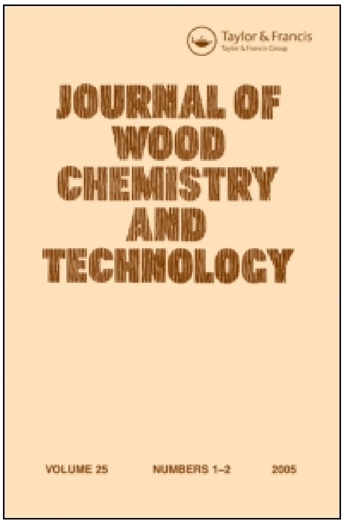

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CONDENSATION REACTIONS OF SOFTWOOD AND HARDWOOD LIGNIN MODEL COMPOUNDS UNDER ORGANIC ACID COOKING CONDITIONS

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ABSTRACT

In order to examine the condensation reactions of softwood and hardwood lignin during organic acid cooking, mixtures of benzyl alcohol type lignin model compounds with guaiacyl and syringyl units as the sources of benzyl cations and creosol and 5-methoxycreosol as the sources of electron-rich aromatic carbons were cooked under acidic pulping conditions.

From the yield of the condensation products in the initial reactions, it was shown that the carbonium cations of guaiacyl nuclei were more reactive than those of syringyl nuclei.

Syringyl type aromatic ring carbons had higher reactivities than guaiacyl type ones.

The cleavage of the benzyl ether bond in syringyl compounds was slower than that of guaiacyl compounds.

The diphenylmethane structures formed by the condensation reaction between veratryl alcohol and 5-methoxycreosol were found to be unstable under the strong acidic cooking conditions.

It is concluded that the condensation reactions between benzylic cations from the guaiacyl compounds and the electron rich aromatic ring carbons of syringyl ones are very fast, but the condensation products are unstable under the strong acidic pulping conditions.

When the guaiacyl nuclei react as an electron-rich aromatic carbon, the reaction is slower but the condensation product is much more stable.

These differences in reactivities, and the stabilities of the condensation products, may contribute to the resistance of softwood toward complete delignification on acid pulping.

INTRODUCTION

Solvolysis pulping generally aims at the development of a new pollution free pulping process and/or the total utilization of forest biomass resources. Various solvolysis pulping methods have been studied since 1970. The main processes examined were alcohol[1,2], phenol[3,4] and organic acid[5-7] pulping. Some of them have proceeded to pilot plants. However, they are not yet able to compete with the kraft pulping process because of their problems such as low paper strength, difficult recovery of chemicals, inefficient utilization of extracted lignin, and so on.

Recently, acetic acid pulping (acetosolve pulping)[8,9] and performic acid pulping have been proposed as effective pulping processes. Delignification mechanisms of these pulping processes have also been proposed[10-12]. Acidolysis, formation of the enol ether structures, esterification, and condensation have been shown to be the important reactions. Among these, the effect of the inter- and intramolecular condensation reactions on delignification is very important, because they affect not only delignification but also the properties of the dissolved lignin which is the by-product of the process.

The acidic condensation reactions of lignin mainly take place between the side chain benzylic carbons and the electron rich carbons on aromatic nuclei (fig.1). In other words, these reactions are formed between the benzylic cations and the electron-rich aromatic carbon on aromatic rings of lignin. The

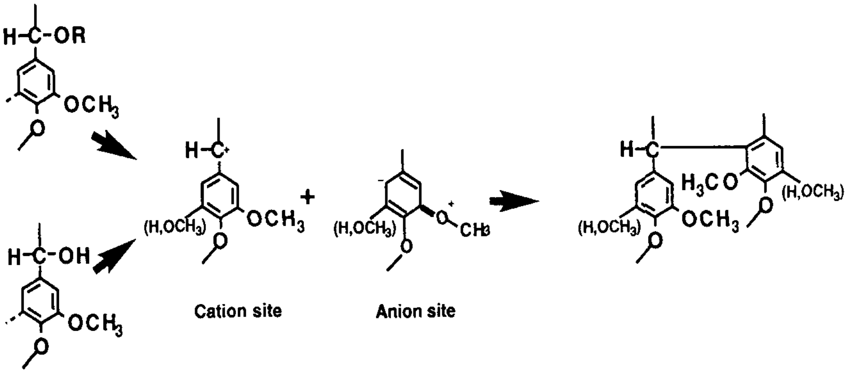


FIGURE 1. Acid Catalyzed Condensation of Lignin

condensation rections at the benzylic carbons interfere with the formation of enol-ether structures in lignin which leads to the cleavage of β-ether bonds in lignin under acidic conditions.

Intramolecular condensation reactions, however, will promote delignification through blocking the benzylic cations which otherwise suffer intermolecular condensation reactions.

Thus condensation reactions are very important reactions in delignification during organic acid pulping processes. Neverthless, little is known about the differences in condensation reactions between softwood and hardwood lignin. This paper deals with the condensation reactions of guaiacyl and syringyl lignin model compounds under formic, acetic and propionic acid pulping conditions. The different responses of hardwood and softwood to the organic acid cooking will be discussed in this paper based on the experimental results of lignin model compounds.

EXPERIMENTAL

Synthesis of Model Compounds

5 - Methoxycreosol: A solusion of 2.5g of syringaldehyde, 4.5g

of $NaBH_4$ in 95 ml of NaOH (10%) was refluxed for 15 hours under an atmosphere of nitrogen. After cooling, the solution was neutralized with 0.5N hydrochloric acid and then extracted with ethyl ether. The ethyl ether layer was washed with water, dried over sodium sulfate and evaporated. Column chromatography of the reduction products on silica gel using n-hexane-ethyl acetate (7:3) gave 5-methoxycreosol as syrup (yield:70%).

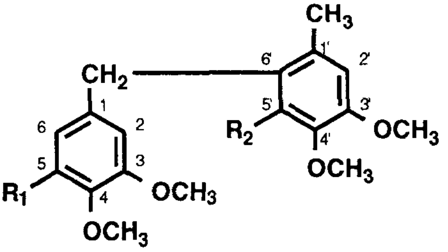
Ethyl ether derivatives of veratryl alcohol and 3,4,5-trimethoxybenzyl alcohol were prepared by the etherification with diethyl sulfate. Both compounds were obtained as syrup. Three compounds synthesized as above were identified by mass and NMR spectra.

Synthesis of diphenylmethane type compounds I, II, III and IV (See Fig.2) were performed in the following manner. A solution of about 2g of veratryl alcohol or 3,4,5-trimethoxybenzyl alcohol and 1.8g of creosol or 5-methoxycreosol in 5 ml 97%(V/V) acetic acid with 0.1%(W/V) HCl was heated at 120℃(oil bath) in a flask with a condenser for 1 hr.

After cooling, the solution was diluted with water and then extracted with chloroform. The chloroform layer was washed with water, and dried over sodium sulfate. The diphenylmethanes were then purified by silica gel column chromatography using n-hexane. Purity was checked by thin layer and gas chromatography, and the structural identifications were performed by mass and NMR spectra. 2-D NMR was used for the assignment of protons and carbons.

Compound I

MS m/z (%) : 288 (M^+ , 100), 273 (27), 257 (24), 150 (40) ; ^{1}H NMR, δ(ppm) : 2.18(s,3H,CH_3), 3.81(s,2H,CH_2), 3.81(s,3H,OCH_3), 3.84(s,3H,OCH_3), 3.85(s,3H,OCH_3), 6.64(dd,*J*=2.0,8.2Hz,1H,6-H), 6.66(s,1H,2-H), 6.66(s,1H,2'-H), 6.68(s,1H,5'-H), 6.76(d,*J*=8.7Hz,1H, 5-H); ^{13}C NMR, δ(ppm): 19.2(q,OCH_3), 38.4(t,CH_2), 55.8(q,OCH_3), 55.9(q,OCH_3), 56.0(q,OCH_3), 111.2(d,5-C), 112.0(d,2-C), 112.9(d,2'-C), 116.1(d,5'-C), 120.6(d,6-C), 127.7(s,1'-C), 132.0(s,6'-C), 133.2(s,1-C), 143.4(s,4'-C), 144.7(s,3'-C), 147.2(s,4-C), 148.9(s,3-C).



$R_1=R_2=H$ I
$R_1=H, R_2=OCH_3$ II
$R_1=OCH_3, R_2=H$ III
$R_1=R_2=OCH_3$ IV

FIGURE 2. Chemical Structures of Condensation Products

Compound II

MS m/z (%) : 318(M^+,100), 180(53), 151(26) ; ^{1}H NMR, δ (ppm) : 2.16(s,3H,CH_3), 3.75(s,3H,OCH_3), 3.81(s,3H,OCH_3), 3.82(s,3H,OCH_3), 3.87(s,3H,OCH_3),3.94(s,2H,CH_2),6.51(s,1H,2'-H), 6.59(dd,J=1.7,8.5Hz,1H,6-H),6.70(d,J=1.7Hz,1H,2-H), 6.72(d,J=8.5Hz,1H,5-H); ^{13}C NMR, δ (ppm) : 19.6(q,CH_3), 31.5(t,CH_2), 55.8(q,OCH_3), 55.9(q,OCH_3), 56.2(q,OCH_3), 60.8(q,OCH_3), 108.7(d,2'-C), 111.1(d,5-C), 111.7(d,2-C), 119.8(d,6-C), 125.0(s,6'-C), 128.0(s,1'-C), 133.6(s,1-C), 136.5(s,4'-C), 145.7(s,3'-C), 145.8(s,5'-C), 147.0(s,4-C), 148.8(s,3-C).

Compound III

MS m/z (%) : 318(M^+,100), 303(20), 150(30) ; ^{1}H NMR , δ (ppm) : 2.20(s,3H,CH_3), 3.79(s,6H,OCH_3), 3.81(s,2H,CH_2), 3.82(s,3H,OCH_3), 3.86(s,3H,OCH_3), 6.34(s,2H,2-H,6-H), 6.68(s,2H,2'-H,5'-H) ; ^{13}C NMR δ (ppm) : 19.3(q,CH_3), 39.1(t,CH_2), 56.0(q,OCH_3), 56.1(q,OCH_3), 60.9(q,OCH_3), 105.7(d,2-C,6-C), 112.9(d,2'-C), 136.4(s,1-C), 143.4(s,4'-C), 144.8(s,3'-C), 153.2(s,3-C,5-C).

Compound IV

MS m/z(%):348(M^+,100), 333(22), 181(57), 151(26) ; ^{1}H NMR , δ (ppm) : 2.17(s,3H,CH_3), 3.77(s,6H,OCH3), 3.80(s,3H,OCH3), 3.88(s,3H,OCH_3), 3.94(s,2H,CH_2), 6.34(s,2H,2-H,6-H), 6.51(s,1H,2'-H) ;

^{13}C NMR, δ(ppm) : 19.7(q,CH_3), 32.2(t,CH2), 56.1(q,OCH_3), 56.1(q,OCH_3), 60.8(q,OCH_3), 60.9(q,OCH_3), 105.2(d,2-C,6-C), 108.6(d,2'-C), 124.5(s,6'-C), 128.1(s,1'-C), 136.0(s,4-C), 136.5(s,4'-C), 136.8(s,1-C), 145.8(s,3'-C,5'-C), 153.1(s,3-C,5-C).

Condensation Reaction

Organic acids used in this experiments were 95%(V/V) formic(FA), acetic(AA) and propionic acid(PA) with 0.1%(W/V) HCl. Boiling temperatures of these acid solutions were 102, 106 and 109℃, respectively.

The following three types of mixtures of lignin model compounds were treated with 0.2 ml FA, AA and PA in a glass tube sealed with a screw cap for 0 to 60 minutes.

a) A mixture of 1.7 mg (10 μmol) of veratryl alcohol, 2.0 mg (10 μmol) of 3,4,5-trimethoxy-benzylalcohol and 17 mg (100 μ mol) of 5-methoxycreosol.

b) A mixture of 1.7 mg of veratrylalcohol, 14 mg of creosol and 17 mg of 5-methoxycreosol.

c) A mixture of 2.0 mg of 3,4,5-trimethoxybenzyl alcohol, 14 mg of creosol and 17 mg of 5-methoxycreosol.

In the experiment for the reactivities of benzyl ether type compounds, a mixture of 1.9 mg of veratryl alcohol ethyl ether, 2.2 mg of 3, 4, 5 - trimethoxybenzyl alcohol ethyl ether and 17 mg of 5-methoxycreosol was treated with the acids under the same conditions.

Analysis of Condensation Products

The condensation products were analyzed by GC, GC-MS and NMR spectrometry. The yields of the condensation products were determined by the calibration curves obtained from the synthesized diphenylmethane compounds. GC conditions were ; 25 m capillary column (CBP1 Shimadzu) with nitrogen as a carrier gas at a flow rate of 0.85ml/min. The column temperature was

140 ~ 250℃(4℃/min). ^1H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ on a JEOL DATUM α500 spectrometer.

RESULTS AND DISCUSSION

Reactivities of Guaiacyl and Syringyl Nuclei

Acid catalyzed condensation of lignin is known to take place between the cationic site from either benzyl alcohol or benzyl ether and the electron-rich aromatic carbon as illustrated in fig.1. Both the cationic site and the electron-rich aromatic carbon can be either a guaiacyl or a syringyl unit in lignin. The differences in the reactivities in these acid condensation reactions between guaiacyl and syringyl compounds may explain the different responses of the softwood and hardwood to the organic acid pulping.

Reactivities of cationic site:

In order to investigate the reactivities of the benzylic cations of softwood and hardwood lignin, the mixtures of veratryl alcohol and 3,4,5-trimethoxybenzyl alcohol as cationic site model compounds of non-phenolic guaiacyl and syringyl nuclei and 5-methoxycreosol with electron-rich aromatic carbons in the molar ratio of 1:1:10 were treated with the organic acids. The yields of the condensation products are listed in table 1.

In most cases, the yield of compound Ⅱ was higher than that of compound Ⅳ (where Ⅱ: condensation product from veratryl alcohol and 5-methoxycreosol, Ⅳ: that from 3,4,5-trimethoxybenzyl alcohol and 5-methoxycreosol) and the molar ratio of Ⅱ/Ⅳ was higher especially in the initial reaction period. After 30 min. in FA cooking, however, compound Ⅳ showed higher yield than compound Ⅱ, indicating the higher stability of compound Ⅳ in this strong acid. At the low temperature (0℃, 1 min.) of FA treatment, the value of Ⅱ/Ⅳ increased to 24.3. These results clearly indicate that the carbonium ions derived from the guaiacyl compound has a higher reactivity.

However, the reactions in a strong acidic solvent like FA are too fast to observe the reactivities. In other words, the cation

TABLE 1

Yield of Condensation Products in Various Organic Acid Cooking of the Mixture of Veratryl Alcohol, 3,4,5-Trimethoxybenzyl Alcohol and 5-Methoxycreosol

	Time (min)	Yield (μ mole)		Molar ratio
		II	IV	II/IV
FA	0.5[1]	8.6	3.2	2.7
	3	10.3	9.6	1.1
	30	6.8	8.8	0.8
	1[2]	9.7	0.4	24.3
AA	3	5.2	0.6	8.7
	15	10.2	9.8	1.0
	30	9.2	8.6	1.1
PA	3	4.8	0.3	16.0
	30	10.5	4.5	2.3
	60	9.7	5.3	1.8

Note: 1) Room temp. 2) 0℃
FA(formic acid), AA(acetic acid) PA(propinic acid),
Cooking conditions;95% acids with 0.1%HCl, at 110℃
Compounds II,IV(see Fig.2)

formation rate of guaiacyl nuclei is faster and/or the cations are more stable than syringyl ones.

Previously, it was suggested by Yasuda et al[13] that benzylic cations with guaiacyl and syringyl nuclei have similar reaction rates and reactivities in sulfuric acid treatment. This is probably because the acidic conditions used were too strong to see the reactivities. The condensation reactions at the initial reaction period would be very important for pulping, because it would affect the subsequent delignification. (The yields of the condensation products was found to be FA>AA>PA; in the order of acidity of the solvents.)

Reactivities of electron-rich aromatic carbon:

To see the differences in reactivities of electron-rich aromtic carbons between guaiacyl and syringyl nuclei, two reaction mixtures A:(veratryl alcohol, creosol and 5-

TABLE 2

Yields of Condensation Products in Various Organic Acids Cooking of the Mixture A and B

		A		B	
Acid	Time(min.)	Yield (μ mole)		Yield (μ mole)	
		I	II	III	IV
FA	0.5[1)]	1.0	6.2	0.3	1.8
	3	2.6	8.5	3.2	9.8
AA	3	0.2	9.1	0.5	3.8
	30	0.3	8.0	1.2	6.4
PA	3	0.8	6.0	0.1	0.2
	30	2.0	10.2	1.0	6.8

Note ; 1) Room temp. I ~ IV; see Fig.2

A : mixture of veratryl alcohol, creosol and 5-methoxy creosol

B : mixture of 3, 4, 5 - trimethoxybenzyl alcohol, creosol and 5-methoxycreosol, in the molar ratio of 1:10:10

methoxycreosol) and B:(3,4,5-trimethoxybenzyl alcohol, creosol and 5-methoxycreosol) in the molar ratio of 1:10:10 were treated with these organic acids. The results are shown in table 2.

At any reaction time and in any organic acid, the yields of condensation products from veratryl alcohol (or 3,4,5-trimethoxybenzyl alcohol) and 5-methoxycreosol (compound II or IV) were higher than those from veratryl alcohol (or 3,4,5-trimethoxy benzyl alcohol) and creosol (compound I or III). The amounts of condensation products were higher in mixture A. In addition, the reaction selectivity depended on the organic acids used. These facts suggest that the reactivities of the aromatic carbons of syringyl nuclei are higher than those of guaiacyl ones. The yields of condensation products were also influenced by the acidity of the solvents.

On the basis of these data, it seemed reasonable to assume that higher reactivities of syringyl nuclei depend on the higher electron density of syringyl nuclei due to the presence of another methoxyl group as an electron donating group.

Reactivities of Benzyl Ether Structures of Guaiacyl and Syringyl Nuclei

The ether linkages at α-carbon of lignin (benzyl ether) known to be present as α-O-4, phenylcoumaran, pinoresinol and lignin carbohydrate complex (LCC) are also hydrolyzed and expected to be precursors of benzylic cations in acidic cooking. The amounts of these benzyl ether structures in lignin are estimated to be about 0.2 per C9 unit[14].

The differences in hydrolysis rates of benzyl ether structures containing guaiacyl and syringyl nuclei were investigated by determining the yield of the condensation products. The two types of mixture, C: (veratryl alcohol ethyl ether, 3,4,5 trimethoxybenzyl alcohol ethyl ether and 5-methoxycreosol) and D (veratryl alcohol, 3,4,5-trimethoxybenzyl alcohol and 5-methoxycreosol) at the molar ratio of 1:1:10 were treated with organic acids under the same conditions. The results were shown in fig. 3 and table 3. The recovery of the starting substances from etherified compounds were higher compared to non-etherified compounds. In addition, the recovery of syringyl type compounds was also higher than that of guaiacyl compounds. Though veratryl alcohol in the mixture D was consumed completely in 10 minutes, approximately 30% of 3,4,5-trimethoxybenzyl alcohol ethyl ether in the mixture C still remained after 1 hr under 95% PA treatment. The formation of condensation products from the ethyl ether of 3,4,5-trimethoxybenzyl alcohol showed the tendency to be lower compared to those of veratryl alcohol . The ratios of compounds II and IV in the mixture C to those in the mixture D are shown in table 4. In the initial reaction time, the ratio of compound II in the mixture C to compound II in the mixture D was 3 to 4 times that of compound IV in the mixture C to compound IV in the mixture D (table 4).

The facts indicate that the ether derivatives of syringyl-type benzyl alcohol have a rather higher positive blocking effect on the

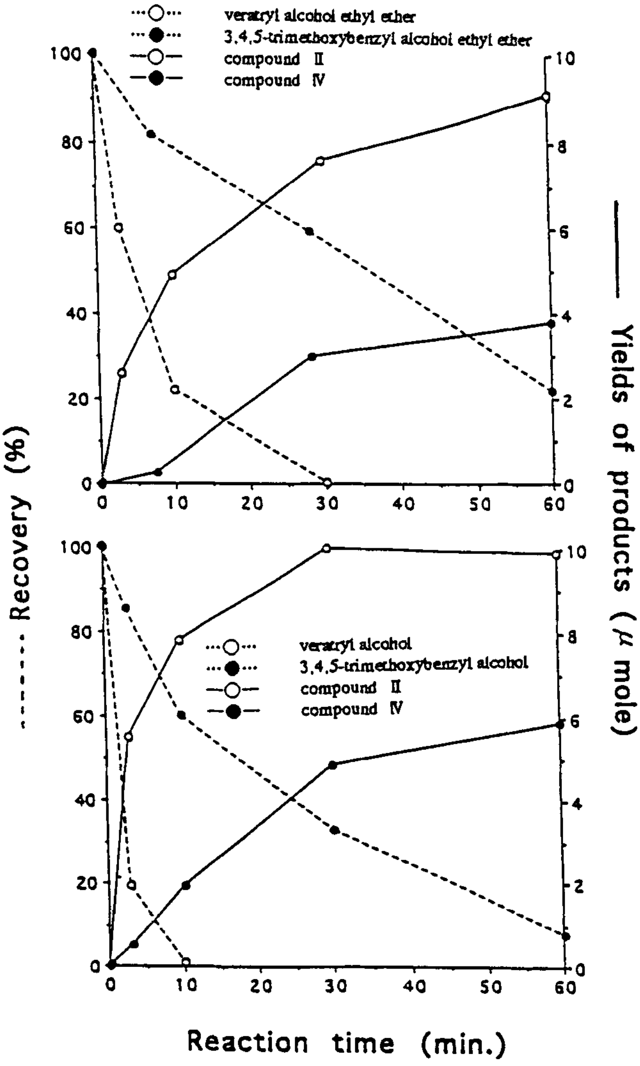


FIGURE 3. Recovery of Original Model Compounds and the Yield of Condensation Products after PA Cooking.
C: Etherified, D : Non-etherified Compounds

TABLE 3

Yields of Condensation Products II and IV after PA Cooking of the Mixture C and D

	C			D		
	Yield(μ mole)		Molar ratio	Yield(μ mole)		Molar ratio
Time(min.)	II	IV	II / IV	II	IV	II /IV
3	2.3	0.1	23.0	5.6	0.5	11.2
10	5.0	0.3	16.7	7.6	1.6	4.8
30	7.2	3.3	2.2	10.2	4.7	2.1
60	8.4	4.1	2.0	9.4	5.6	1.8

Note ; Compounds II, IV (see Fig.2), Cooking condition ; 95% PA with 0.1%HCl, temp.; 110℃, C ; mixture of veratryl alcohol ethyl ether, 3,4, 5-trimethoxybenzyl alcohol ethyl ether and 5-methoxycreosol, D ; mixture of veratryl alcohol,3, 4, 5 -trimethoxybenzyl alcohol and 5-methoxycreosol in the molar ratio of 1:1:10.

TABLE 4

Effect of Etherification of Benzyl Alcohol on the Formation of Condensation Products in PA and AA Cooking

Acid	PA			AA		
Time(min.)	3	10	30	$0.5^{1)}$	3	10
II_C/II_D	0.41	0.68	0.75	0.57	0.91	1.00
IV_C/IV_D	0.10	0.26	0.52	0.22	0.71	1.00

Note: 1) Room temp. Compound II,IV(see Fig.2)

IIC/IID : the ratio of compound II in C to compound II in D

IVC/IVD : the ratio of compound IV in C to compound IV in D

C : the mixture of veratryl alcohol ethylether, 3,4,5-trimethoxybenzyl alcohol ethylether and 5-methoxycreosol,

D : the mixture of veratryl alcohol, 3,4,5- trimethoxybenzyl alcohol and 5-methoxycreosol in the molar ratio 1:1:10

formation of benzylic cations than that of guaiacyl-type benzyl alcohol especially in the initial reaction period.

Stability of Diphenylmethane Structures During Organic Acid Cooking

On the acid pulping, it has been suggested that various diphenylmethane type units were formed resulting from condensation reactions. The diphenylmethane structures thus formed are generally considered to be very stable under acidic conditions, and this may be the cause for the difficulty of performing complete delignification.

To elucidate the stability of diphenylmethanes under the organic acids cooking conditions, four types of diphenylmethane compounds Ⅰ ~ Ⅳ (see fig.2) were synthesized and treated with PA, AA and FA. The percent decomposition of the diphenylmethanes were listed in table 5.

The decomposition of diphenylmethane structures was observed only in the case of FA treatment, but the compounds Ⅰ and Ⅲ consisting of guaiacyl nuclei (as elctron-rich aromatic carbon sites when they were formed) were found to be very stable even under FA treatment conditions. When compound Ⅱ was treated with FA under the presence of excess amount of creosol, most of the compound Ⅱ was converted to compound Ⅰ. After the reaction, 5-methoxycreosol was found in the reaction solution. This fact explains that benzylic cations formed by the decomposition of compound Ⅱ under the strong acidic conditions condensed with another electron rich carbon of creosol. The newly formed condensation product (compound Ⅰ) was very stable and accumulated in the solution. The results suggest that hardwood lignin consisting of syringyl nuclei rapidly forms condensation products but they are decomposed easily under the strong acidic conditions. This behavior supports the observation that syringyl lignin is easy to be removed under acidic cooking conditions. The tentative decomposition mechanism of compound Ⅱ under FA cooking was illustrated in fig.4. The first step of the reaction is the protonation to the π-electron of aromatic rings and then follows the route just reverse to its formation reaction. The

TABLE 5

Percent Decomposition of Diphenylmethanes under the Organic Acids Cooking

Diphenylmethane types	PA	AA	FA
I	0	0	2
II	0	0	86
III	0	0	0
IV	0	0	21

Note : I ~ IV (see Fig.2), Cooking conditions ; 95% organic acids with 0.1%, HCl, 110℃ ,60min.
Figures show the percent of decomposition.

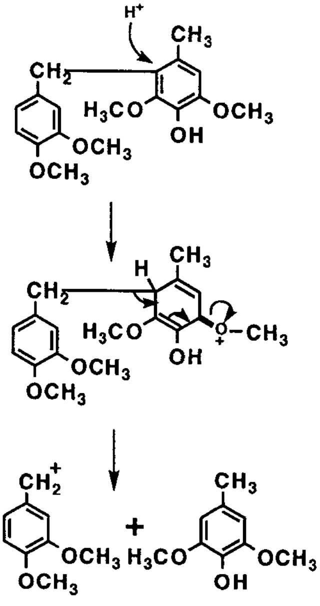


FIGURE 4. Tentative Decomposition Mechanism of Compound II under FA Cooking

higher π-electron density of syringyl nuclei compared to guaiacyl ones which is caused by an extra methoxy group explains the higher reactivity.

CONCLUSION

The reactivities of guaiacyl and syringyl lignin in condensation reactions during organic acid pulping have been examined by using corresponding model compounds.

At the initial reaction period, higher reactivities in condensation reactions were observed between carbonium cations of guaiacyl nuclei and syringyl type aromatic carbons compared to other combinations.

The cleavage of benzyl ether bonds of syringyl nuclei was slower than that of guaiacyl nuclei. In addition, the diphenylmethane structures formed by condensation reaction between carbonium cations of guaiacyl compounds and electron rich aromatic ring carbons of syringyl compounds were found to be unstable during the strong acidic cooking. These reactivities may contribute to the easier delignification characteristics of hardwood.

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