STRATEGIE OF PRETREATMENT OF LIGNOCELLULOSIC BIOMASS FOR BIOETHANOL PRODUCTION AS BIOFUEL

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Bioethanol is recognized as a valuable substitute for renewable energy sources to meet the fuel and energy demand, considered an environmentally friendly resource obtained from agricultural residues such as sugarcane bagasse, wheat straw, corn and rice straw. Lignocellulosic biomass (LCB) is the point of attention in replacing the dependence on fossil fuels. The recalcitrant structure of the lignocellulosic biomass is disrupted using effective pretreatment techniques that separate complex interlinked structures among cellulose, hemicellulose, and lignin. Recently, the thermophysical method or high-temperature steam explosion treatment of lignocellulosic biomass under pressure has become more popular. The method of decompression or steam explosion changes the biostructure of the product, destroys lignin bonds and affects the composition of the obtained products. The optimal conditions for explosive defibrillation are preliminary moistening of the product with water, a heating temperature of up to 200 ºC and a processing time of 10 minutes, which contributes to the transition of cellulose into a more accessible amorphous form, which later becomes available for enzymatic hydrolysis under the action of cellulases with the formation of sugars, which are fermented by yeast in ethyl alcohol - glucose, fructose.

The obtained results show that with an increase in the processing temperature from 150 to 200 ºC, the delignification of cellulose-containing raw materials increases, which is evidenced by a decrease in the content of residual lignin by 2.2 times, a decrease in the residual content of hemicelluloses in the product from 16.76 to 2.6%.

Keywords: bioethanol, biofuel, lignocellulosic biomass, pretreatment, steam explosion

DOI: 10.24263/EDSD-2024-6-31

Received 29.04.2024
Received in revised form 18.10.2024
Accepted 12.11.2024

Introduction

In the last 20 years, the crude oil crisis causes an increasingly high demand of renewable energy, especially biofuels. America and Brazil are the two leading countries in producing bioethanol from sugarcane and corn. Ethanol is predominantly used as a renewable «drop-in» transport fuel and ethanol-based value chains towards other compounds, including jet fuel and polyethylene (Tran, Le & Nguyen, 2019). In 2022, 103 billion liters of ethanol were produced by yeast-based fermentation of agriculture-derived carbohydrates. Of this volume, approximately 30% was produced from Brazilian cane sugar (mainly consisting of sucrose) and approximately 54% from corn starch-derived glucose, mainly in the United States of America. However, the production of biofuels from starches and sugars vigorously violates against the world's food security for humanity.

In an attempt to find an alternative approaches to bioethanol production, lignocellulosic biomass raises an intensive attention as cellulose is similar to starch and sugar because it is also a polymer of glucose. Bioethanol is produced from waste agricultural feedstocks, such as sugarcane bagasse, wheat straw, corn and rice straw. On evaluating the total production of various agricultural residues globally, the sugarcane bagasse (SCB) biomass is considered one of the abundant agricultural residues that hold the key to solving the global energy problem and environmental concern (Ajala, Ighalo & Ayanshola, 2021). According to recent research, the potential for lignocellulose biomass contributed from SCB worldwide annually is 243 million tonnes, which translates to producing 4.3 EJ of energy, which covers 6.8% of the present global supply of bioenergy (Pan, Zabed & Qi, 2022). Similarly, corn straw production in 2021–2022 was approximately 120 MT globally and has the potential to produce 23–53 billion tons of bioethanol in the United States alone (Ruan, Wang & Liao, 2019). The use of such biomass makes the feedstocks base for obtaining fuel ethanol practically inexhaustible.

Lignocellulosic biomass (LCB) is a complex structure consisting of fermentable and non-fermentable sugar. Cellulose is the most common component of lignocellulosic biomass, the content of which is 33–47%, depending on the type of raw material (Singh, Srivastava, and Shukla, 2016). Another copious compound in the LCB is hemicellulose (19–27%) in composition. Non-fermentable part of biomass are lignin (5–24%) and silica (18.3%) component which forms lignin–carbohydrates complex and hinders the further process of hydrolysis by binding with cellulose, reducing the exposed surface area for enzymatic action (Akhtar, Goyal, and Goyal, 2016) as well as forms a hindrance against external encroachment and prevents degradation. Both hemicellulose and lignin form cover over a cellulosic portion of biomass and reduce the efficiency of enzymatic hydrolysis and fermentation which ultimately lowers the product yield.

The bioethanol production scheme from lignin-cellulosic biomass consists of the following stages:

- Pretreatment of lignocellulosic biomass;
- Enzymatic hydrolysis of cellulose;
- Fermentation;
- Distillation of ethanol
- Production of biofuel

Pretreatment of lignocellulosic biomass is carried out to remove lignin, increase the porosity of fibers and enhance hydrolysis in the process of processing biomass into bioethanol. It is carried out by physical, chemical and biological methods.

Pretreatment with steam explosion, which is one of the main and widespread methods of physical and chemical pretreatment. Steam explosion is also considered an environmentally friendly method of delignification of plant biomass, since it uses high-pressure water vapor and does not emit any harmful emissions into the atmosphere (Rezania et al., 2020). If we compare 2 known environmentally friendly pretreatment methods – steam explosion and biological treatment, the results show that the cellulose content in the steam-treated biomass is 39.5%, while the cellulose content in the biomass after biological treatment is 37.6%. (Shen et al., 2019). This pretreatment method is performed at 1,5-2,8 MPa pressure and a high temperature of 160–260 °C in different residence times, i.e., 15, 30, and 60 min, along with sudden depressurization. It was evaluated that the total sugars were less concentrated when the material was exposed to the pretreatment for longer periods. As a result, applying steam explosion increased the quantity of total sugar accessible in comparison to such material that had no prior treatment. Therefore, it indicated that the operation of steam to dissolve the cellulose's protective hemicellulose and lignin structure was adequate (Bernier-

Oviedo, Rincon-Moreno & Vaquiro-Herrera, 2018; Shukla et al., 2023). According to this method, raw materials are processed under the pressure created by water vapor at a temperature of 160-200 °C for a short time, followed by a rapid release of pressure to atmospheric pressure (steam explosion effect). Under such conditions, hemicelluloses are hydrolyzed, the fibrous amorphous parts of the polymer chains of cellulose are hydrolyzed, leaving the crystalline segments of the chains in an unchanged state ([Bernier-Oviedo, Rincon-Moreno & Vaquiro-Herrera, 2018). After pretreatment, the degree of depolymerization of cellulose decreases from 1000 units for original cellulose up to 100-400 units for cellulose obtained by the steam explosion method (Cai et al., 2017). Rapid decompression of the material during such treatment helps to separate cellulose, hemicelluloses and lignin in the raw material, which makes it possible to more efficiently carry out enzymatic hydrolysis of cellulose to obtain bioethanol. Major drawbacks associated with it are partial lignin removal and the production of some toxic chemicals such as acetic acid, furfural, and hydroxymethylfurfural. During the process, inhibitory removal is required as it disturbs the sustainability of enzymes during hydrolysis and fermentation which sometimes results in high production costs.

The purpose of the work is to study the influence of the processing of lignin-cellulosic biomass by steam explosion on the composition of the formed products of explosive defibrillation. The results of the study are aimed at achieving one of the most important goals of sustainable development - affordable and clean energy.

Materials and Methods

Materials

The wheat straw was obtained from local farmers. Relative humidity was 6,4%. Before the steam explosion, the straw was crushed to a particle size of 2–3 cm using an electric shredder. The composition of wheat straw is shown in Table 1.

Table 1. The composition of wheat straw

Content	Indicator
Moisture, %	6.43
Ash, %	6.51
Cellulose, %	43.56
Hemicellulose, %	20.71
Lignine, %	24.47

The steam explosion was carried out in a laboratory reactor. 500 g of dried and shredded wheat straw (moisture content 6,4%) was mixed with water in a ratio of 1:1 and steam explosion was carried out at the specified residence time and temperature conditions at a pressure of 1,5 MPa.

Research Methods

The moisture content of cellulosic raw materials was determined by drying to constant weight at a temperature of 100-105 C°. Lignin content - by direct method by hydrolysis with a mixture of concentrated hydrochloric acid and 72% sulfuric acid [Schoorl method]. The amount of polysaccharides, easily and difficultly hydrolyzed, was determined by the number of monosaccharides by reducing ability determined by the Maquenne-Schoorl method [Schoorl method].

Results and Discussion

We studied samples of cellulose-containing raw materials (wheat straw) treated with water, followed by explosive decompression (steam explosion). Processing conditions - temperature 150ºC, duration of processing 20 minutes and 200ºC, duration of processing 10 minutes. The steam explosion method makes it possible to completely separate hemicellulose and a significant amount of lignin, while leaving almost completely activated cellulose. At the same time, the effectiveness of this method increases with increasing temperature and contact time.

The results of the analysis of intermediate products of explosive defibrillation are shown in Table 2.

Table 2. Physico-chemical composition of samples of explosive defibrillation products under different processing conditions

Content	Processing conditions	
	Temperature 150ºC Duration of processing 20 min	Temperature 200ºC Duration of processing 10 min
Dry solids, %	33.2	9.34
Moisture, %	66.8	90.66
pH	4.36	5.19
Amount of polysaccharides, easily hydrolyzed (hemicellulose), %	20.2	19.1
Mass content of reducing substances in the polysaccharide hydrolyzate, easily hydrolyzed, %	0.029	0.184
Amount of polysaccharides, difficultly hydrolyzed (cellulose), %	43.56	63.11
Mass content of reducing substances in the polysaccharide hydrolyzate, difficultly hydrolyzed, %,	0.12	0.17
Lignin content, %	22.1	12.1

As can be seen from the Table 2, the conditions of explosive defibration at a temperature of 150 ºC and a processing time of 20 minutes do not meet the requirements of delignification - the moisture content of the product was 66.8%. This indicates an insufficient degree of wetting by water vapor of the product sample, the content of residual lignin in the product is almost did not change and amounted to 22.1%, the hemicellulose content increased by only 6% compared to untreated wheat straw.

As the processing temperature increased from 150 to 200 ºC, the content of cellulose increased from 43 to 63% and hemicellulose decreased from 20 to 19%. However, the content of residual lignin in the intermediate product of explosive defibration remains at the level of 12%, which indicates the incomplete destruction of lignin bonds in the structure of the molecule, which will interfere with the enzymatic hydrolysis of raw materials and reduce the yield of bioethanol. The obtained results are confirmed by the research of other scientists. Thus, Shukla and others treated rice straw with hydrogen peroxide of different concentrations, and then conducted a steam explosion at a temperature of 121°C and a pressure of 130 kPa. At the same time, the cellulose content increased by 1.7 times, while there was a reduction in the hemicellulose and lignin content up to 1.2 and 2 times (Shukla, Kumar & Mohan, 2023).

Conclusions

Due to the presence of lignin in it, which binds cellulose and hemicellulose, wheat straw makes the structure of lignin-cellulosic raw materials stronger and firmer. That is why, when processing this raw material, it is necessary to pre-treat it to remove lignin and increase the porosity of the fibers.It was established that the method of decompression or steam explosion changes the biostructure of the product, destroys lignin bonds and affects the composition of the obtained products. The optimal conditions for explosive defibrillation are preliminary moistening of the product with water, a heating temperature of up to 200 ºC and a processing time of 10 minutes, which contributes to the transition of cellulose into a more accessible amorphous form, which later becomes available for enzymatic hydrolysis under the action of cellulases with the formation of sugars, which are fermented by yeast in ethyl alcohol - glucose, fructose.

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Conflict of interest

The authors state no conflict of interest.

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