents the proximate, ultimate and compositional properties and the heat value of the rice straw. The rice straw was dried at room temperature (25 °C) to a moisture content below 10%. The resultant rice straw was stored in vacuum bags for later pretreatment. The inoculum used in this study was anaerobic digested sludge that was taken from an anaerobic digester that was fed with dairy manure in Chongming Island, Shanghai, China. The anaerobic digester was a 300-m³ continuously stirred digester that had been stably operated at 35 °C for more than 3 years.

2.2. Extrusion combined with alkali pretreatment

The procedure for the extrusion combined with alkali pretreatment is presented in Fig. 1. In brief, a twin-screw extruder (JXM80, Jinwor Machinery Co., Ltd, Nanjing, China) and NaOH were used as the biomass-size-reduction machine and the alkaline reagent, respectively. The dried rice straw was pretreated with the extruder and then passed through a 0.45-mm sieve. The resulting rice straw was pretreated with a NaOH solution. The pretreatment parameters were as follows: a treatment temperature of 35 °C, a treatment time of 3–120 h, a SLR of 1:6 and an ALR of 1.5–6.0%. The variation in the pH and the chemical composition during the alkali pretreatment were analyzed using the following procedure: eight 50-mL plastic centrifuge tubes were prepared with different ALRs (1.5%, 3.0%, 4.5% and 6.0%) for the alkali pretreatment, and the reaction was terminated after 3, 6, 12, 24, 48, 72, 96 and 120 h for sampling and subsequent analysis.

2.3. Methane production from rice straw by AD

The biological methane potential (BMP) of untreated and pretreated rice straw was evaluated using 500-mL batch glass digesters, which each had a 400-mL working volume and a 100-mL head space. First, 10.0 g of volatile solids (VS) from a rice straw sample were weighed and added to each digester. Second, the required amount of sludge was fed into each digester with a substrate-to-inoculum ratio of 1:1 based on the VS. Urea was used to adjust the carbon-to-nitrogen ratio (C/N) of the mixture to 25. Third, distilled water was added to each digester to reach the working volume. The desired pH range of 6.8–7.2 range for AD

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