論 文 の 内 容 の 要 旨

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論文題目　Development of lignocellulosic solution and its application to chemical analysis of plant cell wall components
（リグノセルロース溶液の開発とそれを用いた植物細胞壁構成成分の化学分析）

In this thesis, the researches were focused on the development of solution systems of lignocellulosic materials by the use of common solvents and chemical analysis of plant cell wall components on the basis of these solutions. Dimethyl sulfoxide containing lithium chloride (LiCl/DMSO) was found to be used as a new solvent system for lignocellulosic materials. The dissolution of lignocellulosic materials in LiCl/DMSO was achieved by using two different pretreatment methods, ball milling pretreatment and ethylenediamine pretreatment. Pretreatment conditions were designed so that structural change of cell wall components during the whole dissolution process could be minimized. The new fractionation methods of lignin, lignin-carbohydrate complex (LCC) and polysaccharides from the lignocellulosic solution were established. Main concern of the analyses of obtained fractions was to elucidate the relationships and possible interactions between cellulose, hemicellulose and lignin.

Dissolution of milled wood in LiCl/DMSO

The LiCl/DMSO solvent system completely dissolved milled wood prepared by as short as 2 h of milling pretreatment using a planetary ball-mill. The nitrobenzene oxidation and ozonation analyses indicated that the structural change of lignin caused by the 2 h of milling is not significant. In contrast, the destruction of the cellulose crystalline region in the milled wood was serious even with 1 h of milling. Compared with already reported solvent systems, the advantages of the LiCl/DMSO system, developed in this thesis, are high solubility, low degradation of lignin and the simplicity of the solvent itself. Thus this solvent system can be applied widely to the spectral analyses of the entire lignin fraction in wood cell wall. For example, at the first time, the structural information of the whole aromatic part of lignin was obtained by measuring NMR of this complete wood solution. The gram absorptivity of lignin at 280 nm was obtained by measuring the UV absorbance of this solution. Interestingly, the absorptivity increased along with milling time, which suggested that gram absorptivity of lignin could be applied only to semi-quantitative determination. The wood solution forms gel at relatively high concentration by standing the solution at room temperature. The critical concentration for gelation increased along with milling time.

Dissolution of ethylenediamine pretreated lignocellulosic material in LiCl/DMSO

Milling pretreatment caused a minor but unavoidable structural change of lignin, cellulose and hemicellulose. Especially, in order to obtain the solution of lignocelluloses with high cellulose DP (degree of polymerization), another pretreatment method is required. From this point of view, the ethylenediamine pretreatment method was established for dissolution of lignocellulosic material. Various lignocellulosic samples, such as microcrystalline cellulose (Whatman CF11), cotton, cellulose I, cellulose II, holocellulose or kraft pulps (softwood, hardwood) including those with relatively high lignin content, were soaked in ethylenediamine for a described period at room temperature and then the bulk of ethylenediamine was removed by freeze drying. These

ethylenediamine pretreated samples can be dissolved in LiCl/DMSO solvent system. Interestingly, even hardwood kraft pulp with as high as 10.5% lignin content gave the transparent solution. After the EDA pretreatment, the crystallinity of the lignocellulosic materials remained as high as the original samples, although the crystal structure changed. Because milling of the sample is not required, degradation of the cell wall components caused by milling does not take place. This is the first time that transparent solutions of underivatized pulps with high lignin content were obtained in a simple organic solvent system. The formation of a lignocellulose-EDA complex seems to be critical for the dissolution in LiCl/DMSO. The NMR spectrum of the EDA treated lignocellulosic solution had good resolution even though the DP of the cellulose in the pulp is very high. A very good relationship between UV absorbance of lignin at 280 nm in pulp solution and corresponding kappa number of pulp was obtained. Although the ethylenediamine pretreatment method is applicable to partially delignified samples, about 70% of the original wood meal without milling was found to be dissolved by repeating ethylenediamine pretreatment and dissolution in LiCl/DMSO.

Fractionation and characterization of wood cell wall components by using LiCl/DMSO system

One new and simple fractionation method of wood cell wall components by the use of LiCl/DMSO solvent system was acheived by varying the dissolving capacity of LiCl/DMSO system, i.e. by changing the LiCl concentration in DMSO. When LiCl concentration was higher than 6%, milling-pretreated wood meal completely dissolved in DMSO/LiCl, but when it was lower than this value, some part of milled wood was always left as an insoluble fraction depending on the LiCl concentration. Accordingly, different LiCl concentration gives different soluble and insoluble fractions, analyses of which must give new insight into the nature of cell wall components.

Nitrobenzene oxidation (N.O.) analysis revealed that the lignin in the insoluble fractions always had higher syringyl ratio, S/(S+V), and higher N.O. products yield, S+V, than corresponding soluble fractions, which indicated that the secondary wall type lignin with higher S/(S+V) ratio was more

difficult to be dissolved than the primary wall type lignin with lower S/(S+V) ratio. With the increase in LiCl concentration in DMSO, the yield of soluble fraction increased and finally reached 100% when LiCl concentration was 6%. The proportion of lignin in each soluble fraction decreased, while the yield of S+V and the S/(S+V) ratio increased with the increase in the LiCl concentration. As to the solubilization behavior of carbohydrates, the most significant trend resulted from the increase in LiCl concentration of the solvent is the increase of the proportion of glucan (most presumably cellulose) in the fraction. It was safely stated that solubilization of cellulose controls the whole solubilization of milled wood. It was also clearly shown that about 40% of lignin and xylan dissolved independently from the cellulose solubilization but the solubilization of the rest was assisted by the cellulose solubilization.

When the concentration of LiCl reached 3%, about 90% of the milled wood dissolved. Although the remaining 10% dissolved completely by increasing the LiCl concentration to 6%, analysis of this fraction seems to give a key to understand the interaction between lignin, hemicellulose and cellulose.