



Enzymatic pulping of lignocellulosic biomass

Xuejiao Lin^{a,1}, Zhengmei Wu^{a,1}, Chenyuan Zhang^{a,d}, Shijie Liu^{a,c}, Shuangxi Nie^{a,b,d,*}

^a College of Light Industry and Food Engineering, Guangxi University, Nanning, 530004, China

^b State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China

^c Department of Paper and Bioprocess Engineering, SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY, 13210, United States

^d Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning, 530004, China



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ABSTRACT

With advances in biotechnology, enzyme technologies have been increasingly applied to pretreat lignocellulosic biomass before the production of pulp. There are several driving forces, which include decreasing environmental impact from the traditional pulp and paper manufacturing processes, decreasing the overall production cost, and improving the product properties. This paper reviews recent developments in the area, particularly, related to the production of bleached pulp, dissolving pulp and pulp refining. This paper focuses on the mechanism and influencing factors of enzymatically assisted pulp bleaching to reduce adsorbable organic halide (AOX) formation and dissolving pulp production and focuses on saving energy in pulp refining. The enzyme technology is in the marketplace of the pulp and paper processes, and it is expected to gain more importance in the future.

1. Introduction

Green technology/practice has been in high demand, particular for the traditional manufacturing industry, such as pulp and paper industry (Balea et al., 2017; He et al., 2016). For this reason, enzyme technologies and their applications to the pulp and paper manufacturing processes have been a hot topic in the research community (Ma et al., 2017; Menezes et al., 2016). With significant advances in enzymes production technology, the market price of enzymes have fallen, which allows the use of enzymes, e.g., xylanase and cellulases, in related processes. For example, biobleaching has become a preferred method for pulp bleaching, and the use of enzymes can be extended to the production of dissolving pulp and mechanical pulp (Sindhu et al., 2016). The great potential for enzyme technology has been demonstrated in reducing environmental pollution and improving pulp properties as well as the comprehensive utilization of lignocellulosic biomass (Meighan et al., 2017).

Lignocellulosic biomass primarily consists of cellulose, hemicellulose, lignin and extracts (Kim et al., 2016; Liu, 2010; Mosier et al., 2005; Song et al., 2016a; Yao et al., 2015b; Zhang et al., 2012). At present, three types of enzymes, namely, cellulases, hemicellulases and ligninases, are used in the lignocellulosic biomass treatment process (Demuner et al., 2011; Nie et al., 2018). Cellulases can be used to improve the performance of dissolved pulp (Duan et al., 2017) and reduce the energy consumption of pulp refining (Singh et al., 2015).

Hemicellulases are primarily used to assist in pulp bleaching for the reduction of environmental pollution load (Maan and Dutt, 2017; Nie et al., 2015). The major ligninases, such as laccase, can be used to treat the lignocellulosic biomass, which can also reduce pollution (Gonçalves et al., 2015; Pei et al., 2016; Wang et al., 2014b).

Dissolving pulp is a type of high-purity chemical pulp that is regarded as an important raw material for producing cellulose derivatives, such as regenerated cellulose fiber, cellulose rayon, acetate fiber and cellulose ethers (Duan et al., 2017; Tian et al., 2014; Wang et al., 2015c). Utilization of lignocellulosic biomass to prepare highly reactive dissolving pulp is now facing shortcomings in terms of low pulp purity and poor fiber reactivity. The enzymatically assisted preparation of dissolving pulp can hydrolyze or oxidize the non-cellulose components, based on the specificity and high efficiency of the enzymes. Therefore, the pulp purity and fiber reactivity can be improved, and the fiber viscosity can be reduced. The technology of pulp bleaching assisted by enzymes is a reliable and green technology (Aracri and Vidal, 2011). Xylanase is the most commonly used enzymes in pulp bleaching. Xylanase can hydrolyze hexenuronic acid (HexA), formed during cooking, and xylan in fiber, thereby enhancing the permeability of the pulp (Saleem et al., 2012). To activate and relax the fiber surface to promote the water absorption and fibrillation of the fiber, enzymatic pretreatment with high activity cellulases or hemicellulases was employed, thereby improving pulping performance and reducing energy consumption of pulp refining (Cebreiros et al., 2017; Yang et al., 2011).

* Corresponding author at: College of Light Industry and Food Engineering, Guangxi University, Nanning, 530004, China.

E-mail address: nieshuangxi@gxu.edu.cn (S. Nie).

¹ These authors contributed equally to this work.

The objective of this paper was to review and summarize the applications of enzymes in pulp bleaching, production of dissolving pulp and in the pulp refining. The mechanism and influencing factors of enzymatically assisted pulp bleaching to reduce adsorbable organic halide (AOX) formation, to control factors for enzymatic assisted production of dissolving pulp and to assess the mechanism of energy saving in the enzymatically assisted pulp refining process were summarized. It is our aim to aid the development of clean pulp bleaching and the efficient production of dissolving pulp and enzymatic pulp refining with low energy consumption, as well as to boost the application of enzymes and further increase biotechnological applications in the pulp and paper industry.

2. Enzymatic treatments for pulp bleaching

Bio-bleaching is a process of improving pulp bleachability or directly enhancing the brightness through the degradation of lignin, which depends on the reaction between enzymes with the chemical constituents of the pulp. The main enzymes used in the pretreatment of pulp bleaching are hemicellulases and ligninases. Hemicellulases primarily consist of xylanase and mannanase. The xylanases are a group of complex enzymes that can degrade xylan into oligosaccharides and xylose. The lignin-carbohydrate complex (LCC) is destroyed during the degradation of xylan, and more active groups are exposed. Meanwhile, the fiber cell wall becomes loose and helps to expose lignin to bleaching agents and alkali, which will improve the bleachability of the pulp (Maan and Dutt, 2017). Ligninases primarily include laccases, lignin peroxidases and manganese peroxidases. Laccases combined with redox mediator can degrade phenolic and non-phenolic lignin. Laccase pretreatment reduces the chromophores of the pulp and provides a favorable basis for subsequent bleaching (Bholay et al., 2012). The greatest advantage of bio-bleaching is to reduce the consumption of chlorine-based bleaching agents to reduce the formation of AOX and improve paper performance.

2.1. Reduction of AOX formation

2.1.1. AOX formation mechanisms

AOX is the most common parameter to indicate and evaluate the environmental impact of bleaching processes (Lehtimaa et al., 2010; Nie et al., 2014a). In the global pulp and paper industry, chlorine dioxide has now become the most basic bleaching agent in ECF bleaching (Nie et al., 2013; Yao et al., 2017). Many researchers have studied the formation pathway of AOX (Bjorklund et al., 2004; Ni, 1992). There are seven major chlorine species in the bleaching liquid during chlorine dioxide bleaching. The graphical model for the reaction between chlorine compounds during chlorine dioxide bleaching is presented in Fig. 1 (Nie, 2015).

During chlorine dioxide bleaching, the main factors that affect the

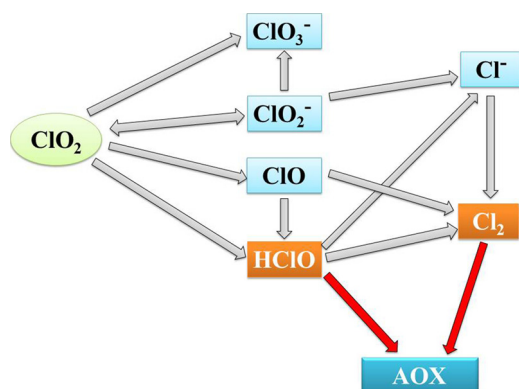


Fig. 1. A simplified scheme of the reactions during chlorine dioxide bleaching.

formation of AOX are the concentration and structure of lignin, the available chlorine dosage, the reaction temperature, the pH and the HexA content (Nie et al., 2014b). To reduce the formation of AOX, the key is to improve the delignification rate and reduce the amount of bleaching chemicals (Nie et al., 2016; Yao et al., 2015a). Common methods of enzymatic assisted pulp bleaching include xylanase bleaching, laccase bleaching and the synergistic bleaching of enzymes.

2.1.2. Reduction of AOX by xylanase pretreatment

Xylanase is the most common hemicellulases used in pulp bleaching. HexA is formed in the cooking process of hardwood and nonwood, and the residual xylan in the fiber can be hydrolyzed by xylanase, thereby enhancing the permeability of the pulp (Saleem et al., 2012). With increasing improvement of enzyme production technology, the market price of enzymes is falling significantly. Studies of xylanase-assisted chlorine dioxide bleaching have gradually increased. This is mainly because xylanase bleaching has many advantages as compared to traditional bleaching. The primary advantage is to reduce the pollution load of the bleaching wastewater (especially the reduction of AOX formation) (Dedhia et al., 2014; Sharma et al., 2014). Senior and Hamilton (Senior and Hamilton, 1992) employed xylanase to decrease the formation of AOX in softwood and hardwood kraft pulp bleaching. They found that xylanase pretreatment can yield high-brightness, up to 90%ISO, and resulted in a reduction of chlorination charges of 26% and 35–45%. In their further studies, they found that AOX formation could decrease by up to 40% after xylanase pretreatment in a standard (CD) EDED sequence (Senior and Hamilton, 1993).

In recent years, numerous studies on xylanase-assisted bleaching have been published by multiple research institutions. Nie et al. (Nie et al., 2015) employed xylanase-assisted chlorine dioxide to treat bagasse pulp and found that chlorine dioxide was reduced by 12.5%–22%, and the production of AOX was reduced by 21.4%–26.6% when the same degree of brightness was obtained. Similarly, Dai et al. (2016) employed chlorine dioxide to bleach bagasse pulp after xylanase pretreatment. They found that the HexA and kappa number both decreased after xylanase pretreatment, and AOX emissions decreased by 29.8%. Cheng et al. (2013) employed xylanase-assisted chlorine dioxide to bleach eucalyptus kraft pulp. They found that xylanase exhibited good thermal stability, and the pulp brightness increased by 12.9%, the kappa number decreased by 27.4%, and the chlorine dioxide consumption was reduced by 17% when the temperature was below 60 °C and when the pH increased from 6 to 8. Maan and Dutt (2017) utilized natural xylanase to pretreat kraft pulp, and the results showed that the consumption of bleaching chemical was reduced by 17.16%, while the formation of AOX decreased significantly. Ghafoor et al. (2016) employed acid and oxygen pretreatment for wheat straw pulp to remove partial metal ion before xylanase treatment. The results showed that xylanase treatment can not only improve the brightness of pulp to 76% but also greatly reduce the use of bleaching chemicals, therefore decreasing the amount of harmful substances such as AOX.

Xylan on the fiber surface can be effectively degraded by xylanase during pretreatment, and the fiber cell walls swell and soften as a result. Lignin can therefore be extracted more easily from the fiber. Xylanase can also degrade hemicellulose and destroy the connections between carbohydrates and lignin. The residual lignin can be contacted more easily by chlorine dioxide and can be removed more easily after xylanase treatment. The goal of using less chlorine dioxide to obtain the same bleachability can be realized after xylanase pretreatment, which enables the generation of less AOX (Sharma et al., 2014). In addition, HexA formed during the cooking process can be removed by xylanase. HexA is closely related to the brightness and kappa number of the pulp and the formation of AOX, which will consume more chlorine dioxide and increase AOX amounts (Andreu and Vidal, 2014). Based on the previous study, Nie et al. (2015) found that HexA is contained in the main and branched chain of hemicellulose and can be removed from the fiber due to the degradation of the hemicellulose chain during

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