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主 論 文 の 要 旨

Structure of water solubilized sulfuric acid lignin by hydrothermal reaction and its functional development

論文題目 (水熱反応により水溶化した硫酸リグニンの構造と機能発現)

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論 文 内 容 の 要 旨

In recent decades, the depletion of traditional fossil fuel resources and irreversible climate change attributed to anthropogenic carbon dioxide emissions have been viewed with increasing concern. This concern drives a strong global interest in carbon-neutral renewable energy sources and has promoted considerable efforts to tap into these sources. The use of lignocellulosic acid saccharification process using sulfuric acid to produce bio-ethanol has enormous potential because of the abundance and renewable nature of lignocellulosic materials. However, the procedure also produces large quantities of sulfuric acid lignin (SAL), which shows variability in its physical-chemical properties and an extremely low reactivity, limiting its industrial uses greatly. Therefore, the development of value-added polymers and bioproducts from SAL is considered to be of utmost importance, not only to develop this acid-hydrolysis-based saccharification process for achieving a sustainable economy, but also because of the increasing importance to add value to lignin produced as a bio-residue.

In recent study, it was found that hydrothermal reaction can convert SAL into a water-soluble polymer (HSAL). In this thesis, the structural characteristics of hydrothermally treated SAL were analyzed, and the its functional development were investigated.

Investigation of chemical structure of HSAL:

The effect of hydrothermal reactions on enhancing the solubility and reactivity of SAL was discussed. A hydrothermal reaction was firstly conducted on SAL from *Cryptomeria japonica* to obtain a completely water-soluble lignin. Fourier-transform infrared spectroscopy, gel permeation chromatography, gas chromatography, and NMR analyses revealed that the hydrothermal reaction of SAL caused depolymerization,

demethylation, and the introduction of phenolic hydroxyls. Furthermore, another experiment was conducted on synthesizing a lignin polymer model compound (DHP) ¹³C-labelled on the aromatic ring, followed by hydrothermal reaction and acetylation. The detailed structural information of DHP under the hydrothermal reaction was obtained by solid-state cross-polarization magic-angle spinning NMR analysis. The results showed that the reactivity of the hydrothermally treated SAL was enhanced by the hydrothermal reaction, through the reversed increase in the phenolic hydroxyl/aliphatic hydroxyl ratio in the condensed lignin units.

Utilization of HSAL for flocculant and dispersant:

Two kinds of ionization applications on HSAL were presented. Firstly, HSAL-based cationized flocculants were synthesized by a reaction with glycidyl trimethylammonium chloride (GTA). Dye removal tests were performed using three kinds of organic dyes and the GTA-HSAL-based flocculants. The results indicated an ideal dye removal ratio on GTA-HSAL (higher than 90% for all the dyes used), which suggested that GTA-HSAL has huge potential, as the core molecule, to develop a highly efficient dye flocculant. Then, carboxymethylation of HSAL with bromoacetic acid was conducted to obtain a HSAL-based anionic dispersant. Dispersibility tests using gypsum paste showed that the carboxymethylation product (CHSAL) has an equivalent dispersibility weaker than that of commercial lignosulfonate. The highly condensed structure of CHSAL may have been the reason for this result.

Investigation of the physiological activity of HSAL on plants:

A hydroponic cultivation system with the addition of HSAL showed that it greatly promotes the elongation of the root system. Furthermore, HSAL has some positive effective on the growth of the main root, lateral root, and thick lateral root, but less effect on the L-type lateral root. EdU staining shows that this phenotype is related to the promotion of root cell division. Detailed mechanisms require further research.

In conclusions, the hydrothermal reaction can convert sulfuric acid lignin (SAL) into a soluble lignin in neutral water and an insoluble lignin in organic solvents. Depolymerization, demethylation, introduction of phenolic group and aromatic ring cracking were determinate during the hydrothermal reaction. Then, results of ionization applications of HSAL suggested that HSAL has an expectant potential character as a raw material with some chemical modification to give it various industrial uses (GTA-HSAL as a flocculant; CHSAL as a dispersant). Finally, HSAL shows an unexpectedly high physiological activity on plants, especially on promoting the elongation of the root system dramatically. EdU staining shows that this phenotype is related to the promotion of root cell division.