



Modification of industrial softwood kraft lignin using Mannich reaction with and without phenolation pretreatment



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ABSTRACT

The amination of industrial softwood kraft lignin was conducted using the Mannich reaction to modify the lignin structure for value-added applications. To understand the reaction mechanism and to quantify the amount of amine groups that were introduced, different types of NMR analyses were performed. The lignin was also pretreated by phenolation to increase its reactivity and the amount of the amine groups that were introduced. The Mannich reaction was very selective at the C-5 position of the guaiacyl units and complete under acidic conditions with ~11-fold amounts of reagents of dimethylamine and formaldehyde over either model lignin (4-hydroxy-3-methoxyacetophenone, HMAP) or industrial spruce kraft lignin (LignoBoost lignin, LBL). For LBL, 28 amine groups were introduced over 100 aromatic rings. By weight, the nitrogen content was 2.5%. The aminated lignin was found to possess a higher molecular mass, reaching a Mp of 4.9×10^3 Da compared to the original 3.9×10^3 Da, and with a considerably increased dispersibility, especially in a dilute aqueous solution of hydrochloric acid (pH = 3), namely 5.2 mg/ml. With a preceding phenolation treatment, which increased the amount of phenolic aromatic rings available for the Mannich reaction, an introduction of 42 amine groups over 100 aromatic rings, or a nitrogen content of 4.8%, was obtained, which caused a further increase of the molecular mass to 5.1×10^3 Da (Mp) and of dispersibility in the aqueous solution of hydrochloric acid up to 32.0 mg/ml. The aminated lignins with or without the phenolation pretreatment formed very stable colloidal suspensions in water, with large particle sizes (391 and 39 nm), high zeta potentials (31.6 and 27.2 mV), and large charge densities (1.6 and 1.2×10^{-7} equiv./ml, respectively). The potential value-added applications of these modified lignins with high amine contents include use as surfactant chemicals, polycationic materials and slow-release fertilisers, among others.

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1. Introduction

Lignin is the second most abundant component next to cellulose in biomass (Bolker, 1974). In Sweden, large quantities of lignin are produced as a by-product in the pulp and paper industry when converting wood, e.g., spruce, into chemical pulp fibers for subsequent conversion into paper and board products. The lignin is dissolved in the process liquor, forming the so-called black liquor. Although there is a complete energy and chemical generation system using the black liquor in the predominating kraft pulping process, the energy generated by burning the black liquor is greater than the process demand, and the recovery boiler is the limiting factor for increasing the pulping capacity. A LignoBoost process has therefore been established as a complete system for extracting lignin, the

by-product component from the wood with a high heating value, from the black liquor. This process serves as a good solution to the “bottleneck” problem. The LignoBoost lignin obtained from spruce kraft pulping is a relatively pure lignin that can be used as a biofuel or as a raw material for the production of various bio-based materials and chemicals (Oehman et al., 2006). However, the industrially produced lignin is generally known being of low value (Stewart, 2008) due to heterogeneous structures and poor properties. For value-added applications, structural modifications of the lignin are required.

Lignin modification has long been an attractive and challenging topic. The investigated modifications of lignin include demethylation (Campion and Suckling, 1998), hydroxymethylation (Zhao et al., 1994), phenolation (Effendi et al., 2008), oxidation (Xiang and Lee, 2000), reduction (Meister, 2002) and hydrolysis (Wahyudiono et al., 2008); however, amination is one of the most promising modifications (Meister, 2002) because the amine groups that are introduced are ionizable and positively charged under acidic conditions. The modified lignin is highly hydrophilic and it still possesses

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a high molecular mass, which renders it useful for many potential applications, e.g., for polycationic materials (Jiao, 2010), as a reagent for enzyme immobilization (Fang et al., 2009) and for use as slow-release fertilisers (Ramirez et al., 1997).

Chemically, there are many applicable methods for the introduction of amine groups. Among these various methods, the Mannich reaction is the simplest and the most straightforward method. Traditionally, the Mannich reaction is one of the most important fundamental reactions in organic chemistry (Carey and Sundberg, 1983). For example, this reaction is a powerful method that is typically used for the synthesis of various β -amino ketones or esters, which are, for example, useful synthetic building blocks for the preparation of many biologically important nitrogen-containing compounds (Trost and Fleming, 1991). Many investigations have been conducted on the lignin structure, which are summarized in two reviews (Liu et al., 2007; Yue et al., 2001). The Mannich reaction has been performed on model lignin (Nie et al., 2012) and on various industrial lignins, with the objective of producing cationic asphalt emulsifiers (Wang et al., 2000; Zhang et al., 2006a,b), cationic surfactants (Matsushita and Yasuda, 2003b), anion-exchange resins (Brezny et al., 1988; Matsushita and Yasuda, 2003a) and retention aids (Matsushita et al., 2004). In addition, the Mannich reaction of lignin has been conducted to investigate the synthetic mechanism (Mikawa et al., 1956) and to investigate the lignin structures after performing a subsequent Phosphorous-31 Nuclear Magnetic Resonance ($^{31}\text{PNMR}$) analysis (Jiang and Argyropoulos, 1998).

Mannich reactions can be conducted under alkaline, neutral or acidic conditions. More commonly, the amination of lignin structures has been investigated by charging different types of amines and formaldehyde under alkaline conditions (Kong et al., 2010; Schilling and Brown, 1988; Slack et al., 1998). In 2003, the Mannich reaction was comprehensively investigated for the chemical conversion of highly condensed acid-hydrolysed lignin, a main byproduct from the wood hydrolysis industry, into a cationic structure under acidic conditions (Matsushita and Yasuda, 2003b). In this field, understanding the reaction mechanisms and the effective introduction of amine groups are of theoretical and practical importance, respectively, for which structural characterization and nitrogen content determination are needed. To date, elementary analysis (EA) has almost exclusively been the quantification method for evaluating the effects of nitrogen introduction, but EA cannot supply additional information concerning structural changes, e.g., about the bonding positions and side reactions, etc. It is well known that nuclear magnetic resonance (NMR) is a modern and very informative method. However, NMR analysis has only been applied in a few studies and only on the model lignin structure (Matsushita and Yasuda, 2003b). On the other hand, investigations concerning the amination modification of lignin are still being conducted, and a new patent application has recently been reported (Kong et al., 2010). In addition, to obtain higher amine contents, a phenolation pretreatment to increase the lignin's reactivity has been conducted for sulphuric acid lignin (Matsushita and Yasuda, 2003b).

The aim of the present study was to use the Mannich reaction in the structural modification of industrial LignoBoost spruce kraft lignin to understand the Mannich reaction mechanism and to introduce high amounts of amine groups under acidic conditions. This study started from the study of model lignin using the conditions reported in (Matsushita and Yasuda, 2003b). Various types of NMR analyses were then performed to establish the NMR methods for qualitatively monitoring the structural changes and for quantifying the content of the introduced amine groups, both of which are important to eventually control the reaction in terms of tailoring the structure and properties. Furthermore, determination of the total

nitrogen content was also performed. Phenolation of the industrial lignin was conducted, which was followed by the Mannich reaction to obtain an even higher introduction of amine groups. Finally, the dispersibility and colloidal properties of the aminated lignins were determined to evaluate their potential in applications.

2. Experimental

2.1. Materials and chemicals

4-Hydroxy-3-methoxyacetophenone (HMAP), purchased from Aldrich-Chemie (Sweden), was used as a lignin model. LignoBoost lignin (LBL) from spruce kraft black liquor was obtained from the Wallenberg Wood Science Center (WWSC) in Sweden. A 40% dimethylamine aqueous solution, a 37% formaldehyde aqueous solution, acetic acid, and 1,4-dioxane were all of AR grade and were purchased from Fisher Scientific.

2.2. Phenolation pretreatment

A mixture of 0.5 g (~2.5 mmol) LBL and 3.0 g (~32 mmol) phenol was stirred in 7.5 ml of 72 wt% sulphuric acid at 60 °C for 6 h, followed by dilution in water to 3.0% sulphuric acid. Then, the solution was autoclaved at 125 °C for 1 h. The solid precipitates, termed as phenolized LignoBoost lignin (P-LBL), were filtered, washed with warm deionised water until neutral pH, and dried in a 105 °C oven.

2.3. Mannich reaction

The lignin model (HMAP) in an amount of 33 mg (0.2 mmol) was dissolved in 1.0 ml dioxane followed by additions of 2.2 mmol 40% dimethylamine aqueous solution, 2.2 mmol 37% formaldehyde aqueous solution, and 0.2 ml acetic acid successively, as described in (Matsushita and Yasuda, 2003b). Then, the mixture was heated up and kept at 60 °C for 4 h under stirring. The reaction was terminated by adjusting the solution pH to approximately pH 9 with 2 M NaOH, followed by extraction with ethyl acetate. The obtained ethyl acetate solution was dehydrated over sodium sulphate and further evaporated to dryness by film evaporation.

In the cases of lignin samples, 100 mg (~0.5 mmol) LBL or P-LBL was dissolved in 1 ml of an 80% dioxane aqueous solution, followed by the successive addition of 5.5 mmol of a 40% dimethylamine aqueous solution, 5.5 mmol of a 37% formaldehyde aqueous solution, and 0.2 ml of acetic acid. Then, the mixture was heated and maintained at 60 °C for 4 h under stirring. The final product mixture was evaporated under vacuum to remove most of the organic reagents, purified by dialysis with a molecular weight cut-off of 1000 Da and then freeze-dried. The obtained products were used for the analyses mentioned below.

2.3.1. HMAP

MS m/z : 237.7 (silylated M^+); ^{13}C NMR δ : 26.61 (CH_3), 55.97 (OCH_3), 111.33 (aromatic C-2), 115.32 (aromatic C-5), 124.00 (aromatic C-6), 129.23 (aromatic C-1), 147.91 (aromatic C-3), 152.07 (aromatic C-4), 197.37 (C_α of side chain), 26.61 (C_β of side chain).

2.3.2. Aminated HMAP

MS m/z : 295.2 (silylated M^+); ^{13}C NMR δ : 26.13 (CH_3), 43.94 [$\text{N}(\text{CH}_3)_2$], 55.52 (OCH_3), 60.00 (CH_2), 110.13 (aromatic C-2), 121.92 (aromatic C-5), 122.88 (aromatic C-6), 127.43 (aromatic C-1), 147.27 (aromatic C-3), 152.18 (aromatic C-4), 195.95 (C_α of side chain), 26.13 (C_β of side chain).

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