Abstract of the Dissertation

DECOMPOSITION BEHAVIORS OF LIGNIN IN HYDROTHERMAL TREATMENT OF LIGNOCELLULOSICS

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The lignocellulosic cell wall consists mainly of cellulose, hemicellulose and lignin, and these components are composed in intricately artful manner to enforce the cell wall, having a resistance to water and most organic solvents. Among the natural polymers, lignin is not uniformly distributed within the cell wall and its chemical structure is depending on the species, cell types and morphological regions, thus its utilization is quite difficult. For the utilization of lignocellulosics, the hydrothermal treatment is a promising technology. However, the detailed decomposition behaviors of lignin are not clarified yet. Thus, the main objective of this dissertation is to elucidate the decomposition behaviors of lignin in hydrothermal treatment of lignocellulosics, consisting of 7 chapters.

In *Chapter 1*, the background of this dissertation is briefly summarized, which includes taxonomy of lignocellulosics, topochemistry of lignin, and various decomposition methods of lignin [1].

In *Chapter 2*, Japanese cedar (*Cryptomeria japonica*) as one of gymnosperms was treated by two-step semi-flow hot-compressed water (1st stage: 230°C/10 MPa/15 min, 2nd stage: 270°C/10 MPa/15 min), and the hot-compressed water-soluble portion and water-insoluble residue were obtained. For the hot-compressed water-soluble portion, it was separated during standing for 12 h under ambient condition to be water-soluble

portion and precipitates, which were retrieved by the filtration. The lignin-derived products in the obtained "water-soluble portion", "precipitates" and "insoluble residue" were then quantified and characterized with the analytical instruments [2]. For the lignin-derived products in water-soluble portion, 17 kinds of aromatic monomers were determined by gas chromatography/mass spectrometry analysis, and all of them contained methoxyl and phenolic hydroxyl groups. The lignin-derived products in precipitates were composed of relatively higher molecular weight distribution. Furthermore, according to the alkaline nitrobenzene oxidation, the lignin-derived products in precipitates were rich in ether type linkages. In contrast, the insoluble residue was mostly composed of lignin (0.875 g/g), rich in condensed type linkages. Based on these lines of evidence, condensed type lignin must be resistant to hot-compressed water and remain as insoluble residue after two-step treatment.

As mentioned in *Chapter 1*, the distribution of lignin is depending on the species, cell types and morphological regions. In *Chapter 3*, therefore, the difference in delignification between Japanese cedar (one of gymnosperms) and Japanese beech (*Fagus crenata*) (one of dicotyledonous angiosperms) was investigated from a topochemical viewpoint as treated by hot-compressed water [3]. As a result, through the microscopic observations of insoluble residues, the delignification was preferentially occurred for both species from the secondary wall compared to the compound middle lamella. This result was supported by the methoxyl content analysis of the residual lignin. Furthermore, the residual lignin was rich in condensed type lignin, indicating that the lignin in the compound middle lamella would be rich in condensed type linkages. Such information must reveal the importance of topochemistry in the clarification of decomposition behaviors of lignin.

In *Chapter 4*, in order to explore the utilization possibility of the obtained lignin-derived products, the author focused on the precipitated lignin among the obtained lignin-derived products by hydrothermal treatment. The precipitated lignin from Japanese beech was characterized and compared with the milled wood lignin (MWL), which is widely considered to be a good representative of the original lignin [4]. According to Fourier transform-infrared spectroscopy and two-dimensional nuclear magnetic resonance spectroscopy analyses, their structures were relatively similar. However, the precipitated

lignin contained higher syringyl (S) lignin as compared to MWL. This would be because the precipitated lignin is derived mainly from the fiber secondary wall because of the richness of S lignin in the fiber secondary wall. Furthermore, the precipitated lignin contained higher contents of phenolic hydroxyl groups and ether type linkages compared to MWL, which should increase the potential of the precipitated lignin to be utilized as the value-added aromatic materials.

In *Chapter 5*, the hydrothermal treatment was applied on the corn (*Zea mays*) cob, which is one of the monocotyledonous angiosperms, in order to gain better insight into the whole species [5]. As a result, 98.8 wt% of corn cob was decomposed and dissolved into hot-compressed water. Among the decomposed products, more than 80 wt% was quantitatively determined such as saccharides, lignin-derived aromatic compounds, dehydrated compounds, fragmented compounds and organic acids. As for the lignin, 95.6 % of the initial lignin was decomposed and dissolved into hot-compressed water. In the water-soluble portion, monolignols derived from all of guaiacyl, syringyl and *p*-hydroxyphenyl lignins, and ferulic and *p*-coumaric acids were obtained. Accordingly, it was found that the hot-compressed water is a good medium to decompose corn cob.

In *Chapter 6*, for the further understanding of the delignification behaviors by hydrothermal treatment, phenol was applied for the subcritical treatment of the woods for its high ability to delignify lignocellulosics. Then, the delignification behaviors of Japanese beech as treated by subcritical water and phenol were compared from a topochemical viewpoint [6]. As a result, based on the preferential cleavage of ether type linkages in lignin, the lignin in the secondary wall of the fiber and vessel was easily delignified in both subcritical water and phenol. Lignin in the compound middle lamella showed resistance to subcritical water, while it was delignified in the subcritical phenol. Through the structural analyses of water- and phenol-soluble portion, it was found that the differences would be due to the influence of solvolysis. Accordingly, the differences in the course of both the treatments are due more likely to the intrinsic characteristics of lignin in various morphological regions and the properties of solvents.

Finally, concluding remarks of these investigations are summarized in *Chapter 7* along with the future prospects for this dissertation.

References

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