



Improvement of direct liquefaction of technical alkaline lignin pretreated by alkaline hydrogen peroxide

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ABSTRACT

Technical alkaline lignin was first pretreated with alkaline hydrogen peroxide and then liquefied using methanol-water mixture or methanol solvents. When the technical lignin was pretreated by 0.5% H₂O₂ at 80 °C, the liquid yield of the liquefaction in methanol-water mixture and methanol increased from 84.2% to 93.5% and from 79.2% to 90.5%, respectively. The alkaline lignin (AL), pretreated lignin (PL) and resulting liquid (RL) were characterized by using GPC, FT-IR, and ¹H NMR methods. The GPC results illustrated that the pretreatment by 0.5% H₂O₂ could decrease the weight average (M_w) and number average (M_n) molecular weight from 1692 to 1354 g/mol and from 1376 to 1207 g/mol, respectively. The FT-IR and ¹H NMR results confirmed that some phenols were oxidized to quinone or aliphatic chain structures, and parts of side chains were separated from lignin.

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1. Introduction

Lignin is the second most abundant natural polymer after cellulose in wood. It is a biopolymer which consists of hydroxyphenylpropane groups such as *trans-p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; these units are connected with ether and carbon-carbon linkage using a helical structure [1,2]. Currently, the industrial production of lignin was from paper pulping factories as well as biorefineries. These by-products have been viewed as a waste or low-value products; no more than 2% of lignin has been isolated from pulping black liquors and used for some industrial products [3]. However, the aromatic structure of lignin suggests that this biopolymer might be a substitute source for petroleum to produce aromatic chemicals if its linkage bonds can be broken using thermochemical methods [4–6].

Direct liquefaction is a promising technology to produce liquid oil and chemicals as the products are water insoluble and include a range of aromatic chemicals [7,8]. Suitable solvents and conditions could provide a high oil yield and various kinds of products with and without catalysts. After Song et al. [9] screened several common

solvents for native lignin catalytic conversion, methanol proved to be most effective. Singh et al. [10] compared methanol and ethanol liquefaction at 200 °C, 250 °C and 280 °C, and maximum yield of 85% was observed at 200 °C for 30 min residence time using methanol. When guaiacol was used for pine wood liquefaction at 300 °C and 60 bar [11], up to 93% oil was obtained; moreover, it was found that wet (10 wt% on total feed basis) biomass resulted in higher oil yields than dry biomass. Supercritical fluid consisting of carbon dioxide, acetone, and water was used for converting organosolve lignin to phenolic oil and aromatic monomers [12]. Yuan et al. [13] degraded alkaline lignin in ethanol and NaOH solutions, and found that over 99% oil was produced at 260 °C.

Besides solvents and reaction conditions, pretreatment of raw materials may be another way to promote high oil yields. Mild pretreatment on cornstalk using acid-chlorite, for example, increased the hydrothermal liquefaction oil yield from 23.4% to 31.4% in ethanol [14]. Among the biomass pretreatment methods, hydrogen peroxide pretreatment is an effective and environmentally-friendly pretreatment way that has been applied to wood waste [15], straw [16], sugarcane bagasse [17] and furfural residue [18]; these studies have showed an outstanding delignification rate. Hydrogen peroxide had a more reactive oxidant than oxygen [19]. In the alkaline medium, the reduction potential of the H₂O₂/H₂O pair was +0.994 V, which was higher than the O₂/H₂O pair of +0.401 V. Its hydroperoxide anions could oxidize unsaturated side chain such as

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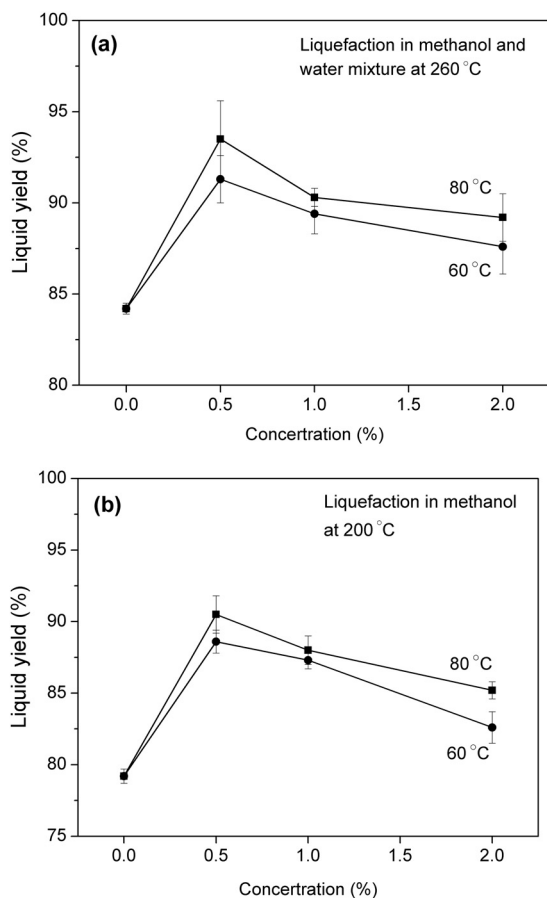


Fig. 1. Effects of the H₂O₂ concentration on liquefaction yields in methanol-water mixture (a) and methanol (b), respectively.

3-(4-hydroxy-3-methoxyphenyl)-2-acrole to produce *p*-hydroxy benzaldehyde, *p*-hydroxy benzoic acid and *p*-hydroxyl guaiacol [20,21] and these fragments can be further converted to quins [22]. Also, the aromatic rings have been cracked through the dissociative peroxy acid groups, attacking the multiple reaction sites offered by *o*- and *p*-quinone rings. This process resulted in producing ring opening products. As de- and re-polymerization happened simultaneously during liquefaction [23,24], the hydrogen peroxide cracked the lignin, reduced the activity of some groups, overcame re-polymerization, and promoted degradation in solvent effectively.

To our knowledge, there has not been any recorded study on alkaline lignin pretreatment using hydrogen peroxide. In this work, hydrogen peroxide was used to break alkaline lignin before degradation. Since aromatic ring-opening reactions favor acidic buffers, an alkaline condition was used to protect the aromatic structure of lignin [19]. The raw and pretreated lignin were directly liquefied, as a result, products were characterized by FT-IR, NMR and GPC to understand the change in the technical lignin. Meanwhile, GC-MS was used to determine the various monomers obtained from the liquefaction.

2. Materials and methods

2.1. Lignin preparation

Alkaline lignin was isolated from the black liquor residue of poplar wood soda pulp, which was kindly provided by Shandong Chenming Paper Group Co., Ltd. Through a typical isolation process, 100 mL of black liquors were diluted in 900 mL of distilled water

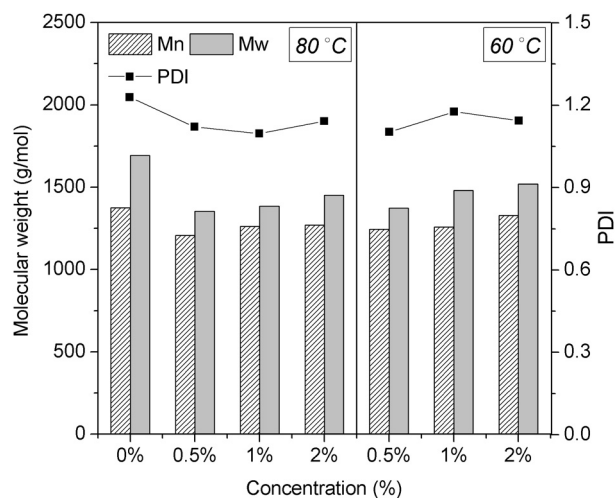


Fig. 2. The GPC results of pretreated lignin over different concentrations.

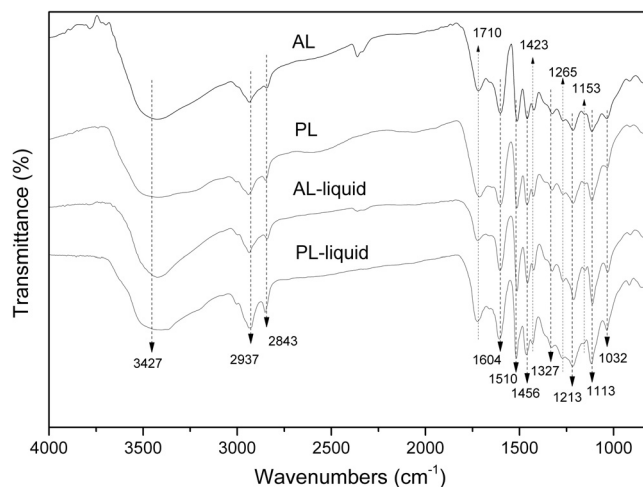


Fig. 3. FT-IR results of alkali lignin and their resulting liquids. AL was alkali lignin, PL was pretreated lignin over 5% H₂O₂ and liquid was resulted product.

and the pH of the mixture was adjusted to 2 by adding 4 M HCl. After being deposited overnight, the crude lignin was separated by centrifugation and washed by deionized water several times until the washings were rendered neutral. The lignin was vacuum dried and finally milled into powders. According to TAPPI T211, the ash content of 2.4% was obtained by combusting the lignin at 525 °C for 4 h. This raw alkaline lignin was named as AL.

2.2. Pretreatment of the alkaline lignin

Alkaline lignin pretreatments were conducted at 5% substrate solids (w/v) in the pressure tube reactor. The solution concentration and pretreatment temperature were screened. For solution concentration, 30% H₂O₂ was diluted to 0.5%, 1%, and 2% and adjusted to pH 11.5 with 4 M NaOH solutions. Each concentration was settled at 60 °C and 80 °C for 1 h, respectively. After the pretreatment, 4 M HCl was loaded in the mixture and its pH was adjusted to 2. Samples derived from the pretreatment were centrifuged and then vacuum dried at room temperature for 10 h. Based on the different solution concentration, three kinds of pretreated lignin were obtained and named as PL-0.5, PL-1, and PL-2.

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