

Occurrence of Diphenylmethane Type Condensation in Lignin during Heating and Sulfuric Acid Treatment of Wood

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Abstract

The formation and quantity of diphenylmethane type structures in lignin during heating and sulfuric acid treatment of wood were investigated quantitatively by a method combining nucleus exchange and nitrobenzene oxidation. More than 60% of non-condensed units were rapidly converted to diphenylmethane type units at early stage of the treatment with concentrated sulfuric acid. After that, further condensation of lignin scarcely occurred. The formation ratio of diphenylmethane type to other type condensed units was about three during the treatment with concentrated sulfuric acid. The modification of lignin during heating of wood began above 120°C and was mainly diphenylmethane type condensation. About 40 and 75% of non-condensed units were converted to diphenylmethane type units by heating dry and wet wood meals at 220°C, respectively. The conversion rate to diphenylmethane type units doubled by increasing the temperature from 180 to 220°C and by the presence of water.

Key words: Acid hydrolysis, Heating, Lignin condensation, Diphenylmethane, Nucleus exchange reaction

Introduction

Wood is a complex of carbohydrates (cellulose and hemicellulose) and polyphenol (lignin), which are totally different in structure and property. Aiming at the total utilization of wood constituents, wood should be separated into carbohydrates and lignin first. However, those are intertwined with each other at molecular level in the cell wall so that the separation usually needs drastic conditions such as high temperature and pressure. Lignin is subjected to two major reactions during these treatments. One is the depolymerization by the cleavage of ether linkages. The other is the polymerization by the condensation between building units. The latter occurs to larger extent with increasing severity of conditions^{1,2}, resulting in the rigidity of lignin molecule.

α -Positions of lignin side chains, the most reactive sites, are attacked rapidly by adjacent phenyl nuclei under both acidic and alkaline conditions to form C_{α} -aryl linkages (diphenylmethane type structures)^{3,4,5}. Diphenylmethane (DPM) type structures are readily oxidized to give colored mesomeric quinonemethides⁶, which form strong hydrogen bonds with hydroquinones or phenols⁷. Namely, DPM type structures formed in lignin greatly influence the color or the properties of lignin molecule such as the reactivity and solubility. The information on the formation and quantity of DPM type structures in lignin during various modifications is very

important for the process control and the utilization of products. However, compared with the depolymerization, there are few quantitative data on the condensation of lignin, especially on DPM quantitative data on the condensation of lignin, especially on DPM type units in highly-condensed lignins. This is mainly due to the rigidity and less reactivity of highly-condensed lignins and to the lack of the method to selectively cleave only specified C-C linkages in lignin.

The nucleus exchange method is a novel technique for the selective and quantitative cleavage of methylene linkages in DPM type structural units^{4,8,9,10}. This method is applicable directly to wood without isolating lignin for analysis. In the present work, the behavior of lignin condensation, especially the formation and quantity of DPM type structures, during heating and acid treatment of wood were investigated quantitatively by a method combining nucleus exchange and introbenzene oxidation.

Experimental

1. Heating of wood

Preparation of dry and wet wood meals

Yezo spruce (*Picea jezoensis* Carr.) wood meal (80 mesh pass) was extracted for 48 hours with ethanol-benzene (1:2, V/V) and dried over P₂O₅ (Dry wood meal, W-0).

Air-dried extractive-free wood meal was spread on a dish in a desiccator with water on the bottom and was kept in it for 4 days with stirring of the water layer (Moisture content 22%, dry base, W-22).

Water was gradually added to air-dried extractive-free wood meal until saturated with water (Moisture content 340%, dry base, W-340).

Heating

About 1.5 g (dry base) of wood meal were placed and sealed into a 17 ml volume stainless steel autoclave. The sample was heated at a prescribed temperature for 1 hour in an oil bath. After heating, the sample was transferred to a dish and dried over P₂O₅.

Table 1. Treatment conditions of wood with sulfuric acid

Treatment	Time (hr)	
	First Hydrolysis* ¹	Second Hydrolysis* ²
	72% H ₂ SO ₄ Room temp.	3% H ₂ SO ₄ Reflux
I	1	—
II	2	—
III	3	—
IV	4	—
V	4	1
VI	4	2

*¹ 20 ml of 72% H₂SO₄/g of wood.

*² After the first hydrolysis the reaction mixture was diluted with water to 3% concentration of sulfuric acid and boiled.

2. Treatment of wood with sulfuric acid

Extractive-free Yezo spruce wood meal (80 mesh pass) was treated with sulfuric acid under a prescribed condition (Table 1). After the reaction, the hydrolyzates were filtered through glass fiber filter paper, washed with cold and hot water, and dried over P_2O_5 .

3. Nucleus exchange treatment

The degradation reagent was prepared by mixing phenol (19 parts), xylene (10 parts) and boron trifluoride-phenol complex (4 parts). Eighty five mg of sample and 3 ml of the reagent were placed and sealed in a 5 ml stainless steel autoclave. The reaction mixture was heated at 180°C for 4 hours in an oil bath. The reaction products (guaiacol and catechol) were converted to their trimethylsilyl derivatives and analyzed by gas chromatography. The detailed procedure was described in previous papers^{8,10}.

Apparatus: YANAGIMOTO G3800

Column: Crosslinked methyl silicone capillary column (Quadrex S2006, 0.25 mm I.D. \times 50 m Length \times 0.25 μ m Film thickness)

Column temperature: Initial 170°C, 15 min
Rate 5°C/min
Final 180°C

Injection temperature: 230°C

Carrier gas: Helium

Detector: FID

4. Alkaline nitrobenzene oxidation

Sample (40 mg), 2N sodium hydroxide (3.2 ml) and nitrobenzene (0.2 ml) were placed in a 5 ml stainless steel autoclave, and heated at 170°C for 3 hours in an oil bath. The products (vanillin and vanillic acid) were converted to their trimethylsilyl derivatives and analyzed by gas chromatography. The same gas chromatograph system as described above was used. However, the column temperature was 160°C initially and was raised after 15 min to the final temperature of 250°C at a rate of 5°C/min.

5. Estimation of lignin structural units

It was done according to a combination analysis of nucleus exchanges and nitrobenzene oxidation¹¹. The calculations are summarized below:

Abbreviations

NEP_o and NEP_m: Nucleus exchange products (guaiacol and catechol) from original and modified lignins, respectively.

NOP_o and NOP_m: Nitrobenzene oxidation products (vanillin and vanillic acid) from original and modified lignins, respectively.

NC_o and NC_m: Non-condensed units in original and modified lignins, respectively.

DPM: Diphenylmethane

Original lignin

Non-condensed units (Type A), mole%, =NEP_o

Condensed units (Type B), mole%, = $100 - \text{NEP}_o$

Maximum conversion of non-condensed units into NOP

$$= \text{NOP}_o / \text{Non-condensed units}$$

$$= \text{NOP}_o / \text{NEP}_o$$

Modified lignin

Non-condensed units (Type A), NC_m , mole%,

$$= \text{NOP}_m / (\text{NOP}_o / \text{NC}_o)$$

$$= \text{NOP}_m / (\text{NOP}_o / \text{NEP}_o)$$

DPM type units (Types A' and B'), mole%,

$$= \text{NEP}_m - \text{NC}_m$$

$$= \text{NEP}_m - \text{NOP}_m / (\text{NOP}_o / \text{NEP}_o)$$

Condensed units (Type B), mole%,

$$= 100 - \text{NEP}_m$$

Figs. 1 and 2 show the relationship between the lignin structures and the yields of NEP and NOP, and the lignin structural units groups as non-condensed, condensed, and DPM type units in the above calculations, respectively.

As obvious from the relationship between NEP and NOP, the difference in the yield between NEP and NOP is getting larger with increasing amount of diphenylmethane type units in lignin.

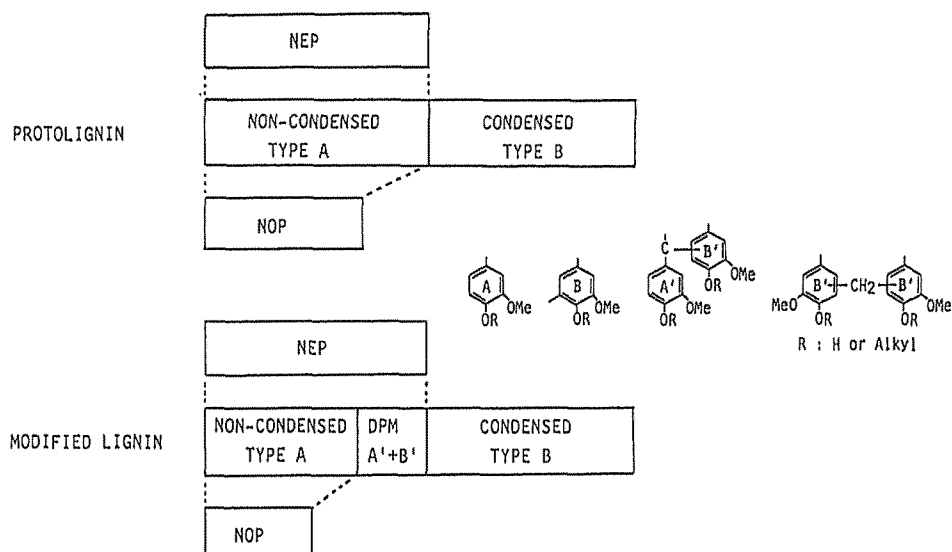


Fig. 1. Relationship between softwood lignin structures and yields of NEP and NOP.

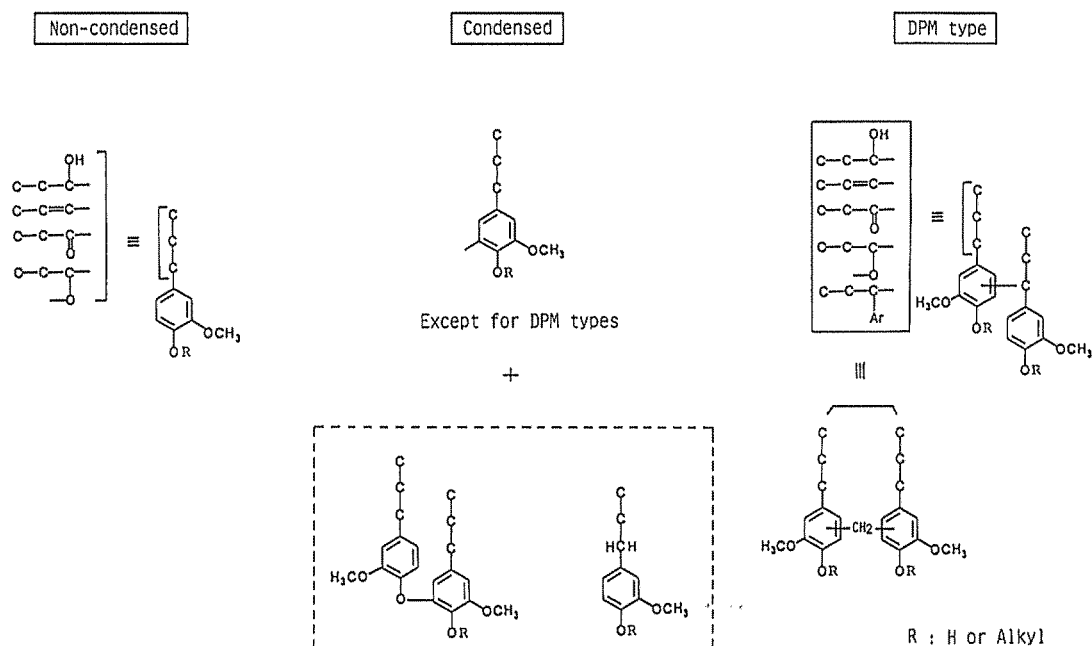


Fig. 2. Lignin structural units grouped as non-condensed, condensed and DPM type units by a combination analysis of nucleus exchange and nitrobenzene oxidation.

Results and Discussion

Condensation of lignin during heating

Fig. 3 shows the variations of NEP and NOP yields during heating. NEP yields remained almost constant below 180°C, above which those slightly increased in wet wood meals (W-22 and W-340), due to the increase in the proportion of lignin caused by the degradation of carbohydrates. On the other hand, NOP yields decreased dramatically with increasing temperatures above 120°C. These facts indicate that the modification of lignin during heating of wood began above 120°C and was mainly DPM type condensation.

The decrease rate of NOP yield above 120°C was larger in the heating of wet wood meals (W-22 and W-340) than in that of dry wood meal (Fig. 3), indicating that water contained in wood accelerated the condensation of lignin. One of the reasons for this is the flow of lignin at a lower temperature because water decreases the softening temperature of lignin¹²⁾. The other is the decrease in pH by the organic acid, mainly acetic acid derived from hemicellulose. The variation patterns of NEP and NOP yields were almost the same, independent of moisture content, between wet wood meals (W-22 and W-340).

The formation rate of DPM type units in lignin during heating is shown in Fig. 4. Lignin was not subjected to any condensation reactions up to 120°C, above which only DPM type condensation occurred. About 40 and 75% of non-condensed units were converted to DPM type units at 220°C in dry and wet wood meals, respectively. The conversion rate to DPM type units doubled by increasing the temperature from 180 to 220°C and by the presence of water.

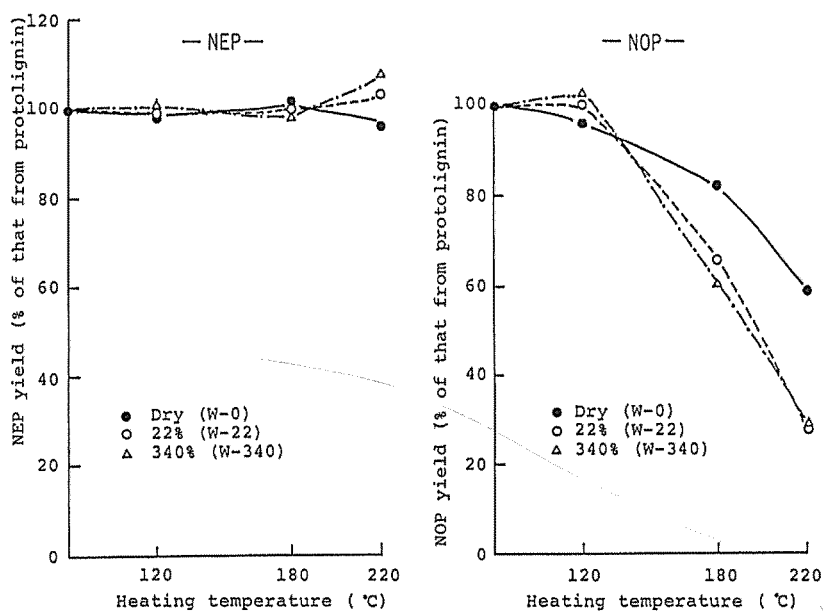


Fig. 3. Variations of NEP and NOP yields from lignin during heating of wood.
Heating time: 1 hour.

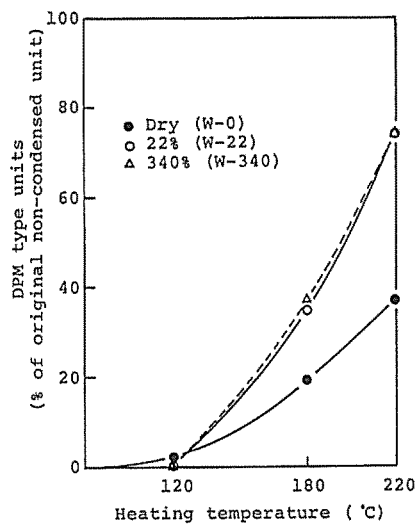


Fig. 4. Conversion of non-condensed to DPM type units during heating of wood.
Heating time: 1 hour.

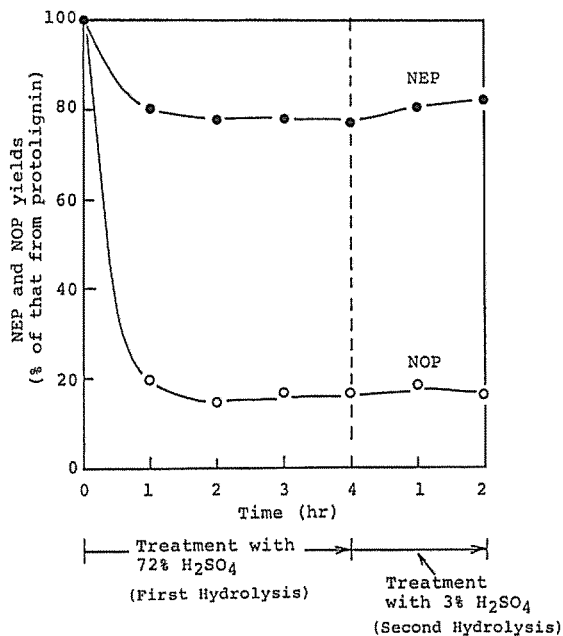


Fig. 5. Variations of NEP and NOP yields from lignin during the treatment of wood with sulfuric acid.

Condensation of lignin during the treatment with sulfuric acid

Fig. 5 shows the variations of NEP and NOP yields during sulfuric acid treatment. NEP yields remained

almost constant with 20% decrease to that from original lignin during the treatment with 72% sulfuric acid. On the other hand, NOP yields decreased dramatically to less than 20% of that from original lignin by the treatment for 1 hour, after which those did not vary considerably. These facts indicate that lignin was heavily condensed at early stage of the treatment with concentrated sulfuric acid and that the condensation of lignin during the treatment was mainly of DPM types. Furthermore, no variation in NEP and NOP yields implies that neither DPM type nor other type condensation of lignin occurred any more after heavy condensation at early stage.

NEP yields slightly increased again during refluxing with 3% sulfuric acid (Fig. 5). This increase was possibly caused by the conversion of acid soluble to acid insoluble fractions through condensation at benzyl positions and/or by the conversion of original and secondarily formed condensed units (Type B) to NEP producing structures. The latter is due to the rearrangement of diphenylethane type units (original phenylcoumaran and 1,2-diaryl propane or secondarily formed condensed structures at β -positions) to NEP producing structures such as stilbene type units by acidolysis¹³.

More than 60% of non-condensed units were converted to DPM type units (Types A' and B') by the treatment with 72% sulfuric acid within 1 hour (Fig. 6). Other type condensed units (Type B) were about 20%. Namely, the formation ratio of DPM type to other type condensed units was about three.

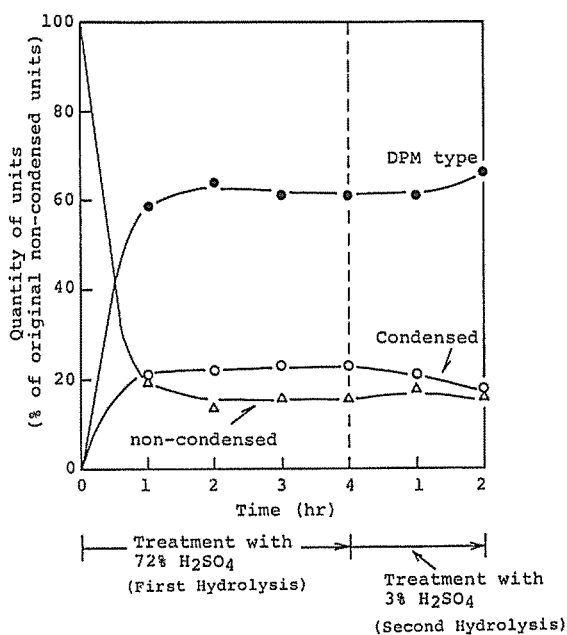


Fig. 6. Structural change of non-condensed units in lignin during the treatment of wood with sulfuric acid.

Only DPM type units (Types A' and B') were formed by heating wood, whereas the treatment with concentrated sulfuric acid is drastic so that other type condensed units (Type B) were also formed in addition to DPM type units. However, it is of interest that the conversion rates of non-condensed to condensed type units are similar between sulfuric acid treatment (total of DPM and other types, 80%) and heating (DPM type, 75%) of wood. Also, further condensation of lignin was scarcely observed after heavy condensation at early stage.

These suggest that the maximum conversion of non-condensed to condensed type units is around 80% because of the rigidity of the molecule. DPM type condensation occurs preferentially between C_α and C_6 under acidic conditions¹⁴⁾. Therefore, DPM type structures can be formed in both non-condensed and condensed units. The present results on structural change of non-condensed units strongly indicate that DPM type condensation occurs in high frequency in whole lignin molecule under drastic conditions.

Lignin utilization has been tried in various fields, but it is still unsuccessful. One reason for this difficulty is in the complexity of lignin structures. In general, treatments of lignin under drastic conditions have not been considered to be desirable for the utilization because of its heavy condensation. However, lignin is always subjected to some modification in any treatment. Drastic treatments such as heating at high temperature or treatment with concentrated sulfuric acid convert the lignin molecule to a highly-condensed form linked mainly through DPM type linkages. Changing the point of view, this is a simplification of lignin structure. Of course, highly-condensed lignin is rigid and less reactive. However, DPM type polymers are rapidly depolymerized by nucleus exchange treatment^{15,16)} to give reactive oligomers which can be easily processed for utilization (Fig. 7). Therefore, the lignin modification via DPM type condensation might offer a new route for its utilization.

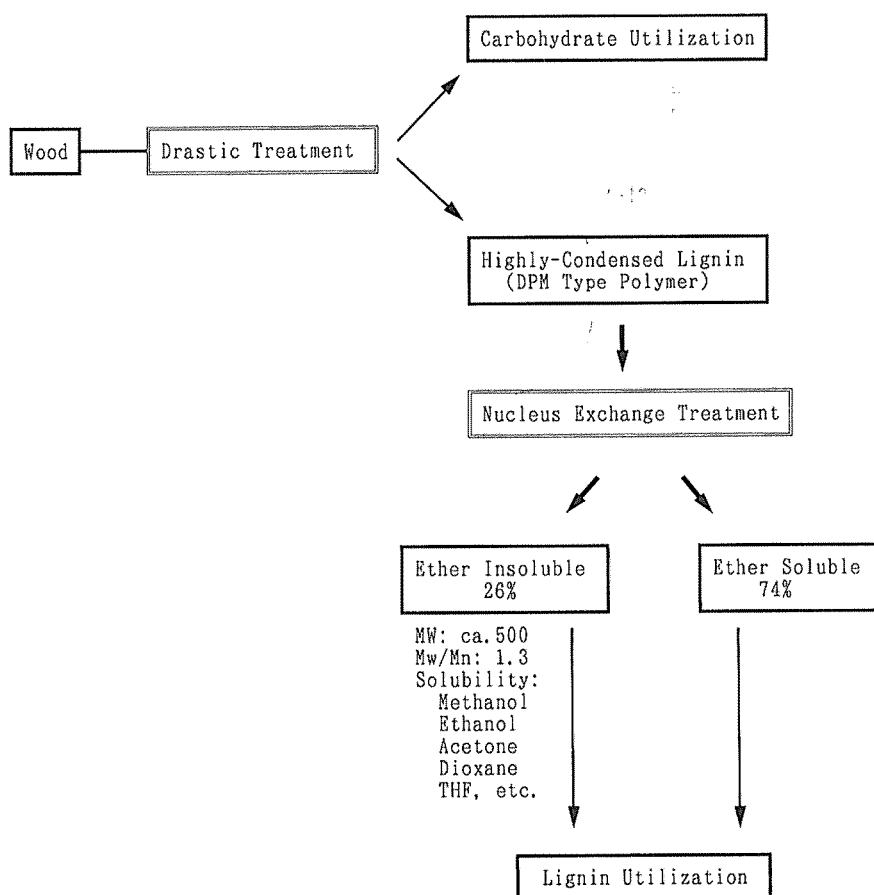


Fig. 7. Proposed utilization process of lignocellulosics.

Conclusions

The formation and quantity of DPM type structures in lignin during heating and sulfuric acid treatment of wood were investigated quantitatively by a method combining nucleus exchange and nitrobenzene oxidation.

- (1) The modification of lignin during heating of wood began above 120°C and was mainly DPM type condensation.
- (2) Water accelerated the DPM type condensation of lignin.
- (3) About 40 and 75% of non-condensed units were converted to DPM type units by heating of dry and wet wood meals up to 220°C, respectively. The conversion rate to DPM type units doubled by increasing the temperature from 180 to 220°C.
- (4) At early stage of the treatment with concentrated sulfuric acid, more than 60% of non-condensed units were rapidly converted to DPM type units.
- (5) The formation ratio of DPM type to other type condensed units was about three during the treatment with concentrated sulfuric acid.
- (6) Neither DPM type nor other type condensation of lignin occurred any more after the heavy condensation at early stage of the treatment with concentrated sulfuric acid.

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酸触媒オルガノソルブリグニンの構造特性

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オルガノソルブリグニンの有効利用に関する基礎的知見を得るため、Aspen チップがメタノール-水系で処理され、溶出リグニンの構造が蒸解液 pH との関連で論議された。pH 3.2 以上では、溶出リグニンの組成はオリジナルリグニンと類似していたが、pH の低下とともに縮合反応が開始され、C α -アリアル縮合構造が形成された。低 pH で流出するリグニンは、グアイアイアシル単位にリッチであった。