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Lignin: Its Functions and Successive Flow

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Summary: Phenolic lignin-based polymers with structure-variable function have originally been designed, and a process has been developed for synthesizing them directly from native lignins. The key point of the process is to set up two different solvents, which are immiscible each other, for selective modification and separation of lignin and carbohydrates: hydrophobic solvent for hydrophobic lignin and hydrophilic solvent for hydrophilic carbohydrates. The native lignins, three dimensional network polymers, are subjected to selective modifications at the interface between both phases to give linear type polymers (lignophenols) composed mainly of 1,1-bis(aryl)propane type units, almost quantitatively. The process provides a new system for successively utilizing lignocellulosics in the molecular level.

Keywords: lignin, lignocellulosics, lignophenols, phase-separation, recycling

Introduction

Lignin is an amorphous, aromatic network polymer, second to cellulose in natural abundance. The biosphere is estimated to contain $3\text{x}10^{11}$ tons of lignin with an annual biosynthesis rate of about $2\text{x}10^{10}$ tons.[1] However, in contrast to the importance and potential of lignin in nature, lignin-based products have scarcely been in human life. This strange situation is due to the fact that lignin molecules lack stereoregularity, and repeating units in its molecule are too heterogeneous and complex. In addition, non-selective modifications during isolation from the cell wall make lignin molecules much more heterogeneous.

Lignin-based functional polymers (lignophenols) have originally been designed and their synthesis process from native lignins has been developed.[2-5] This process includes the phase-separation reaction system composed of phenol derivatives and concentrated acid. In the present paper are described the design of lignin-based polymers (lignophenols) with the structure variable function, the selective conversion process for lignocellulosics and the features of the resulting lignophenols.

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Design of Lignin-based Polymers

The native lignin is constructed through two reactions: one is the random radical coupling of precursors, and consequently the linkages with adjacent building units are formed at phenolic OH, C5 or C1 position of aromatic nucleus, and C2-position of side chain in each unit. The other includes the addition of adjacent nucleophiles, H_2O, lignin units and carbohydrates, to quinonemethides which C2 radicals have. The structures formed by the latter are very important for controlling the lignin functionalities, because of their high reactivity and frequency.

Lignin acts as hydrophobic, phenolic network polymers in the cell walls. Aiming at synthesizing structure- and reactivity controllable phenolic lignin-based polymers with the original functions of native lignin, the following guidelines have been designed:

- *Replacement of reactive C1-functional groups with phenol derivatives*

Selective phenol grafting at C*1*-positions gives 1,1-bis(aryl)propane type units in the lignin molecules, leading to both of improved phenolic functionality and decreased heterogeneity in structures and reactivities.

- *Release of network structures by the cleavage of benzyl aryl ethers*

The selective cleavage of benzyl aryl ethers, the most labile linkages, leads to linear type subunits retaining original functions of native lignins.

- *Retain of blocked phenolic functions*

Native lignins are latent phenolic materials, in which phenolic hydroxyl groups are blocked to give alkyl aryl ethers such as C2-aryl ethers and methoxyl groups. These latent reactive structures should be retained in the first lignin derivatives for the successive structure control.

- *Design of intramolecular switching units*

The 1,1-bis(aryl)propane-2-O-aryl ether units are formed frequently through above modifications. This structural units can be utilized as switching devices for the structure control (phenolic functionality and molecular weight).

Selective Structure Control of Lignin

The originally designed process includes the phase-separative reaction system composed of phenol derivatives and concentrated acid, which are immiscible each other. The concentrated acid is a solvent for carbohydrates, and works as a catalyst for the fragmentation and phenolation of lignin, and phenol derivatives act as phenolation agents, a barrier to minimize the attack of acid on the lignin, and a solvent for the lignin fractions.

Lignocellulosic particles are solvated with hydrophobic solvents (for example, alkylphenols) first, and then, are contacted with the acid at the interface between both solvents. The carbohydrates are swollen, partially hydrolyzed, and lignins are depolymerized through the selective cleavage of reactive benzyl aryl ethers, resulting in the release of the interpenetrating polymer network structures in the cell wall. The hydrophilic carbohydrates pass through the interface to the aqueous phase, and lignins always stay in the hydrophobic solvents, leading to the separation of carbohydrates and lignin (Figure 1). This separation process works within 60min without any heating and pressing. The resulting lignin-based materials (lignophenols) were of high brightness comparable to milled wood lignin, and quickly dissolved in solvents such as methanol, ethanol, acetone, dioxane and pyridine.

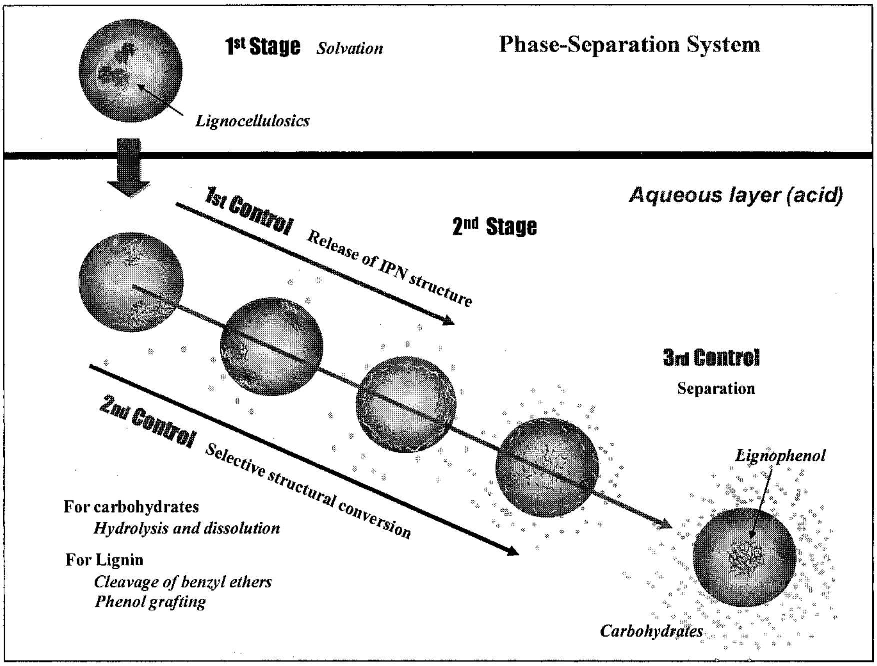

Fig. 1. Structural modifications and separation of lignocellulosic components through the phase-separation process.

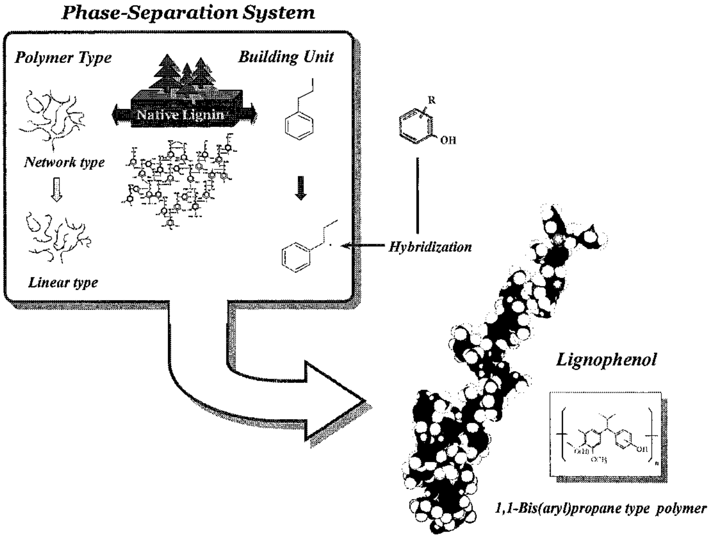

Fig. 2. Conversion of native lignins to lignophenols through the phase-separation process.

The amount of grafted phenols is about 25% (about 0.65 mol/C_9) in softwood lignophenol and about 30% (about 0.9 mol/C_9) in hardwood lignophenol. The difference between the species is due to both the flexibility of the molecule and the frequency of reactive functional groups in the side chains. Seventy seven % of grafted phenols are linked to lignin benzyl-positions through carbon-carbon linkages, 16% to C3-positions, and the remaining 7% etherified to lignin side chains through its phenolic hydroxyl groups. The TMA curves of lignophenols indicate an apparent change of the phase at ca.130 °C in hardwood and at ca.170 °C in softwood, at which those are transformed to clear liquid state. That is, native lignins, three dimensional network polymers, are converted to linear-type polymers with high frequency of 1,1-bis(aryl)propane-2-O-aryl ethers during the process (Figure 2).

It usually takes a long time to perfectly swell and dissolve cellulose within lignocellulosics by the acid treatment. This is due to the belt effect of lignin with highly rigid structures which are formed through the self-condensation in the early stage of acid treatment. However, this effect of lignin to cellulose disappears by the effective phenolysis of lignin during the phase-separation treatment, leading to the rapid separation of both constituents. Furthermore, the rapid and selective phenol grafting of native lignin is due to the lignin distribution within the organic phase: native lignins, which are rich in hydrophilic functional groups, are distributed near the interface with the aqueous phase, resulting in frequent contact with acid to give rapid structural modifications. The resulting lignin derivatives (lignophenols), which are much more hydrophobic than native lignins, are moved far from the interface area to escape from the frequent attack by the acid.

This process has been termed "Phase-separation process". The system plant for the conversion of lignocellulosics through the phase-separation process has been constructed in Mie University campus in 2001 (Figure 3).

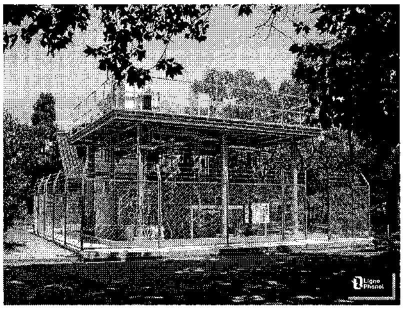

Fig. 3. System plant for the phase-separation conversion of lignocellulosics.

Design of Switching Units for the Functionality Control

In order to utilize lignophenols successively through detailed structural conversion, the important functionalities such as phenolic properties and molecular weights should be controlled so as to meet the requirements. The characteristic units in lignophenols, 1,1-bis(aryl)propane-2-O-aryl ethers, can be used as switching devices for the structural control[6-13]: the phenoxide ions of grafted phenols readily attack the electron deficient C2 nucleophilically, resulting in the cleavage of C2-aryl ether linkages with the exchange of phenolic functionality from C1-grafted nuclei to lignin nuclei (Figure 4). Since this type of neighboring group participation is very quantitative, the functionality of lignophenols can strictly be adjusted by the frequency control of C2-attackable phenolic nuclei (switching devices) within the molecules. The switching devices are divided into two types: one is the reactive device with a reactive point on the nucleus, and the other is the stable device without any reactive point. The phenols linked to lignin side chains through *p*-position to phenolic hydroxyl group do not work as switching devices, due to the steric factor and can be used as control devices for controlling the frequency of switching devices within the molecule. There is a good correlation between the controlled molecular weights of lignophenols and the frequency of switching devices within the molecule (Figure 5). Using reactive- and stable devices, network type- and linear type polymers can be prepared, respectively. By mixing both devices, the polymer network structures from lignophenols can be controlled (Figure 6). The resulting lignophenol polymers can be readily released to subunits using the switching function, producing new raw materials for the next industrial system.

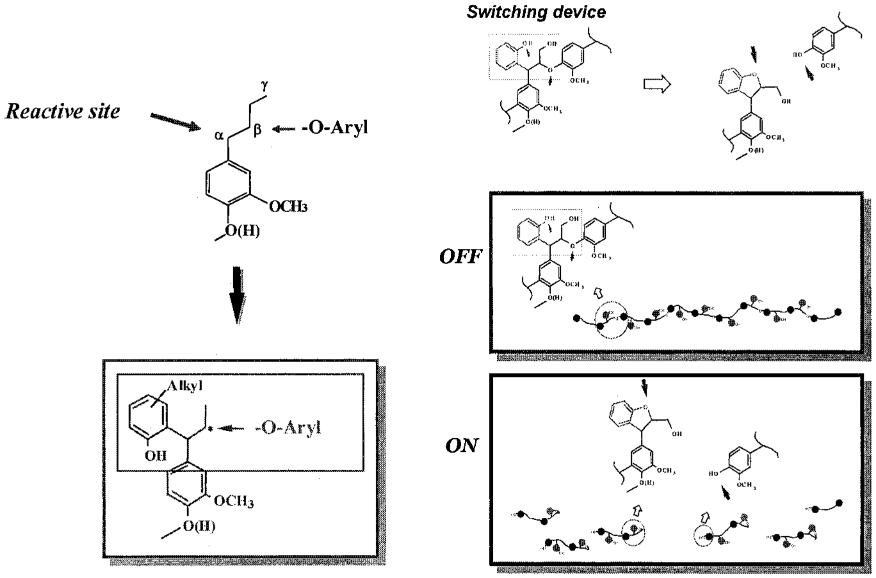

Fig. 4. Design of intramolecular switching units and the second structural control of lignophenols.

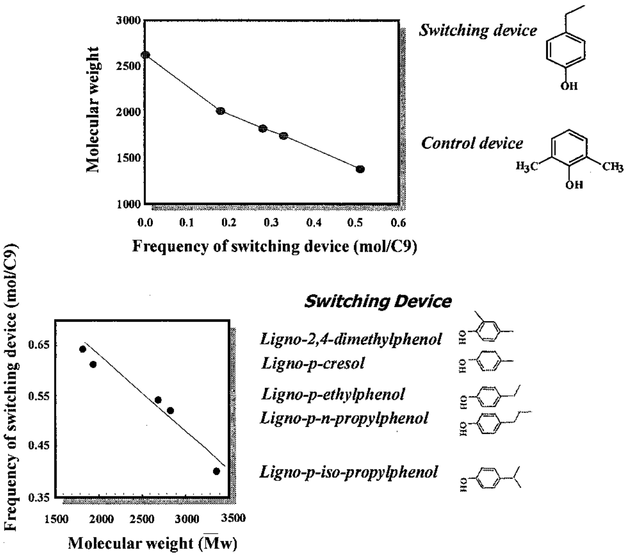

Fig. 5. Relationship between the frequency of switching units and controlled molecular weights.

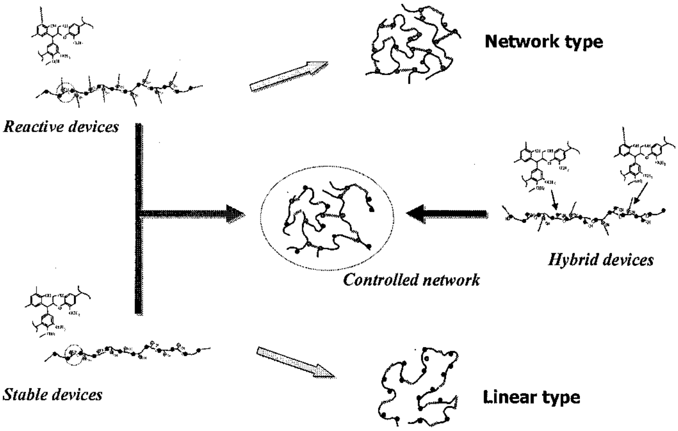

Fig. 6. Second structural control of lignophenols using the intramolecular switching devices.

New Application Fields of Lignin

Lignin is a natural polymer with very complicated network structures. The complexity is due to the random linking between building units, phenylpropanes. The side chain carbon (C1) combined with aromatic unit has a reactive substituent (hydroxyl group, carbonyl group or ether linkage). Therefore, the selective grafting of monomeric phenol derivatives to C1-positions of propane units leads to the formation of new phenylpropane units between grafted phenolic units and lignin propane units. This results in a dramatic change of the original lignin functions, forming a new type of lignin-based polymers composed mainly of 1,1-bis(aryl)propane type units.

New application fields of lignophenols are shown below.

- Recyclable composites with cellulose, biopolyesters, and inorganic materials (glasses, metals)[12,14-17]
- Raw materials for recyclable polymers[7]
- Detachable adhesives[8,13,15-17]
- Switching devices for material recycling[8,13,15-17]
- Electromagnetic shielding materials[18-20]
- Carbon molecular sieving membranes[21-24]
- Enzyme supports for bioreactors and affinity chromatography[25]
- Adsorbents for proteins and metals[25]
- Performance control agents for lead-acid battery and enzymes[25,26]
- Photoresists[27]
- Antioxidants[28]
- UV barriers[14]

Although lignophenols can be applied in various fields as a new type of phenolic polymers with structure-variable function, their application fields would be greatly extended through its secondary functionality control, leading to a new type of lignocellulosic industry.

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