学位論文内容の要旨

博士の専攻分野名称：博士（農学）　　氏　名：Linping Wang

学位論文題名

Analysis of solution structure of isolated lignins and their related compounds with size-exclusion chromatography equipped with a multi-angle light scattering detector

（光散乱検出器を備えたサイズ排除クロマトグラフィーを用いた単離リグニン及び関連化合物の溶液構造の解析）

Lignin is the second abundant biomass component after cellulose in terrestrial plants. The isolated lignins, which are separated from the lignocellulose, have gained much attention in both academic and industrial research. The pulping industry can produce a large amount of technical lignins, which are considered to be a promising alternative feedstock to petrochemicals. However, their inhomogeneity of chemical structure impedes their utilizations. Molar mass (MM) determination of technical lignins is one of the important subjects to elucidate their chemical structures. Currently, size-exclusion chromatography (SEC) with tetrahydrofuran (THF) as an eluent and a conventional calibration curve, which is made from polystyrene standards, is widely used for MM determination of acetylated lignins. However, this method gives the relative MM, but not the absolute MM. On the other hand, SEC combined with multi-angle laser-light scattering detector (SEC-MALS) enables to obtain number-average MM (Mn), weight-average MM (Mw) and molar mass dispersity ($Đ_M$) of polymers based on the absolute MM, because the MALS detector can directly measure it at any retention volume of SEC. One problem of SEC-MALS for lignin MM determination is self-fluorescence of lignin, which increases light scattering intensity and leads to overestimation of MM. The self-fluorescence is caused by the conjugated structures of technical lignins.

In this study, SEC-MALS was used for lignin MM determination, and its practical conditions were investigated to minimize the self-fluorescence of lignin as much as possible. The solution structure of technical lignins were also investigated with respect to molecular size and their branched structure.

1. Determination of acetylated hardwood kraft lignin via SEC-MALS using different wavelength laser light

Two types of MALS detector with different laser lights at the wavelength of 658 nm and 785 nm were used to determine MM of acetylated hardwood kraft lignin (Ac-HKL) with the SEC-MALS method. The MM of Ac-HKL measured at 658 nm was

much larger than that measured at 785 nm. This meant that the short wavelength detector overestimated MM due to the self-fluorescence of lignin. Thereby, the long wavelength detector could remove the self-fluorescence, and gave us accurate MM. Mn and Mw of Ac-HKL determined by the SEC-MALS at 785 nm in THF were 6.2 and 6.5 times, respectively, larger than those estimated by SEC with the conventional calibration curve created with authentic polystyrene. The Mark-Houwink-Sakurada (MHS) equation for Ac-HKL was established based on the Mw of Ac-HKL fractions, which was obtained by solvent precipitation with hexane and had different MM range. The MHS equation ($[\eta] = kM^a$) was $[\eta]/mL\ g^{-1} = 0.320\ M^{0.24}$ in THF and $[\eta]/mL\ g^{-1} = 0.142\ M^{0.26}$ in DMSO. These values of parameter "a" in the equation for HKL demonstrate that Ac-HKL has a more compact solution structure in THF than polystyrene. The compact solution structure of Ac-HKL may be caused by its branched structure.

2. Relationships between MM of acetylated lignin and its frequency of branched linkage

To confirm the relation of the compact structure with the branched structure of KL, SEC-MALS measurements were conducted for *8-O-4'* type of acetylated polymeric lignin model compound (Ac-M-8O4') as a non-branched lignin besides acetylated softwood KL (SKL) and HKL. Furthermore, the frequency of 5-5' interunitary linkage, which was a branching point, in the lignin was determined by a combination analyzing method of the alkaline nitrobenzene oxidation and ^{1}H-NMR.

As a result, the plot of MM for Ac-M-8O4' vs. retention time of SEC was similar to that of polystyrene, which revealed that Ac-M-8O4' exhibited a similar swelling behavior in THF to that of polystyrene. When the frequencies of 5-5' linkage was plotted against MM at a given retention time of SEC, a linear relationship between MM and 5-5' frequency was observed in the high MM region. This indicated that the branched structure provides kraft lignins a large molar mass and a denser morphology.

3. Conclusion

MM is very important to characterize a chemical compound. In 1960's, Mn and Mw of several lignins were reported to be in the digit range of 10^3-10^5 g mol^{-1}. However, their recent values were in the range of 10^3-10^4 g mol^{-1}, which were measured by using a conventional SEC with a calibration curve of polystyrene. In this study, the reason for a big difference in MM estimation was clearly elucidated by using a SEC-MALS system; the conventional SEC system ignored the relation between MM and hydrodynamic radius of lignin, and underestimated MM. Thus, this study pointed out invalidity of the conventional SEC system, and demonstrated to measure accurate MM with SEC-MALS system. Henceforth, an accurate MM determination of technical lignins is enabled based on this research result and measurement protocol.