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Review of Pretreatment Technology for Corn Straw Anaerobic Digestion

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Abstract **Review Article**

Corn straw is mainly composed of hemicellulose, cellulose, and lignin, which together form a crystal structure with extremely high stability. Anaerobic fermentation is an important means of straw resource utilization. Due to the complex composition of corn straw, the hydrolysis rate during anaerobic fermentation is limited, which affects the gas production efficiency. Therefore, it is necessary to pretreat corn straw. This article analyzes the advantages and disadvantages of different pretreatment methods and their applications in anaerobic digestion in order to provide optimal pathways for the pretreatment of corn straw.
Keywords: Anaerobic digestion, Corn straw, Pretreatment.

1. INTRODUCTION

China is one of the world’s major agricultural countries, with an annual crop straw production of about 1 billion tons, mainly corn, rice, and wheat straw, of which corn straw accounts for approximately 35%. However, a large amount of crop straw is not effectively utilized, some of which is discarded or burned, leading to resource wastage and environmental pollution, while also hindering the sustainable development of agriculture. There is potential to more fully utilize these resources by exploring new utilization methods, which can contribute to promoting sustainable development. The government is actively promoting the “straw-biogas-fertilizer” agricultural production model, in which anaerobic digestion (AD) of straw plays a key role in biogas production and can not only solve the problem of organic pollution but also generate clean energy, with high economic and environmental benefits.

Despite the substantial biogas potential of corn straw anaerobic digestion, this technology is still encountering challenges. The primary challenge is the high content of lignin, cellulose, and hemicellulose in straw, with the elevated lignin content impeding the action of cellulase. The removal of lignin can effectively enhance the rate of cellulose hydrolysis. Furthermore, the cellulose crystallinity and polymerization degree also influence the hydrolysis rate, where extensive molecular entanglement makes degradation difficult, consequently diminishing gas production efficiency. Research indicates that pretreatment technology can disrupt the extensive molecular structure in straw, thus aiding in enhancing the efficiency of anaerobic fermentation gas production. Currently, prevalent straw pretreatment methods encompass physical, chemical, and biological treatments.

2. PHYSICAL PRETREATMENT

Physical pretreatment encompasses the utilization of physical methods to modify the shape or structure of agricultural crop straw. Mechanical, heating, steam explosion, and ultrasound are the prevailing techniques applied to enhance the efficacy of primary biomass processing steps.

2.1 MECHANICAL PRETREATMENT

Common mechanical methods such as cutting, crushing, grinding, and high-temperature ball milling are frequently used in biomass pretreatment [1]. These methods not only serve to disrupt the wax layer on the surface of the biomass but also increase the contact area between anaerobic microorganisms and the substrate, or facilitate digestion by disrupting the cell wall structure [2]. Dela Rubia *et al.*, found that the methane production during the anaerobic digestion of sunflower seed oil cake was influenced by particle size, with the highest methane production observed at a particle size of 1.4-2.0 mm among the three treatments [3]. Zhao *et al.*, demonstrated that the density of corn straw increased by 0.2747 t/m^3 after crushing and soaking, with particles smaller than 2 cm accounting for approximately 80% of the total quantity [4].

2.2 HEATING PRETREATMENT

Heat treatment is a process that alters the internal structure and properties of a material by heating it. Commonly used heat treatment methods include drying, carbonization, and hot pressing. Drying is used to remove moisture from straw and reduce its water content; carbonization converts straw into charcoal through high-temperature pyrolysis; hot pressing induces physical changes in straw, such as increased brittleness and ease of grinding, by applying heat and pressure. Bai *et al.*, found that adding 2% NaOH by weight to straw during hydrothermal treatment significantly increased gas production compared to untreated straw, under the conditions of 50℃, 60% moisture content, and 12 hours of pretreatment. Their results indicate that adding NaOH during hydrothermal pretreatment effectively enhances the biogas production of corn straw [5].

2.3 STEAM EXPLOSION

Steam explosion is a method in which crop straw is placed in a high-pressure steam environment, and the structural destruction of straw is achieved through the instantaneous release of impact force generated by steam. Steam explosion can improve the degradability and enzymatic efficiency of straw, thereby better utilizing it as a biomass feedstock. In the study by Wang *et al*., crushed corn straw was subjected to steam explosion treatment using the QB-200 steam explosion pilot plant at different pressures (1.5, 2.0, 2.5, and 3.0 MPa) and times (60, 90, and 120 s) [6]. The study found that the methane conversion rate in corn straw subjected to steam explosion at moderate temperature was higher than that under normal temperature fermentation conditions. This may be due to the insufficient utilization of straw and fermentation products by methane-producing bacteria under normal temperature conditions, requiring higher temperatures to be more effective. Additionally, the study also found that the methane conversion rate during mesophilic AD increased by 320 mL/g with increasing pressure. Li *et al*., found that the energy conversion efficiency of corn straw subjected to steam explosion followed by anaerobic fermentation was 1.38 to 1.92 times higher than that of untreated straw, with the highest energy conversion efficiency reaching 11.68% [7].

2.4 ULTRASOUND PRETREATMENT

Ultrasonic treatment utilizes the energy of ultrasonic waves to alter the structure and properties of agricultural straw. Ultrasonic waves can generate shear forces and vortex effects, disrupting the fiber structure and fiber bundles of straw, thereby increasing its surface area and biodegradability. Different ultrasonic devices, such as ultrasonic baths, ultrasonic oscillators, and ultrasonic sprayers, can be employed for ultrasonic treatment. Research by Zou Shuzhen *et al.*, demonstrated that suitable ultrasonic pretreatment significantly increases the total gas production of anaerobic fermentation ($p < 0.05$) at 40 kHz and 0.20 kW [8]. Mixing cow dung pretreated for 17.68 minutes with corn straw pretreated for 19.94 minutes for AD resulted in the highest methane yield of 177 mL/g, significantly higher than the untreated group ($p < 0.05$), with the highest energy efficiency of 1835 J/g. Research by Liu *et al*., revealed that pretreating straw with thermal alkali ultrasound can enhance its methane conversion rate in the AD of straw slurry [9]. Ninomiya *et al*., found that combining ultrasonic pretreatment with choline acetate pretreatment can significantly improve the cellulase hydrolysis efficiency of bamboo powder. By combining these two pretreatment methods and pretreating at 25℃ for 60 minutes, a cellulase hydrolysis rate of up to 92% was achieved [10].

3. CHEMICAL PRETREATMENT

The chemical pretreatment of straw includes methods such as acid treatment, alkali treatment, ammonia treatment, and ozone oxidation, all of which can disrupt the stable structure of lignocellulose in straw, break the chemical bonds connecting lignin with cellulose and hemicellulose, thereby improving the accessibility of structural carbohydrates and facilitating their subsequent utilization and resource utilization. Therefore, chemical pretreatment plays a key role in the process of straw utilization.

3.1. ACID TREATMENT

Acid treatment is commonly carried out using organic and inorganic acid solutions, with similar mechanisms mainly involving the disruption of hydrogen bonds between corn straw components. Acid solutions have the ability to dissolve hemicellulose and lignin, thereby removing some hemicellulose and lignin, reducing the crystallinity of cellulose, and more effectively separating cellulose. Depending on the concentration of the reagent, treatment methods are usually divided into dilute acid and concentrated acid. Generally, concentrated acid presents stronger corrosion and harm to equipment. Hence, people tend to use dilute acid for pretreating stover. Research results from Amnuaycheewa *et al*., revealed that oxalic acid pretreatment resulted in the highest enzymatic saccharification efficiency of stover, 2.6 times higher than untreated stover; while citric acid pretreatment led to the greatest increase in methane production, 7.4 times higher than untreated straw [11]. Chai *et al*., carried out pretreatment experiments on ensiled corn straw using various concentrations of sulfuric acid, acetic acid, and phosphoric acid, finding the highest cumulative gas production from stover in the control group (0% sulfuric acid), 4% acetic acid, and 6% phosphoric acid treatments. Particularly, the highest gas production from stover was observed in the 6% phosphoric acid treatment group, demonstrating that phosphoric acid could significantly enhance the methane conversion rate of stover at a certain concentration. In comparison, the effect of dilute sulfuric acid pretreatment was relatively poor, possibly due to insufficient structural disruption of stover, leading to reduced degradability. Acetic acid and phosphoric acid as pretreatment acids showed superior effects compared to dilute sulfuric acid, likely because they could more effectively break down the structure of stover and improve its biodegradability [12].

3.2. ALKALI TREATMENT

Alkali treatment involves using alkaline reagents (sodium hydroxide) to remove part of the hemicellulose and lignin in the straw, in order to disrupt the dense structure inside the straw. Research has shown that the effect of sodium hydroxide is relatively good. Zhang *et al*., used 2% sodium hydroxide to treat straw powder, and compared its effect with 2% dilute sulfuric acid, 10% Triton-X-100 and 1% polyethylene glycol (PEG-4000) at 37°C. The results show that, from the perspective of total sugar, NaOH treatment is superior to other reagents [13]. Ke *et al*., demonstrated that mixing 0.176% (w/v) NaOH solution with 0.9% (v/v) H_2O_2 solution, followed by mixed treatment of corn straw and mixed liquid at a solid-liquid ratio of 1:50, can achieve a higher conversion rate of reducing sugars. In addition, the reduction of lignin contributes to the hydrolysis of cellulase [14]. Mancini *et al*., studied the effect of trace elements and NaOH pretreatment on the anaerobic digestion of rice straw, and the results showed that alkaline pretreatment promoted the accumulation of methane production. The final biogas methane yield increased by 21.40%, while the addition of trace elements did not bring significant differences [15]. Zhang *et al*., found that NaOH pretreatment at different times and concentrations significantly affected the mesophilic anaerobic fermentation of corn straw. Among all the experiments, the 4‰ NaOH pretreatment had the best effect, especially at 9.48 days. Moderate NaOH pretreatment helps to improve the efficiency of mesophilic anaerobic fermentation of corn straw and increases methane production [16].

3.3. AMMONIATION TREATMENT

Ammoniation treatment, as an alkali pretreatment method, can break the ether bonds between cellulose, hemicellulose, and lignin in straw, dissolve some lignin and outer surface cuticle waxes of straw, reduce the crystallinity of straw, increase the surface area of straw, and facilitate the adhesion of microorganisms. The alkalinity of ammonia can neutralize the acidic organic matter in straw, improve the activity of anaerobic microorganisms, and thus increase the digestibility of straw [17]. Researchers such as Li found that under ammonia water treatment (such as ammonium carbonate solution), the solid-liquid ratio of corn straw was 5:2, and the treatment time was 11 days. Under the same conditions, compared with direct enzymatic hydrolysis, the reducing sugar yield was increased by 51.80% with ammoniation treatment [18]. Another study conducted by Xu *et al*., proposed a novel extremely dilute mixed alkali (SDMA) pretreatment method, which combined alkali treatment (1 g/L NaOH) and ammoniation treatment (2 g/L NH3), and applied it to pretreatment and anaerobic fermentation for biogas production from corn straw. The study indicated that corn straw treated with the extremely dilute mixed alkali resulted in higher cumulative methane production, with an increase of 184.65% and 55.6% compared to untreated and 2% NaOH-treated corn straw, respectively [19].

3.4. OZONE OXIDATION

The most typical way of oxidant pretreatment for straw is Fenton pretreatment, in which the Fenton reagent is an oxidation system composed of Fe^{2+} and H_2O_2. In the study by Yang *et al*., pretreatment of corn straw was conducted by activating PS with Fe^{2+} followed by anaerobic fermentation. The results showed that the methane accumulation in the experimental group (Fe^{2+}/PS pretreatment without washing) was higher than in the control group (Fe^{2+}/PS pretreatment with washing after). Washing after pretreatment can lead to the loss of soluble sugars and small molecular organic compounds in the pretreatment solution, which are the main nutritional sources for methane-producing bacteria. Therefore, the methane accumulation after washing is reduced compared to the methane accumulation without washing after Fe^{2+}/PS pretreatment [20]. In the study by Tian *et al*., a mixture of phosphoric acid and H_2O_2 was used for pretreating wheat straw and corn straw. The results indicate that almost all hemicellulose was removed under this pretreatment method, with lignin removal rates reaching 83.50% and 90.00% respectively, and the removal rate of lignin is proportional to the concentration of hydrogen peroxide [21].

4. BIOLOGICAL PRETREATMENT

Biological pretreatment involves the synergistic action of one or more microorganisms on straw, through solid-state or liquid fermentation, to depolymerize lignocellulose and metabolize intermediate products necessary for anaerobic digestion, thereby providing a more easily utilizable metabolic substrate. The microorganisms used in microbial pretreatment include fungi, bacteria, and actinomycetes. Noonari *et al*., isolated three wood cellulose-degrading bacteria, A.sojae, A.niger, and A.terreus, from rice roots, and used them for pretreatment of rice straw before anaerobic fermentation. The methane production after 15 days of pretreatment was highest for strains *Aspergillus sojae*, *Aspergillus niger*, and *Aspergillus terreus*, at 167.60, 181.30, and 204.7 mL/g respectively, which were 17.2%, 23.5%, and 32.2% higher than the control group [22]. Zhang *et al*., obtained a highly efficient gas-producing composite microbial agent from biogas slurry, compost, and tree soil, and found that the gas production was affected by the ratio of straw mass to microbial agent, with the highest gas production when the ratio was 50:1 [23]. Wan *et al*., pretreated corn straw, sorghum stalks, and hardwood for 18 days, and found that the glucose yield after enzymatic hydrolysis increased 2 to 3 times compared to untreated raw materials [24]. Jing *et al*., used a microbial-enhanced hydrolysis pretreatment of corn straw, and under optimal hydrolysis conditions (6% mixed microbial agent addition, 30°C hydrolysis temperature, 8 hours hydrolysis time), achieved a maximum methane production of 227 mL/g VS after 30 days of anaerobic fermentation, which was 77.3% higher than the control group [25].

5. CONCLUSION

The advantages of physical pretreatment include simple equipment operation and no environmental pollution. However, it has high energy consumption, high power requirements, and high costs. Chemical pretreatment has obvious effects, low costs, and low energy consumption, but it is difficult to handle in subsequent processes and can be harmful to the environment. Biological pretreatment has the advantages of low cost, low energy consumption, environmental friendliness, and safety, making it a widely studied research focus. However, there are issues with the enzymatic efficiency of cellulase enzymes produced by the microorganisms used in the pretreatment process, including incomplete enzyme systems, low activity, harsh enzyme action conditions, and long processing cycles. The enormous production of lignocellulosic biomass and the efficient utilization of straw resources can not only solve energy issues but also reduce adverse environmental impacts such as field burning, promote sustainable agricultural development, and to some extent alleviate the current energy shortage. Despite the existing problems, people are actively exploring and innovating in search of an efficient, green, and environmentally friendly method for straw pretreatment to enhance anaerobic fermentation gas production efficiency and increase straw resource utilization efficiency.

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