Comparison of Condensation Reactions of Lignin at C_α-Positions in Kraft and Acid Sulfite Delignification of Western Hemlock

Masamitsu Funaoka*, Vincent L. Chiang**, Kari Kolppo**
and Douglas D. Stokke**

*Faculty of Bioresources, Mie University

**School of Forestry and Wood Products,

Michigan Technological University

Abstract

Acid sulfite delignification of western hemlock (*Tsuga heterophylla*) was carried out from 90°C to a final temperature of 145°C.   Kraft pulping was also carried out from 90°C, but to a final temperature of 170°C. At various stages of delignification structural units condensed at C_α-positions in residual lignins were determined directly without isolating their lignins.   In kraft pulping, the formation of structural units condensed at C_α-positions started at the point where about 50% of the lignin were removed.   In acid sulfite pulping, the formation of those occurred when 65–70% of the lignin were removed.   About 55% of the phenyl nuclei were found associated with condensed structures at C_α-positions in the residual lignins in both kraft and acid sulfite pulps having a kappa number about 35.

Key words: Kraft pulping, Acid sulfite pulping, Lignin degradation, Condensation, Diphenylmethane

Introduction

During pulping, lignin macromolecule is depolymerized mainly through the cleavage of ether linkages to become dissolved in pulping liquor.   In kraft pulping[1], the first step of delignification involves the formation of a quinone methide intermediate from the phenolate anion by the elimination of a hydroxide, alkoxide, or phenoxide ion from the benzylic carbon.   Then this intermediate is attacked by the nucleophilic hydrosulfide ions with formation of a thiirane structure and simultaneous cleavage of the β-aryl linkage.   The cleavage of aryl ether linkages results in increasing hydrophilicity of lignin because of the liberation of phenolic hydroxyl groups.   The depolymerized lignin fragments are dissolved in the cooking liquor as sodium phenolates.   On the other hand, during acid sulfite pulping[1] the α-hydroxyl and the α-ether groups are cleaved readily under simultaneous formation of benzylium ions irrespective of whether phenolic hydroxyl groups are free or etherified.   The cleavage of open α-aryl ether linkages represents the only noteworthy fragmentation of lignin during acid sulfite pulping.   The benzylium ions are sulfonated by attack of hydrated sulfur dioxide or bisulfite ions, resulting in increasing hydrophilicity of lignin molecule.   The extent of delignification depends largely on the degree of sulfonation as well as the depolymerization.

As described above, in the course of kraft and acid sulfite delignification, the reactivity of benzylic carbons is

greatly enhanced resulting in the attack of nucleophilic agents, due to the formation of quinone methides and benzyl cations, respectively.   The attack of hydrosulfide or bisulfite ions to α-carbons which is very important for dissolution always competes with that of phenolic nuclei[2,3].   In general, the latter leads to increased molecular weight of lignin and the solubilization of lignin is retarded or inhibited.   For example, lignin dissolution is retarded particularly during the final phase of kraft pulping as a result of condensation[4].   Also, pine heartwood having reactive phenolic extractives such as pinosylvin and its monomethyl ether cannot be delignified by the conventional acid sulfite process[4].

The condensation at benzyl carbons during kraft and acid sulfite pulping leads to diphenylmethane type structures[1-3].   In order to achieve the overall understanding and perfect control of pulping reactions, the information on when and how frequently the condensation occurs is of the utmost importance.   Especially, secondarily condensed moieties in residual lignins give a great influence to the color of pulp and its bleachability[5]. The quantity of diphenylmethane type units in pulp residual lignin directly reflect the extent of condensation reactions within the wood during the pulping.   In the present work, at various stages of kraft and acid sulfite delignification, structural units related to condensation at C_α-positions in pulp residual lignins were analyzed and discussed.

Materials and Methods

The wood chips were cut from the sapwood portion (20–73 annual increment) of a 73 year old western hemlock (*Tsuga heterophylla*) log to a constant chip size ($2.5 \times 2.5 \times 0.3$ cm^3).   The chips were air dried, after which the moisture content was 7–8%.

Pulping

Kraft liquor: Effective alkali (EA) 17.1% (as Na_2O on OD wood, corresponding to 44.15 g/l of NaOH) and the sulfidity 24.9%.

Acid Sulfite liquor: A solution of 15.6 g/l of NaOH was adjusted to pH 1.5 with SO_2, corresponding to about 27.6 g/l of total SO_2.

Thirty grams of oven dry wood was used, and the liquid to wood ratio used was 5 : 1.   After soaking 24 hours at room temperature (about 25°C) in the digester or in the shaker, the cooking system was transferred to a preheated, rocking digester (94°C).   As soon as the temperature in the digester decreased to 80°C, the system was heated at a rate of 1°C/min until the temperature reached 170°C (kraft) or 145°C (acid sulfite).   The samples were then pulped to various lignin contents by keeping them in the digester for different lengths of time. Delignified wood or pulps were filtered off, followed by thorough washing and air drying.   The samples (wood or pulps) were ground to pass 80 mesh.   The meals were extracted with ethanol-benzene (1 : 2) for 48 hours and dried over P_2O_5.

Isolation of milled wood lignin (MWL)

The isolation and purification of the MWL's were done according to LUNDQUIST et al.[6], and BJÖRKMAN[7]. The elemental compositions of MWL are as follows: C%, 61.42; H%, 5.67; O%, 32.91; OCH$_3$%, 13.44.   Based on these information, the molecular formula per C_9 unit is $C_9H_{8.32}O_{3.12}(OCH_3)_{0.83}$ and the molecular weight per C_9 unit is 192.28 g/mol.   The MWL was used as a reference sample for the determination of lignin by acetyl

bromide method.

Lignin content determination

The lignin content was measured using the Klason+acid soluble lignin determinations.   Klason lignin was determined using a TAPPI standard T222, and the acid soluble lignin was measured according to TAPPI UM 250.   The lignin content at the late stages of pulping was also checked using acetyl bromide lignin determination. The procedures of JOHNSON et al.[8] and MARTON[9] were followed, with the modifications according to VAN ZYL[10] and CHIANG and FUNAOKA[11].

Structural analysis of pulp residual lignins

It was done by a combination of nucleus exchange and nitrobenzene oxidation.   Detailed procedures for these two reactions and the product analysis by gas chromatography are described in detail in the previous papers[11−16].

Results and Discussion

The dissolution of lignin during a standard kraft and a standard acid sulfite pulping of western hemlock is shown in Fig. 1.   As can be seen in this figure, both systems are able to remove about 95% of the lignin and the general pattern of lignin dissolution is rather similar for these systems.

Phynyl nuclei in softwood protolignin are classified into non-condensed (Type A) and condensed (Type B) guaiacyl units (Fig. 2).   Guaiacyl units in residual lignins are divided into non-condensed (Type A), those (Types A' and B') associated with diphenylmethane moieties[1,5,17,18] and other types of condensed (Type B) units (Fig. 2).   The quantities of A, B, A' and B' types of structural units in residual softwood lignins can be obtained from the yields of their monomeric derivatives, guaiacol+catechol (NEP), after direct degrading of pulps by nucleus exchange reaction (Fig. 3), and, vanillin+vanillic acid (NOP), after nitrobenzene oxidation (Fig. 4)[11−16].   The nucleus exchange reactions is a combination of alkylation and dealkylation reactions in the presence of boron trifluoride and excess phenol[19,20].   This reaction converts quantitatively the non-condensed (Type A) and diphenylmethane type (Types A' and B') phenyl nuclei into guaiacol which is partially demethylated to catechol according to the reaction temperature (Fig. 3).   Thus the sum of guaiacol and catechol (NEP, mol%) represents
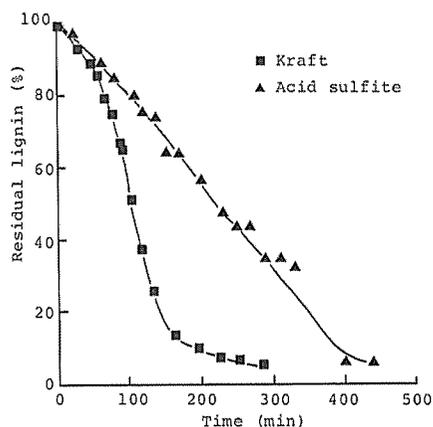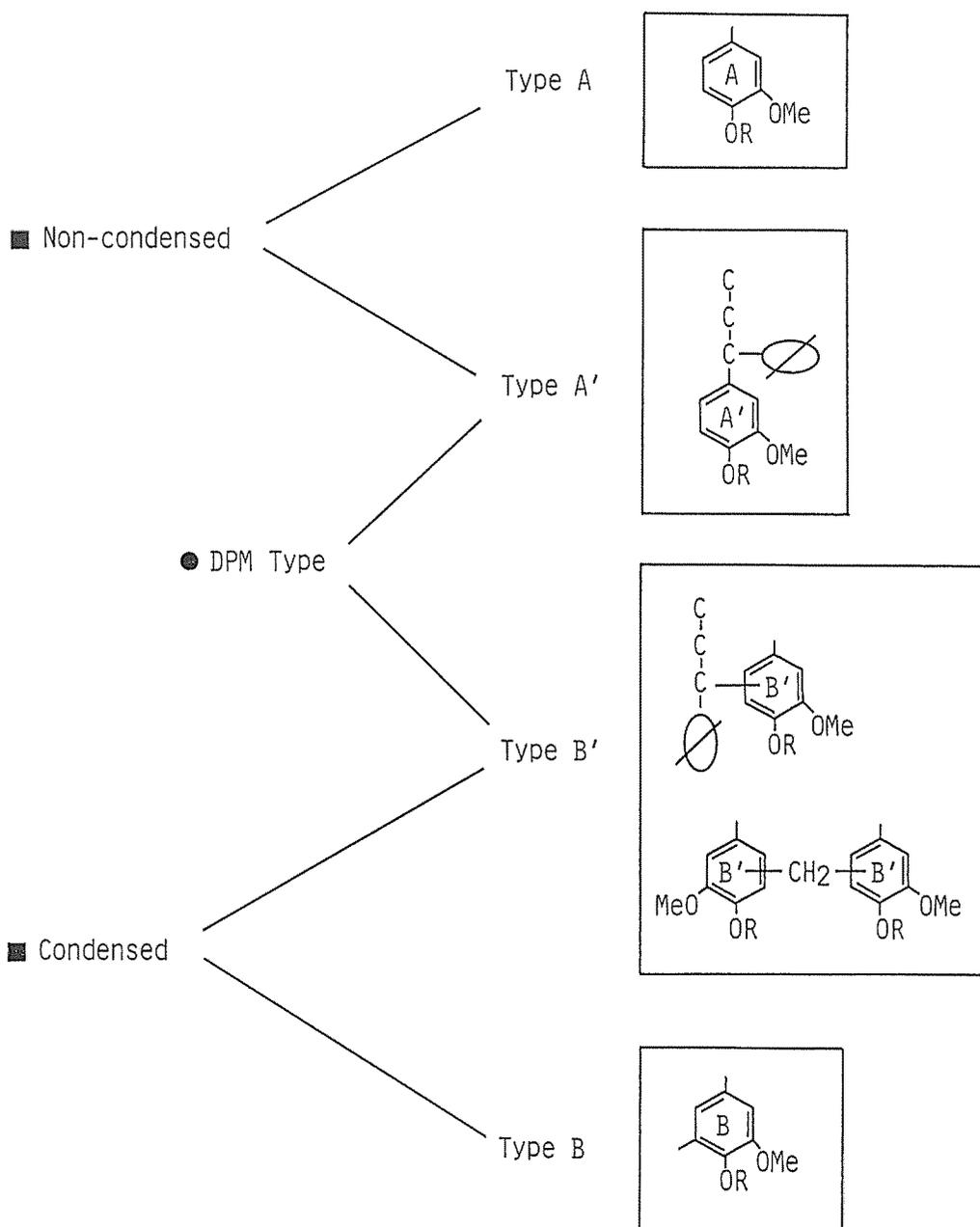

Fig. 1. Kraft and acid sulfite delignification of western hemlock.

Fig. 2.   Types of structural units in original and modified lignins.

the quantity of non-condensed units in non-delignified wood or the quantities of non-condensed (Type A) and diphenylmethane type (Types A′ and B′) units in delignified wood.   Consequently, in delignified wood sample, by subtracting the non-condensed units (Type A) from the yield of NEP, the quantity of diphenylmethane type
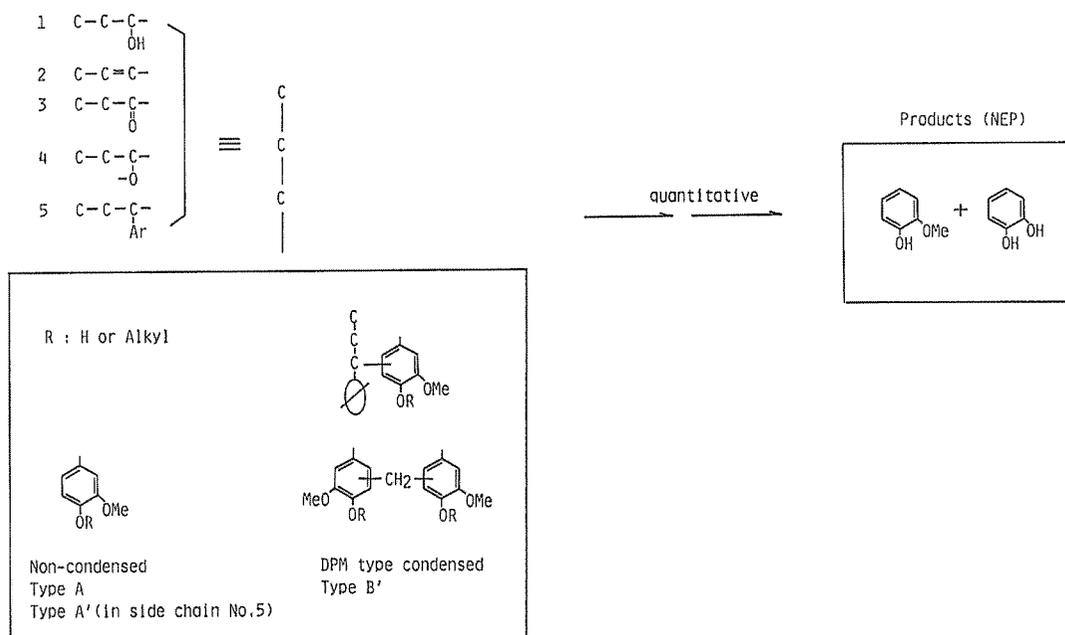
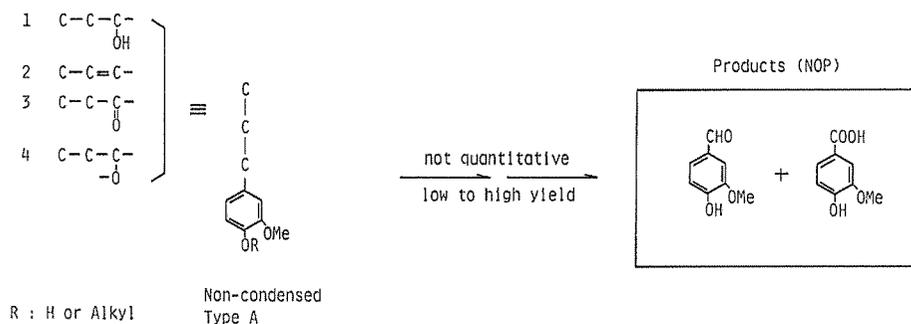Fig. 3.   Lignin structural units giving monomeric products (NEP) by nucleus exchange method.

Fig. 4.   Lignin structural units giving monomeric products (NOP) by nitrobenzene oxidation.

units (Types A′ and B′) can be obtained.   In this calculation, the estimation of non-condensed unit (Type A) is of the utmost importance.   The alkaline nitrobenzene oxidation converts only non-condensed units (Type A) that are not involved in diphenylmethane type units into NOP (Fig. 4)[21].   Therefore, NOP/NEP value in pulp residual lignin is getting lower with increasing amounts of diphenylmethane type structures (Types A′ and B′) in lignin molecule.   Assuming that the conversion rate of non-condensed units (only Type A) to NOP in modified lignin is not so different from that in original lignin, the quantity of non-condensed unit (Type A) can be calculated as follows[22]:

[NOP/(non-condensed, type A)]$_\text{original}$
    =[(NOP/(non-condensed, typeA)]$_\text{residual lignin}$
Non-condensed units (Type A) in residual lignin, mole%,

$$= (\mathrm{NOP})_{\mathrm{residual}} / [\mathrm{NOP}/(\text{non-condensed, Type A})]_{\mathrm{original}}$$
$$= (\mathrm{NOP})_{\mathrm{residual}} / (\mathrm{NOP}/\mathrm{NEP})_{\mathrm{original}}$$

Because, in original lignin, the yield of NEP represents the quantity of non-condensed unit (Type A).   The value of NOP/NEP for the western hemlock original lignin was 0.77.

Fig. 5 shows the variations of NOP/NEP values in residual lignins against the extent of delignification. The overall variation patterns are very similar between both pulping processes.   In kraft pulping, the value got slightly higher in the early stage of delignification, mainly due to the formation of coniferyl type conjugated systems from phenolic β-aryl ether units, giving high yield of NOP[21].   This observation is strikingly similar to a early study on kraft pulping of Douglas-fir[11].   In both processes the variations of NOP/NEP were relatively
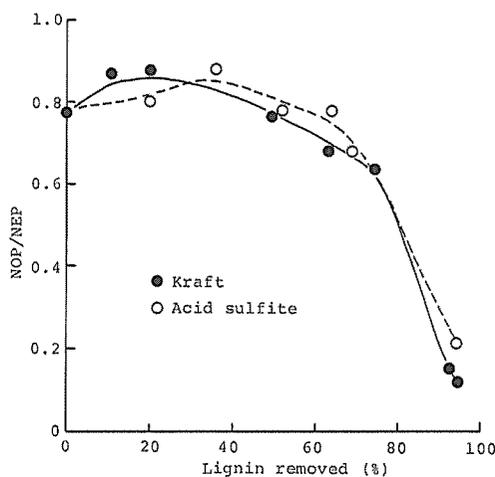

Fig. 5.   Relationship between NOP/NEP values in re-
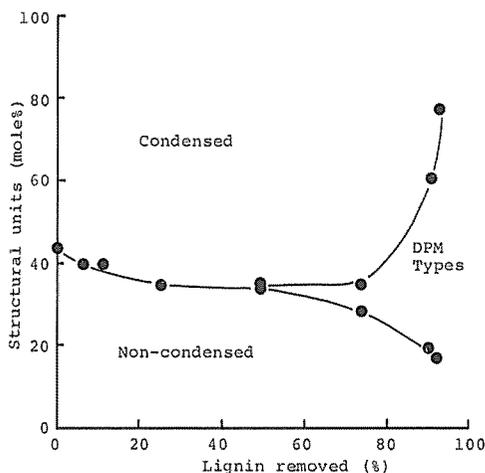sidual lignins and the extent of delignification.

Fig. 6.   Relationship between the composition of residual
lignins and the extent of delignification in kraft
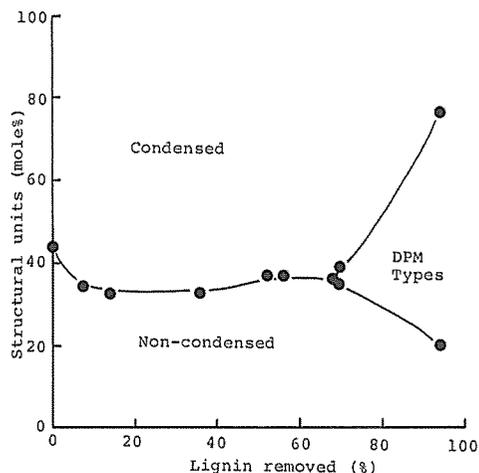pulping of western hemlock.

Fig. 7.   Relationship between the composition of residual
lignins and the extent of delignification in acid
sulfite pulping of western hemlock.

small until the delignification of about 70%, suggesting that lignin structures were not changed dramatically. After that, in the final stage of delignification, the values of NOP/NEP were rapidly dropped to about 0.2. This fact means that the residual lignin in the final stage is of structures quite different from those in the early stages.

The relationships between the compositions of residual lignins and the removal of lignin are shown in Figs. 6 and 7. In kraft pulping the non-condensed units (Type A) were dissolved slightly faster than condensed units (Type B). Acid sulfite delignification also has the same pattern, but the preferential dissolution of non-condensed units was stopped in the earlier stage, compared to kraft delignification. High mobility of non-condensed units in addition to the dissolution resistance of condensed units would permit faster dissolution of non-condensed units in the early stages. Until the delignification reached about 70%, it seemed that there was no dramatic difference between the dissolution of non-condensed and condensed units. In kraft pulping, the residual lignins had the structures condensed at C_α-positions after about 50% of lignin were removed, after which the quantity of diphenylmethane type units increased dramatically in the final stage. In acid sulfite pulping the condensation at C_α-positions occurred at about 65–70% delignification. The delayed formation of diphenylmethane type moieties in acid sulfite pulping was probably due to the competitive reaction of forming sulfonic acid groups at C_α-positions, thus preventing the reactive sites for diphenylmethane formation. On the other hand, in kraft pulping, the cleavage of β-aryl ether linkages results in the formation of reactive conjugated structures, promoting condensation reactions between units[17,23,24]. However, also in acid sulfite pulping, the residual lignins in the final stage had high frequency of condensed structures at C_α-positions. In the combination analysis of nucleus exchange and nitrobenzene oxidation, the units grouped as diphenylmethane types are of originally non-condensed units[22]. Therefore, above results show that in both pulpings originally non-condensed units were left in high frequency in pulp. It would be reasonable that at the final stages of pulpings with lowered sulfide and bisulfite ions reactive non-condensed units were subjected to condensation with adjacent phenyl nuclei at C_α-positions rather than the attack of sulfide or bisulfite ions, resulting in a delayed dissolution.

For both puling systems, condensed structures at C_α-positions became major in residual lignins. About 55% of the phenyl nuclei were found associated with condensed structures at C_α-positions in the residual lignins in both kraft and acid sulfite pulps having a kappa number of about 35.

References

1) Gierer, J.   Chemistry of delignification.   Part 1: General concept and reactions during pulping.   Wood Sci. Technol., 19: 289–312 (1985).
2) Gierer, J.   The reactions of lignin during pulping.   Svensk Papperstidn., 73: 571–596 (1970).
3) Gierer, J.   Chemical aspects of kraft pulping.   Wood Sci. Technol., 14: 241–266 (1980).
4) Sjöstrom, E.   Pulping chemistry-Wood Chemistry: Fundamentals and applications (ed. by E. Sjöstrom, Academic Press, New York) pp. 104–145 (1981).
5) Harkin, J. M.   o-Quinonemethides as tentative structural elements in lignin.   Adv. in Chem. Series, 59: 65–74 (1966).
6) Lundquist, K., P. Ohlsson, and R. Simonson.   Isolation of lignin by means of liquid-liquid extraction.   Svensk Papperstidn., 84: 143–144 (1977).
7) Björkman, A.   Studies on finely divided wood.   Part 1. Extraction of lignin with neutral solvents.   Svensk Papperstidn., 59: 477–485 (1956).
8) Johnson, D. B., W. E. Wayne, E. Moor, and L. C. Zank.   The spectrophotometric determination of lignin in small wood samples.   Tappi, 44(11): 793–798 (1961).
9) Marton, J.   Determination of lignin in small pulp and paper samples using the acetyl bromide method.   Tappi, 50(7):

335–337 (1967).

10) VAN ZYL, J. D.　Notes on the spectrophotometric determination of lignin in wood samples.　Wood Sci. Technol., 12: 251–259 (1978).

11) CHIANG, V. L. and M. FUNAOKA.　The formation and quantity of diphenylmethane type structures in residual lignin during kraft delignification of Douglas-fir.　Holzforschung, 42: 385–391 (1988).

12) FUNAOKA, M. and I. ABE.　The nuclear exchange method for estimation of lignin structure.　Proc. 1983 International symposium on Wood and Pulping Chemistry, 4: 79–84 (1983).

13) FUNAOKA, M. and I. ABE.　Structures of softwood lignins dissolved by successive acidolysis.　Mokuzai Gakkaishi, 29: 781–788 (1983).

14) FUNAOKA, M. and I. ABE.　Analysis of chemical structures of hardwood lignins by nuclear-exchange method.　Mokuzai Gakkaishi, 30: 68–73 (1984).

15) FUNAOKA, M. and I. ABE.　Condensation degree of softwood protolignin.　Bull. Fac. Agriculture, Mie Univ., 73: 347–352 (1986).

16) FUNAOKA, M. and I. ABE.　Selective cleavage of C_α-aryl bonds in lignin.　Bull. Mie Univ. Forests, 15: 97–109 (1987).

17) BRUNOW, G.　Some reactions of lignin in kraft and polysulfide pulping.　Appl. Polym. Symp., 28: 1155–1168 (1976).

18) GIERER, J., F. IMSGARD, and I. PETTERSSON.　Possible condensation and polymerization reactions of lignin fragments during alkaline pulping processes.　Appl. Polym. Symp., 28: 1195–1211 (1976).

19) FUNAOKA, M. and I. ABE.　The reaction of lignin in the presence of phenol and boron trifluoride.　I. On the formation of catechol from MWL, dioxane lignin and kraft lignin.　Mokuzai Gakkaishi, 24: 256–261 (1978).

20) FUNAOKA, M. and I. ABE.　Phenyl-nucleus exchange method for the degradation of lignin.　Wood Sci. Technol., 21: 261–279 (1987).

21) CHANG, H. M. and G. ALLAN.　Oxidation. in Lignins-Occurrence, Formation, Structures, and Reactions (ed. by K. V. Sarkanen and C. H. Ludwig, Wiley-Interscience, New York) pp. 433–485 (1971).

22) FUNAOKA, M.　Application of Nucleus Exchange Technique to Lignin Structural Analysis.　Bull. Fac. Bioresources, Mie Univ., No. 5: 75–97 (1991).

23) MORTIMER, R. D.　The formation of coniferyl alcohol during alkaline delignification with anthraquinone.　J. Wood Chem. Technol., 2: 383–415 (1982).

24) KONDO, R. and K. V. SARKANEN.　Formation and reaction of coniferyl alcohol during alkaline pulping.　J. Wood Chem. Technol., 4: 301–311 (1984).

Western hemlock のクラフトおよび酸性サルファイト蒸解過程における
リグニン側鎖 α 位での縮合反応

船岡正光* ・ Vincent L. CHIANG**, Kari KOLPPO**, Douglas D. STOKKE**

*三重大学生物資源学部，**ミシガン工科大学

　Western hemlock のクラフトおよび酸性サルファイト蒸解過程におけるパルプ残留リグニンの構造変化を定量的に追跡した。リグニンベンジル位での縮合反応は，クラフト蒸解過程においてリグニン除去率約50%の時点で開始したが，一方酸性サルファイト蒸解では65～70%の時点で始まった。クラフトおよび酸性サルファイトいずれにおいても，パルプ (Kappa 価35) 残留リグニンの芳香核の55%以上は側鎖 α 位縮合構造（ジフェニルメタン型構造単位）に取り込まれていた。