論 文 の 内 容 の 要 旨

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論文題目　　Studies on the relationships between hemicellulose composition and lignin structure

（ヘミセルロース組成とリグニン構造の関係に関する研究）

The structure of lignin has not yet been completely elucidated. Milled wood lignin (MWL) and cellulolytic enzyme lignin (CEL) have been used as suitable lignin samples to characterize natural lignin in wood. However, MWL and CEL are isolated from wood meal after rather extensive ball milling, and it has been demonstrated that the structure of lignin could be changed during ball milling. In this dissertation, the first topic was to investigate the relationship between the structure of hemicelluloses and that of lignin by two methods. One is the relationship between syringyl ratio (syringyl / (syringyl+guiaicyl)) and neutral sugar in 65 woods, another one is the analysis of fractions from beech and red pine which were extracted by LiCl/DMSO dissolution system. The second topic was to prepare the CEL by a new pretreatment method. The structure of lignin could be changed during ball milling. Thus, CEL was tried to obtain after mild EDA pretreatment instead of ball milling. As third topic, 65 woods were analyzed by IR spectroscopy to examine if syringyl ratios can be precisely expressed by area ratios of characteristic peaks of aromatic ring in IR spectrum.

Relationships between hemicellulose composition and lignin structure

The compositions and the absolute amounts of neutral sugars were determined for 48

hardwood species (including 17 hardwoods of genera Acacia, 14 hardwoods of genera Eucalyptus and 17 hardwoods of different other genera) and 17 softwood species by alditol-acetate method, and their relationships to the syringyl ratios of lignin, which was determined by nitrobenzene oxidation, were investigated. In 48 hardwood species, with the increase in syringyl ratio of lignin, xylose/glucose ratio and rhamnose/glucose of 48 hardwoods seemed to show upward tendency and mannose/xylose ratios of 48 hardwoods showed downward tendency, while, absolute amounts of glucose of 48 hardwoods remained almost constants. In 17 softwood species, with the increase in lignin contents, mannose /glucose ratio decreased, as well as absolute amounts of glucose, remained almost constants. Therefore, in both hardwoods and softwood, it was hemicellulose but not cellulose that changed in the conjugation with lignin structure and amount. Accordingly, the diversity of hemicellulose was closely related to the structure of lignin.

Relationships between hemicellulose composition and lignin structure of LCC fractions

New fractionation method of wood cell wall components was applied to selected wood species (beech and red pine). Stepwise extraction (Fig. 1, Scheme I) and individual extraction (Fig. 2, Scheme II) were used to obtain fractions.

Finely ground wood meal was first extracted by aqueous dioxane and DMSO to obtain conventional Björkman lignin (MWL) and Björkman LCC. The residue was then subjected to successive extraction by DMSO with increasing content of LiCl (0.5 to 3.0%) in order to obtain new LCC fractions which have not been extracted by a conventional method.

By the analysis of conventional MWL and LCC fractions together with new LCC fractions by stepwise extraction, the following results were obtained. 1) In case of beech, syringyl ratio of soluble fractions was always lower than that of insoluble fractions. 2) For both beech and red pine, lignin structure of S_S1 fraction (MWL) was quite different from other soluble fractions S_S2 to S_S9. 3) Fractions with higher lignin content tended to exhibit higher xylan and lower glucan content in neutral sugar composition in beech. In case of red pine, no clear tendency was observed. 4) Fraction S_S6 of beech and red pine seemed to be very important. Because from S_S6 to S_S9, lignin content, xylan content are lower, and glucan content is higher.

In case of individual extraction, the results indicated that red pine was more difficult to be dissolved than beech. Lignin of red pine seems to be more difficult to be dissolved than lignin of beech. For both beech and red pine, solubilization of milled wood by the LiCl/DMSO solvent system was basically controlled by the solubilization of cellulose. However, lignin of red pine seems to be playing more important role to prevent cell wall

dissolution than lignin of beech.

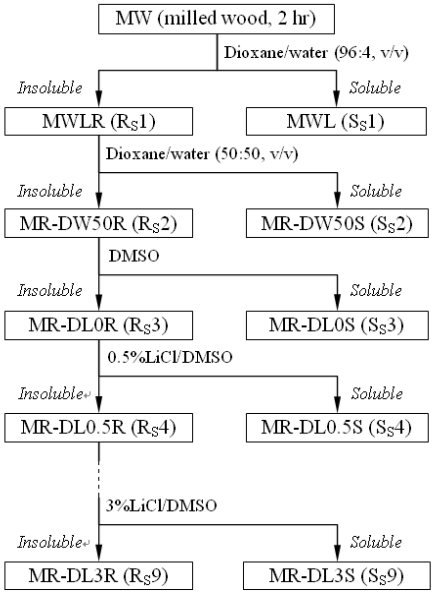

Fig. 1 Scheme I for the isolation procedure of various fractions by the stepwise extraction from milled wood meals

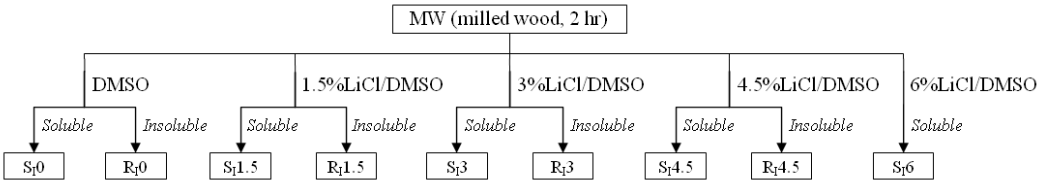

Fig. 2 Scheme II for isolation procedure of various fractions by the individual extraction from milled wood (2 hr)

Isolation of cellulolytic enzyme lignin (CEL) after pretreatment by lignocelluloses dissolution method

Compared to MWL, CEL was considered to be more representative of the total lignin in wood than MWL due to the higher yield. However, both MWL and CEL need to go through rather extensive ball milling pretreatment. In this chapter, EDA pretreatment before enzymatic hydrolysis was used instead of ball milling as shown in Fig. 3. The results show that after pretreatment and enzymatic hydrolysis, more than 80% of lignin was recovered in the residual fraction (WNLi8E), and no obvious change of the structural characteristics of lignin was observed. The carbohydrate content of WNLi8E is 29.5%. Although this value is

higher than that of MWLi6E (usual CEL obtained by the use of ball milling pretreatment), it is quite lower than that of WLi8E (CEL obtained without any pretreatment). It suggested that EDA pretreatment is an effective method for the lignin separation by enzymatic hydrolysis.

Fig. 3 The method to obtain enzymatic hydrolysis lignin

Analysis of lignin aromatic structure based on the IR spectrum

17 softwoods and 48 hardwoods were analyzed by IR spectroscopy to examine if lignin syringyl ratio (syringyl/(syringyl+guaiacyl)) obtained by nitrobenzene oxidation analysis can be precisely expressed by area ratios of characteristic peaks of aromatic ring in IR spectrum. Area ratio of two peaks is referred to as that of two wavenumber domains, represented by "wavenumber 1/ wavenumber 2". Examined peak area ratios were 1595/1509, 1509/1460, 1275/1220, 1130/1032 and 835/(855+815). Among these ratios, log(1595/1509) and log(1275/1220) showed significant linear relationship with the syringyl ratios with a correlation coefficient of 0.98 for all 65 woods. These two ratios could also be used to distinguish all the hardwoods from the softwoods.

Preparation, characterization and Photodegradation of epoxy chloropropane modified rice straw

Whole wood dissolution system (dissolution into 6% LiCl/DMSO after slight ball milling) was applied to dissolve modified rice straw obtained by etherification reaction by the use of epichlorohydrin. The purpose of this modification was to convert straw into a thermoplastic material. From IR analysis, neutral sugar analysis and weight percent gain (WPG), it was suggested that the reaction of cellulose hydroxyl group with epichlorohydrin proceeded well as expected. When the modified rice straw was subjected to whole wood dissolution system, 4 hr milling was required to be completely dissolved instead of 2 hr milling which is usually required for the dissolution of wood. Considering that grasses are usually much easier to be dissolved than wood, the necessity for the longer milling time seemed to be due to the matrix formation in cellulose by the reaction with epichlorohydrin. Moreover, Modified rice straw has good photo degradability as well as natural rice straw.