Application of Feruloyl Esterase in Wheat Straw Pulp Bleaching

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Abstract. The pulp made from wheat straw fiber contains considerable natural cellulose, but there are more carbohydrate-ferulic acid ester-lignin cross-linking structure in the pulp. this cross-linking structure seriously hinders the recognition and binding of hemicellulase and substrate, thus affecting the efficiency of hemicellulose degradation. Feruloyl esterase, as one of hemicellulose degradation enzymes, can hydrolyze hemicellulose side chain branches. Make the plant grid structure loose, it is more important that it can enhance the accessibility of xylanase to the xylan trunk. Therefore, it is of great significance to apply it to the synergistic xylanase-assisted bleaching of wheat straw pulp.

Keywords: feruloyl esterase; wheat straw pulp; bioassisted bleaching.

1. Introduction

In the pulping and papermaking process, the bleaching process is mainly the use of chemicals to remove lignin from the pulp, but the environmental pollution is more serious. The use of biological enzyme bleaching technology to remove residual lignin from pulp is an important measure to speed up the green transformation of the paper industry [1,2]. Enzyme-assisted bleaching can reduce the amount of chemical bleaching reagents and pollution in the bleaching process, so it is a relatively green bleaching technology [3].

The pulp with wheat straw fiber as raw material contains considerable natural cellulose, and there are many carbohydrate-ferulic acid ester-lignin cross-linking structure in the pulp. this cross-linking structure seriously hinders the recognition and combination of hemicellulase and substrate, thus affecting the efficiency of hemicellulose degradation. As one of the hemicellulose degradation enzymes, Feruloyl esterase (Feruloyl esterase, FAE, EC 3.1.1.73) can hydrolyze the ester bond formed by FA between hemicellulose and other macromolecules (lignin, cellulose and pectin), and assist xylanase (one of the important hemicellulose degradation enzymes) to destroy and hydrolyze part of the cell wall structure, open the fiber structure, and make lignocellulose swell [4,5].

In addition, FAE can also promote the hydrolysis of hemicellulose by other hemicellulases, open the dense structure around the lignin layer, and help chemical bleaching agents to better permeate the lignin layer.

2. Research Progress on Bleaching of Wheat Straw Pulp

2.1 Microorganisms Directly Act on the Pulp for Bleaching

Microbial bleaching is studied by using some microorganisms that can degrade lignocellulose, mainly fungi and bacteria. In the study of the degradation of lignin by fungi, some white rot fungi which can secrete extracellular oxidase play a decisive role in the degradation of lignin. Bacteria use lignin or hemicellulose in pulp as carbon source to grow, reproduce and complete corresponding life activities [6]. In the study of Prince Sharma et al, Bacillus haloduransji, which produces xylanase, was inoculated into eucalyptus Kraft pulp for biobleach, and the viscosity of the treated pulp increased, indicating a net increase in the content of cellulose separated from lignin and xylan units in the pulp [7]. However, the direct action of microorganisms on the bleaching process is often not suitable for the requirements of pulping and papermaking process, its treatment cycle is long, and the enzymes produced are formed in the evolution of microorganisms themselves, which are greatly affected by the growth environment. At present, the research focuses on the screening of microbial species, degradation process and degradation mechanism.

2.2 Biological Bleaching of Lignin-Degrading enzymes

At present, lignin peroxidase, manganese peroxidase and laccase are the most common lignin-degrading enzymes. These three kinds of enzymes are a kind of extracellular oxidase secreted by white-rot fungi that can independently degrade plant lignin. However, at the present stage, biological bleaching can not completely replace chemical bleaching because the composition of pulp is complex. The bleaching environment is often accompanied by high temperature, high pressure, heavy metal ions, strong oxidants and extreme pH. The physical and chemical factors of the enzyme have poor resistance, which is easy to cause inactivation, and the effect of single enzyme is often not ideal. The combination of multi-enzyme treatment and compound enzyme preparation is expensive to purchase and apply directly, and its use is often limited.

2.3 Enzyme-Assisted Bleaching

In the study of enzyme-assisted bleaching, xylanase in hemicellulase is the most widely used. Xylanase itself can not degrade lignin macromolecules. The role of xylanase in bleaching is to make the residual lignin in pulp easier to remove in subsequent treatment, which is a bio-assisted bleaching or bleaching-promoting technology [8]. In 1986, Finnish scientists proposed for the first time that the application of xylanase in KP pulp could improve its bleaching performance [9]. Subsequently, Finnish paper mills began to try to apply xylanase in pulp bleaching process. Garg et al. applied xylanase from Bacillus stearothermophilus SDX to pulp-assisted bleaching process to improve pulp whiteness by 4.75% [10] at 60 ℃ for 2.0 h. In addition, with further research, it is found that xylanase-assisted pulp bleaching process can not only improve the delignification rate of pulp, but also reduce the amount of chemical bleaching reagents, thus reducing environmental pollution. Practice shows that when the same whiteness is achieved, the cost of chemical bleaching reagents can be reduced by 5% to 20% [11]. In addition, the physical properties and bleaching effect of pulp can be improved by adding xylanase in ECF and TCF processes.

3. Application of Ferulase in Pulp bleaching

3.1 Overview of Feruloyl Esterase

There are three types of hydroxycinnamic acid in plant cell wall: p-coumaric acid, FA and sinapic acid. The molecular structure is shown in the figure. FA plays an important role in the growth of plant cell wall. It can form cross-linking structure by ester bond and ether bond between lignin and lignin, between lignin and hemicellulose, and between hemicellulose and hemicellulose. FAE exists widely in nature and belongs to a subclass of carboxylic ester hydrolases [12]. It can hydrolyze ferulate which is difficult to degrade in plant cell wall, so as to destroy plant cell wall structure, promote the combination of other enzymes and plant fiber, and finally act on lignocellulose to achieve the purpose of hydrolyzing and delignification.

In 1987, Mackenzie et al.[13] discovered FAE in Streptomyces olivaceus for the first time and was considered to belong to the hemicellulose degradation enzyme system. In 1991, Faulds et al[14] isolated and purified FAE from Streptomyces olivaceus for the first time. Then more and more FAE-producing fungi, bacteria and yeasts were isolated and screened. In 1997, Vries[15] cloned fae from Aspergillus tubingensis and Aspergillus niger for the first time. With the deepening of research, more and more biotechnology functions of FAE have been discovered. It has potential application value for plant biomass conversion and biosynthesis of high value-added molecules, and is widely used in food, feed, fuel, health care, medicine, papermaking and other industries.

According to previous studies, there are many kinds of FAE, and there are great differences in physical and chemical properties and substrate specificity of FAE from different sources[16]. At present, Crepin is widely used in the classification of FAE[17]. Based on the hydrolytic specificity of FAE to four aromatic substrates-methyl ferulate (MFA), methyl caffeate (MCA), methyl erucate (MSA) and methyl coumarate (MpCA), and the ability to release ferulic acid dehydrogenation dimer from the substrate, FAE is divided into four categories A, B, C and D. Udatha et al.[18] collected FAE sequences from 365 different sources, and divided FAE into 12 different categories according to amino acid composition, protein secondary structure and physicochemical properties, but the study of substrate specificity of these categories still depended on A~D classification. It is very important to understand the specific structure related to the function of the enzyme or the analytical crystal structure of amino acid residues. Samad et al found that the conserved sequences and gene sequences of the four kinds of FAE were different, which confirmed that the conserved sequence of esterase gene might be related to the heterogeneity of the substrate.

There are differences in the spatial structure of different types of FAE, and the corresponding catalytic substrates are also diverse, but they are all globulins with compact structure. The whole topological structure is a typical α/β hydrolase structure[19]. The catalytic center is composed of three amino acid residues (Ser-His-Asp). Ser, as a nucleophilic center, is responsible for attacking the ester bond of the substrate, and combines with His and Asp to form a stable tetrahedral transition state structure.

After the ester bond of the substrate is opened, it binds with the enzyme to form an enzyme-acyl complex to attack the tetrahedral intermediate, and then releases phenolic acids such as free FA[20]. This mechanism is the same as that of Ser lipase and protease[21].

3.2 Application of Feruloyl Esterase in Wheat Straw Pulp Bleaching

In the paper industry, FAE is considered to be a good choice for delignification. It can hydrolyze the ester bond between hemicellulose sugar chain and lignin, degrade lignin-carbohydrate complex in conjunction with xylanase and laccase, reduce pulp kappa value and improve lignin removal rate. Record et al.[22] determined the effect of lignin removal from wheat straw by recombinant FAE combined with laccase and xylanase. It was found that the addition of FAE combined with xylanase /laccase reduced the Kappa value to 3.9, and the lignin removal rate reached 74.1%, which was 12.6% higher than that of xylanase / laccase alone. Adding FAE to the pulp biobleaching process can not only increase the paper strength and achieve a better bleaching effect, but also reduce energy consumption and the use of chemical reagents, but also help to protect the environment. The application of FAE as a substitute for bleaching reagent for delignification will become one of the key concerns and research directions of researchers.

4. Summary

The addition of feruloyl esterase to xylanase treated pulp can promote the hydrolysis of hemicellulose by xylanase, reduce the amount of chemical bleaching reagent, improve the hydrolysis efficiency of hemicellulose, and finally enhance the bleaching effect of pulp.

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