Scholars Journal of Engineering and Technology
OPEN ACCESS
Abbreviated Key Title: Sch J Eng Tech
ISSN 2347-9523 (Print) | ISSN 2321-435X (Online)
Journal homepage: https://saspublishers.com

Application of Ammoniation Pretreatment in Anaerobic Digestion of Straw

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DOI: 10.36347/sjet.2023.v11i06.001 | **Received:** 25.04.2023 | **Accepted:** 01.06.2023 | **Published:** 06.06.2023

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Abstract **Review Article**

Straw is a widely available and highly renewable biomass resource with good utilization value. However, its dense structure is not conducive to methane production during anaerobic fermentation and requires pretreatment. To achieve high-value conversion, pretreatment technologies can effectively destroy the rank structure of straw and increase gas production. Ammoniation pretreatment has unique advantages in pretreating straws. This article reviews the ammoniation pretreatment mechanism, the impact of ammoniation pretreatment parameters on anaerobic fermentation, and ammoniation pretreatment technology, providing a reference for the ammoniation pretreatment of straw.

Keywords: Ammoniation Pretreatment, Anaerobic Digestion, Straw.

INTRODUCTION

China is recognized as the world's largest energy consumer. The pattern of a carbon-centric energy structure is not conducive to achieving the carbon peak and carbon neutrality. Thus, energy transformation and the development of renewable energy technologies remain the primary challenges for contemporary China (Huang *et al.*, 2022). In China, crop straw is abundantly available, with an annual yield of approximately 800 million tons. Out of the total straw, 52.8% is directly returned to the fields, and only 7.5% is utilized as fuel energy (Yan *et al.*, 2023). The direct utilization of straw in agricultural areas is challenging to decompose and leads to crop pest infestations. Straw fermentation to produce biogas presents an opportunity for China to generate renewable energy and prevent crop problems resulting from straw's direct return to the field. However, the complex lignocellulosic architecture of straw constrains its efficient biogas production, and straw pretreatment is essential to increase straw utilization and conversion efficiency. The structure of straw mainly consists of 38%~50% cellulose, 20%~35% hemicellulose, and 5%~15% lignin. The structural unit of cellulose is glucose, which forms long chains through β-1,4-glycosidic bonds and aggregates into cellulose microfibrils through hydrogen bonding, with the orderly arranged ones forming the crystalline region, severely inhibiting the decomposition of straw. Hemicellulose is linked to cellulose through hydrogen bonds, and strong hydrogen bonds internally connect lignin and externally form a stable lignin-carbohydrate complex with cellulose through covalent bonds, severely hindering the degradation and utilization of straw by microorganisms (Jin *et al.*, 2009).

The commonly used straw pretreatment practices are physical, chemical, and biological pretreatment techniques. Physical pretreatment techniques refer to modifying the straw's particle size or dense structure to enhance the utilization potential of the straw. The primary physical pretreatment procedures include mechanical crushing, heat treatment, ultrasound pretreatment and high-energy radiation. Biological pretreatment utilizes specific microorganisms such as fungi (white rot fungi, brown rot fungi, and soft rot fungi) and genetically engineered bacteria to degrade lignocellulose in straw. Brown rot fungi mainly decompose cellulose, whereas white rot fungi and soft rot fungi can attack cellulose and lignin (Ding, 2017). Biological pretreatment is a straightforward method with low resource consumption but requires a substantial pretreatment time. Chemical treatments include acidic, alkaline, and organic solvent pretreatments. Among the alkaline pretreatment techniques, ammoniation pretreatment consists of coating the straw with alkaline agents such as urea, ammonia water, liquid ammonia, and carbon ammonia, which is cost-effective and has a faster ammoniation rate.

Ammoniation pretreatment can destroy the ether bonds between cellulose, hemicellulose, and lignin in straw, reduce the crystallinity of straw, and dissolve part of the lignin. It dissolves the cuticle wax silicon layer on the straw's surface, increases its internal surface area, and makes it easy for microorganisms to attach to the straw. At the same time, ammonia and organic matter in straw change to produce ammonium salts, which can serve as a nitrogen source for anaerobic microorganisms and synthesize proteins in microorganisms. Ammonia has alkalinity, which can neutralize acidic organic matter in straw and improve the activity of anaerobic microorganisms, thereby increasing the digestion rate of straw (Li *et al.*, 2011).

1. MAIN FACTORS AFFECTING THE DEGREE OF AMMONIATION OF STRAW

The main factors affecting the degree of straw ammonia pretreatment in the process of straw ammonia are nitrogen source type, straw particle size, straw moisture content, ammonia concentration, and pretreatment temperature.

1.1 Types of Nitrogen Sources

When urea is used to pretreat straw, the urease on the surface of the straw decomposes the urea into NH3 or NH4+, HCO3-. Both gaseous ammonia and liquid ammonia have specific effects on removing lignin in straw (Wang *et al.*, 2020). When ammonia water and ammonium bicarbonate are used to pretreat straw, they are alkaline in water solution. They can break the unstable chemical bonds in straw, weaken the interaction between cellulose and lignin, and achieve the goal of lignin removal. Li *et al.*, (2023) compared the enzymatic hydrolysis and sugar production of corn straw pretreated with urea, ammonium carbonate, and ammonium bicarbonate as ammoniation agents and found that the corn straw pretreated with ammonium carbonate at a concentration of 15% had the highest reducing sugar yield.

1.2 Straw Particle Size

Straw particle size can be reduced by physical methods to increase the effective surface area of straw during utilization and improve microbial utilization during fermentation. Ma *et al.*, (2021) treated corn straw with urea and found that particle size had a more significant impact on anaerobic fermentation than urea concentration or treatment time. Li *et al.*, (2011) studied the effects of ammonia concentration, time, temperature, substrate concentration, and particle size on the pretreatment of corn straw with ammonia. They found that particle size was the main factor affecting the yield of reducing sugar, while ammonia concentration, soaking time, and soaking temperature were the main factors affecting lignin removal.

1.3 Ammonia Concentration

Different concentrations of ammonia have other effects on the pretreatment of raw materials, and the most suitable concentration of ammonia pretreatment should be found when pretreating the raw materials. Ma *et al.*, (2011) studied the effect of different ammonia concentrations on the gas production performance of anaerobic digestion of rice straw and found that 4% NH3 ammonia pretreatment had the best product. Zhao *et al.*, (2016) used different mass fractions of urea to ammoniate rice straw and measured its gas production. The results showed that the best effect was achieved with a 6% concentration of urea pretreatment, with its TS and VS conversion rates increasing by 54.9% and 36.1%, respectively.

1.4 Moisture Content of Straw

The moisture content of straw will affect the pretreatment effect of straw. Yang *et al.*, (2013) used ammonia water to pretreat wheat straws with different moisture contents. They found that wheat straw pretreated with 80% moisture content and 4% ammoniation obtained the maximum methane production at an inlet concentration of 65 g/L. Gas production increased by 36% compared to untreated wheat straw. Zhang (2013) obtained similar results by studying the effect of ammoniation pretreatment on the anaerobic fermentation gas production performance of straw under medium temperature and found that 4% ammonia pretreatment was the best for straw under the condition of 70% moisture content and 65 g/L load.

1.5 Pretreatment Temperature and Time

The pretreatment temperature and time will affect the result, and different pretreatment parameters will lead to different results. Zhang (2018) used different mass fractions of urea to pretreat rice straw and found that the best pretreatment conditions were 5% pretreatment dosage, 25 ℃ pretreatment temperature, and 6.89 d pretreatment time. Wang *et al.*, (2021) found that the best effect of urea pretreatment of soybean straw under high solid content was achieved at 50% TS mass fraction, urea/straw mass ratio of 1:1, pretreatment temperature of 80 ℃, and pretreatment time of 10 d. Qin *et al.*, (2013) optimized the ammonia water pretreatment and found that the pretreatment conditions with high enzyme production were: pretreatment temperature of 180 ℃, ammonia mass fraction of 20%, and pretreatment time of 30 min.

2. AMMONIA PRETREATMENT PROCESS

2.1 Ammonia Fiber Explosion

The ammonia fiber explosion pretreatment process uses liquid ammonia to pretreat biomass at 60~100 °C and a pressure of 1732~2069 KPa. After some time, the valve is opened to release tension, and the ammonia evaporates into the biomass due to the sudden pressure drop. Under external heating, it forms a complex with some hydroxyl groups on cellulose in the form of Cell-OHNH3, causing the cellulose to expand

(Yang *et al*., 2010). Ammonia fiber explosion has the following advantages: it can be used for various woody cellulose materials; the process conditions are easy to control, the temperature is relatively low, and the conversion efficiency is high; most of the nitrogen in the pretreatment process is recycled, and the residual part can be used for subsequent fermentation; ammonia fiber explosion pretreatment does not require washing, and has a high dry matter retention rate. However, during the ammonia fiber explosion process, phenolic substances will be produced, which significantly inhibit the growth of microorganisms in anaerobic fermentation (Qin *et al*., 2016). It was found that the content of acid-soluble lignin increased. In contrast, cellulose and hemicellulose content did not change with the increase of pretreatment temperature in the ammonia fiber explosion process. The hydrophilicity of lignin increased, weakening the adsorption effect between lignin and cellulase during enzymatic hydrolysis, and the higher temperature also produced more phenolic substances (Li *et al*., 2021). It was found that the ethanol yield of whole corn, whole wheat, and whole soybeans increased by 34.8%, 40.1%, and 20.1%, respectively, after pretreatment with ammonia fiber explosion, and the actual conversion rate of corn reached 71.7% of the theoretical value after pretreatment (Shao *et al*., 2013).

2.2 Liquid Ammonia Pretreatment

Due to the difficulty of the ammonia fiber explosion process, Liu Jianjun and others developed the liquid ammonia pretreatment technology based on this process. Liquid ammonia pretreatment increases the temperature of ammonia in the reaction process, transforms the rapid release of ammonia into slow release, and eliminates the depressurization explosion process (Liu *et al*., 2013). Zhao *et al*., (2020) studied the effect of liquid ammonia pretreatment on the chemical structure and enzymatic saccharification of lignocellulosic biomass materials. They found that liquid ammonia pretreatment can reduce the content of oxygen and hydrogen in straw, slightly reduce the straw's crystallinity, and significantly promote the enzymatic hydrolysis of lignocellulose. Liu *et al*., (2013) used liquid ammonia pretreatment to pretreat *Saccharum arundinaceum*. The conversion rates of xylan and cellulose were increased by 573% and 1056%, respectively. The monosaccharide yield was increased by eight times when the water content of the raw material was 80%, the pretreatment temperature was 130 °C, and the mass ratio of liquid ammonia to the biomass was 2:1. The pretreatment effect was similar to that of ammonia fiber explosion.

2.3 Ammonia Circulatory Permeation

Ammonia circulatory permeation is a process in which ammonia water is injected into a circulating reactor, and straw is soaked at 160~180 °C to remove lignin. This process can achieve the recycling of ammonia. Kim *et al*., (2003) used this method to treat corn straw at a concentration of 15% ammonia, a temperature of 170° C, a flow rate of 5 mL/min, and a pressure of 2.3 MPa for 90 minutes and found that the removal rate of lignin in corn straw was 70%~85%, while cellulose was well preserved. This process has a high lignin removal efficiency and a reasonable cellulose retention rate, but 40%-60% of hemicellulose is removed. Kim (2011) used dilute sulfuric acid and ammonium hydroxide to recover hemicellulose from corn straw and remove lignin in a two-stage permeation process. In the first stage, 0.07% dilute sulfuric acid was used to remove hemicellulose, and in the second stage, 15% ammonium hydroxide was used to remove lignin in the ammonia circulatory permeation device. The removal rate of lignin in this process was 81%. After the two-stage pretreatment, the biomass's xylose content was 85%.

2.4 Ammonia Water Circulation Explosion

Ammonia water circulation explosion combines the advantages of ammonia circulatory permeation and ammonia fiber explosion, using ammonia water instead of liquid ammonia, fully contacting the ammonia water with the biomass raw material in a flowing state, which can help reduce the formation of inhibitory substances in the pretreatment process, quickly remove lignin from the biomass and take it away from the surface of the biomass (Li, 2012). Zhang (2010) used an ammonia water circulation explosion to pretreat corn straw and found that the optimal pretreatment conditions were 90°C pretreatment temperature, 80% material moisture content, 9-minute processing time, and 1.5 L/min ammonia flow rate. Under these conditions, the cellulose content of pretreated corn straw was 50.45%, and the cellulose enzymatic hydrolysis rate was 75.61%. Li (2012) systematically studied the effects of pretreatment temperature, time, moisture content, ammonia flow rate, and fluidization time on sorghum straw's components and enzymatic hydrolysis rate after the ammonia water circulation explosion. He found that the optimal pretreatment conditions were 85°C temperature, 25-minute processing time, 60% material moisture content, 3 L/min ammonia flow rate, and 9-minute fluidization time. Under these conditions, the total sugar yield reached the maximum value of 80.14%.

2.5 Low-Moisture Waterless Ammonia Pretreatment

The ammonia process of low-moisture waterless ammonia is to fully contact the gaseous ammonia with a straw with a moisture content of 30%~70% in the reactor, and after a specific time of treatment, open the valve of the reactor to discharge the gaseous ammonia. Then, remove the residual ammonia on the biomass at high temperatures. Research has shown that this process has no effect on the content of each component in straw, breaks the cross-linking of cellulose, hemicellulose, and lignin in biomass, exposes cellulose and increases the contact area of enzymes or microorganisms with cellulose, thereby increasing the enzymatic hydrolysis efficiency or increasing the fermentation products (Yoo *et al*., 2011). Low-moisture waterless ammonia pretreatment eliminates the washing step in traditional ammonia pretreatment, saves the cost of biomass pretreatment, and has good application value (Yang *et al*., 2017). Yasuda *et al*., (2014) used the dry ammonia pretreatment process to pretreat Pennisetum purpureum, and the ethanol yield after simultaneous saccharification and co-fermentation reached 74% of the theoretical value. Yang *et al*., (2017) studied the optimal pretreatment conditions of low-moisture waterless ammonia pretreatment of corn straw in a larger reactor scale (3 L) and found no significant difference compared with laboratory-scale experiments for a water content of 50 wt.%, 72 h, 75 °C, and 0.1 g NH3/g biomass, indicating that this method can achieve a higher glucose enzymatic hydrolysis rate when used on a larger scale.

3. CONCLUSION AND PROSPECT

Straw is a versatile renewable biomass resource. Ammoniation pretreatment technology, as a method that can effectively destroy the complex fibrous structure of straw, not only enhances the utilization efficiency of straw in feed and returning to fields but also introduces nitrogen source, increases the buffering performance of the fermentation system, improves the stability and gas production performance of straw in anaerobic fermentation for biogas system, and promotes the energy utilization of straw. Therefore, ammoniation pretreatment technology has broad prospects in the comprehensive utilization of straw. In addition, many factors affect the ammoniation pretreatment process, and the interactions between these factors should be fully considered during the straw pretreatment. The economic value should be considered to select the optimal pretreatment conditions. Based on the current ammonia pretreatment technology, further exploration still needs to be conducted in order to reduce the energy consumption during the pretreatment process and solve the problem of fermentation inhibition substances produced in the process.

ACKNOWLEDGMENTS

The author of this research is grateful to the Project of Heilongjiang Bayi Agricultural University's scientific research start-up plan for introducing talents (XYB202022) and the Guidance Project of Daqing City (zd-2021-91).

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