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Laccase-TEMPO-mediated air oxidation of galactomannan for use as paper strengthening agent

Jipeng Di[a], Qi Sun[b], Xianliang Song[a,*]

[a] MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, Beijing, 100083, China
[b] Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China

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A B S T R A C T

In this study, galactomannans, which are a type of plant polysaccharide, were oxidized by using a laccase and TEMPO-mediated air-oxidation system. The influence of the oxidation conditions, including the laccase doses, oxidation times, and amounts of oxidizing system, on the properties of the paper were investigated. The results showed that the oxidized galactomannans could improve the paper properties. The optimal conditions were as follows: a 60 U/g enzyme dosage; 6-h oxidization time and a 0.1 g TEMPO dosage. When compared with the control paper, the tensile index and folding endurance have been improved by 28.42% and 88.02%, respectively, when 1.5% oxidized galactomannans were used, and for the recycled paper, the increment could reach 126.97% and 43.85% correspondingly. Also, the results of the elemental, FT-IR, and CP/MAS^{13}C NMR analyses demonstrated that some of the hydroxyl of the galactomannans had been transformed into the carboxyl and aldehyde groups.

1. Introduction

Paper-making additives are auxiliary chemicals, widely used in the paper industry, as they benefit the technical processing performances, as well as the end products. Due to the ongoingshortage of virgin wood pulp fibers, the proportion of recycled fibers has been growing, and recycled fibers have became the main raw material in the paper-making industry (Salam, Lucia, & Jameel, 2015). However, recycled fibers are well known to have low bonding strength due to earlier drying phases, resulting in poor paper properties (Hubbe, 2007). Therefore, paper strengthening agents, such as various types of paper-making additives, are necessary to improve the paper properties when recycled fibers are used (Hubbe, 2006). Polysaccharides and fibers have extensively been used as paper strengthening agents (Ashori & Nourbaksh, 2008; Bai, Hu, & Xu, 2012). However, natural polysaccharides, which are usually modified chemically, do not significantly improve paper strength (Wang, He, & Song, 2017).

Currently, with increasing of environmental protection awareness, it has become ineluctable for various industries to consider potential environmental problems during their production processes. The paper industry has a history of pollution issues. It has made progress over the decades but improvements can still be made in reducing the environmental impacts of its various industrial processes. Therefore, it's necessary to improve the traditional production processes of paper-making additives which consume a large amount of chemical reagents and produce heavy pollutant emissions (Yan, Li, & Song, 2017). The usage of renewable resources has a tremendous application potential in the paper industry.

Galactomannans (GM), mainly derived from Leguminosae seeds, are polysaccharides composed of a linear chain of β-1, 4-D-mannopyranose, to which α-1, 6-D-galactopyranose units are attached, the peculiar structures were found to make them fairly soluble in water at different temperatures, as well as flexible in application, and chemically/biochemically quite reactive (Cheng, Chick, & Rau, 2002). Due to their advantages of renewability, biocompatibility, and environmental friendliness, galactomannans have been widely used in both food and non-food industries (Chen, Zhao, & Liu, 2016). For instance, galactomannans are adsorbed by cellulose fibers, and are used in the paper industry in order to improve the mechanical properties of paper (Lima, Oliveira, & Buckeridge, 2003). The main three commercially used galactomannans in food and non-food industries are guar gum, tara gum, and locust bean gum (Albuquerque, Coelho, Correia, Teixeira, & Carneiro-da-Cunha, 2016). Galactomannans, compared with traditional synthetic polymers, have huge potential environmental benefits as a paper strengthening agent.

Laccase is a polyphenol oxidase which can oxidize both phenolic and non-phenolic substrates (Alfred & Richard, 2002). Due to the low redox potential and substrate inaccessibility, the application of laccase

* Corresponding author.
E-mail addresses: hdmsxl@sohu.com, sxlswd@163.com (X. Song).

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was very limited (Canas & Camarero, 2010). However, the discovery of a mediator for laccase has effectively overcome the limitations of its applications. Using TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy radical) as a mediator, a laccase-TEMPO system has demonstrated the ability to selectively oxidize the primary hydroxyl groups of galactomannans (Nooy, Besemer, & Bekkum, 1995; Parikka et al., 2017). In the cases of TEMPO-mediated reactions, the TEMPO acts as a primary oxidant, and requires a secondary oxidant (usually NaBr/NaClO), which regenerates the TEMPO in the catalytic cycle. Although it has been found to be highly efficient when compared to the enzymatic oxidation process, the presence of sodium bromide, along with the generation of toxic chlorinate, is highly undesirable. The usage of green oxidants, such as oxygen, has effectively made up for these weaknesses. The results have been an increased preference to use O_2 or H_2O_2/enzymes bases in TEMPO systems, rather than salt bases in oxidative systems (Sindhu & Patrick, 2009). First of all, in this laccase-mediator system (LMS), the TEMPO molecule is oxidized by enzymes to an oxonium ion, which can then selectively oxidize the primary hydroxyl groups to the corresponding aldehydes and carboxylates (Viikari, Kruus, & Buchert, 1999). There has been reported that carboxylates could improve paper strength (Law, Daneault, & Guimond, 2007), aldehydes as a transition state before primary alcohols were converted to carboxylic acid, can also improve paper strength, especially the wet-strength (Saito & Isogai, 2006). In the laccase-mediator system, oxygen can be used as the primary oxidant and continuously transform inactiveenzymes to an active one (Bourbonnais, Paice, Freiermuth, Bodie, & Borneman, 1997). In this cyclical system, only oxygen is consumed during the reaction. Therefore, the reaction can continue, as long as the oxygen is present (Aracri, Vidal, & Ragauskas, 2011). In a previous study, primary hydroxyl groups in potato starch were successfully oxidized to corresponding aldehyde and carboxylic acid functionalities using a laccase-mediator system (Mathew & Adlercreutz, 2009). When compared with the traditional chemical systems, NaClO/NaBr system, using an oxygen supported LMS consumes less chemical reagents with near-neutral pH (Bragd, Besemer, & Bekkum, 2001), resulting in a decrease of environmental damages (Baldaro et al., 2012).

In this study, in order to determine a new method to produce paper strengthening agents, the oxidation of galactomannans using a laccase-TEMPO system was examined. The influence of the oxidation conditions, including the laccase doses, oxidation times, and additive amounts of oxydate, on the properties of paper were investigated.

2. Experiment

2.1. Materials

In this study, the laccase from the aspergillus species were obtained from Hefei BoMei Biotechnology Co., Ltd (Hefei, China), the batch No. QL8598, and the CAS No. 80498-15-3. The ABTS and TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy radical) were obtained from Sigma-Aldrich (USA). Aspen kraft pulp was provided by HunanYueyang Paper Group. The pulping conditions were sulfidity 21.8%, active alkali 15.2 g/L, maximum temperature 168 °C, heating up time 1.8–2 h, yield 45%, and beating degree 40° SR.

2.2. Enzyme assay

The laccase activity was determined by oxidation of the ABTS (Bourbonnais, Leech, & Paice, 1998). Laccase could transform ABTS to its cation radical, which has the maximal absorption wave length at 420 nm. The absorbance value increased with the rise of ABTS radical concentration (Niladevi, Sukumaran, Jacob, Anisha, & Prema, 2009). One activity unit (U) was defined as the amount of laccase transforming 1 μmol/min ABTS to its cation radical.

Table 1
Carboxyl content and substitution degree of original galactomannan and oxidized galactomannan.

Laccase amounts (U/g)	Carboxyl content (mmol/kg)	Degree of substitution
0	16.7	0.013
30	66.6	0.096
60	91.8	0.108
90	125.1	0.126

Notes: Oxidied time is 6 h.

2.3. Galactomannan treatment

In this study, 1 g of galactomannan and 0.1 g of TEMPO were placed in a 500 ml beaker. The laccase amounts, as the variable conditions, were added to the beaker, and all the reagents were dissolved in a 100 ml 0.1 mol/L citrate buffer at pH 4. The reaction was followed for variable hours, under constant mechanical stirring (500 rpm) conditions, at 40 °C. When considering the price and potential danger of using pure oxygen, air was considered to be a better choice. Therefore, a suite of bubble generators were used, which consisted of a 20 mm diameter sintered air-stone, and a single outlet air pump. The pump is a kind of air pump used in aquarium, the power consumption of the pump was approximately 2 W, and the output of the air was approximately 1.5 l per minute. Meanwhile, a large number of bubbles would generate in beaker, so it's necessary to setup the mechanical defoaming device (500 rpm), the length of blade is 30 mm. At the end of the reaction, in order to obtain the products in a solid form, two volumes of ethanol were mixed with the product thoroughly. Then, the precipitate was transformed into a final product, following the processes of a vacuum filtration, and drying at room temperature.

2.4. Paper-making and paper testing

According to the ISO 5269-2, the kraft pulp handsheets were made with the addition of variable paper strength agents. The step is that: a certain amount oxidized galactomannans were added to the pulp while stirring, 0.5% $Al_2(SO_4)_3$ based on dry fiber (w/w) was added to the pulp, then the pH was adjusted to 5 by H_2SO_4 solution, and the handsheet was made after stirring for 10 min. The control handsheets were made in the same way but without any other additives. The handsheets were then conditioned at 23 °C, and 50% relative humidity, for at least 24 h before physical testing was performed. Meanwhile, some of the handsheets were taken for the preaparation of recycled paper, these handsheets were immersed in water at room temperature overnight, then were disintegrated into pulp for making handsheets again without any chemical additions.The properties of all the handsheets were then determined according to ISO 534, ISO536, ISO 1924-3, ISO 1974, and ISO 5626.

2.5. Determination of the carboxyl content

A potentiometric titration method was used to determine the carboxyl content of the oxidized galactomannans (Wang, Long, & Xie, 2001).

2.6. Elemental analysis

The elemental contents of C, H, and N were analyzed by using a Vario EL III instrument, and the content of O was calculated by subtracting the C, H, and N contents from the total.

2.7. Degree of substitution (DS)

Exactly 0.2 g of the product was dissolved with 50 ml distilled water

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