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Structural Analysis of Acid-Catalyzed Organosolv Lignins by a Combination of Nucleus Exchange Reaction and Nitrobenzene Oxidation

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Abstract

Aspen (*Populus tremuloides*) chips were treated with methanol: water (70:30 by volume), at 165°C for 2.5 hours, with catalysts ($NaHSO_4$, H_2SO_4 and H_3PO_4), using a liquor-to-wood ratio of 4:1. The structures of the resulting organosolv lignins were analyzed by the combination of nucleus exchange reaction and nitrobenzene oxidation. Above the liquor pH 3.2, the compositions of dissolved lignins were similar to that of original lignin and the condensation reaction did not occur extensively. However, with decreasing liquor pH (below pH 3.0), the condensation occurred dramatically, forming diphenylmethane type structures. The dissolved lignins were rich in guaiacyl units which were mainly of type Gb.

Key words: Organosolv lignin, Acid-catalyst, Condensation, Diphyenylmethane, Nucleus exchange reaction

Introduction

Organosolv delignification was originally studied by KLEINERT and TAYENTHAL[1)] and KLEINERT[2-6)] as a novel method for producing chemical pulps for paper manufacture. Compared to conventional kraft pulping processes, the advantages included substantial reduction in capital costs and higher pulp yields for the same level of delignification. The two broad categories of organosolv processes are "catalyzed and uncatalyzed". The catalysts can be acids or salts : base can also be added[7-9)]. Pilot-plant scale studies are under way using catalyzed and uncatalyzed aqueous ethanol solutions[10)]. Major efforts are ongoing in Europe to develop alkaline organosolv pulping technologies[11-13)]. Pilot- scale efforts are on progress in Germany on at least two of the alkaline processes.

The ability of the organic/aqueous solvent to selectively extract high yields of the lignin fraction or a combination of lignin and hemicellulosic fractions, principally for hardwoods, suggests that potentially these processes could be used as a pretreatment for the production of relatively high purity cellulosic substrates for enzyme hydrolysis. Removal of most of the lignin and xylan fractions would facilitate operation of simultaneous saccharification and fermentation digesters because these inert materials would not occupy 30-40% of the

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digester capacity: in addition, lignin are potentially capable of affecting the downstream enzyme recycle by adsorption of enzyme components[14,15].

It is the utilization of carbohydrates that is greatly improved through organosolv processes. On the other hand, that of the resulting lignin has still remained difficult because of its complexity and heterogeneity in the structure. However, without the effective utilization of lignin fractions, the organosolv process cannot be established as the entire utilization process of lignified biomass. Lots of fundamental data on the molecular weight of organosolv lignin, its reactivity, its functional groups, its condensation degree and others are required for designing new lignin utilization processes. In this connection, the characterization of organosolv lignins by ^{1}H and ^{13}C NMR has been carried out[16]. In the present work, the properties of acid-catalyzed organosolv lignins were discussed using a combination technique of nucleus-exchange and nitrobenzene oxidation.

Experimental

Organosolv treatment and isolation of lignin

Organosolv treatments of aspen (*Populus tremuloides*) chips were carried out in methanol : water (70 : 30 by volume), at 165°C for 2.5 hours, with catalysts ($NaHSO_4$, H_2SO_4 and H_3PO_4) and, for comparison, without catalysts, using a liquor-to-wood ratio of 4 : 1. The delignified woods were filtered off, followed by thorough washing. The filtrate and washings were combined and evaporated to near dryness in a rotary evaporator at temperatures lower than 60°C under reduced pressure. The solid residue was then leached by redissolution of the hemicellulosic fraction in water, followed by filtration (or centrifugation) of the lignins. The isolated lignins were further purified using dioxaneether.

Nucleus exchange and nitrobenzene oxidation

Nucleus exchange treatments of organosolv lignins were carried out with the degradation reagent prepared by mixing 19 parts (by volume) of phenol, 10 parts of xylene and 3 parts of boron trifluoride-phenol complex in a 1.5 ml stainless steel autoclave. One ml of the reagent was used for about 28 mg of lignin. In alkaline nitrobenzene oxidation, lignin (10 mg), 2 N sodium hydroxide (0.8 ml) and nitrobenzene (0.05 ml) were placed in a stainless steel autoclave (1.5 ml in volume) and heated. The detailed procedures for both methods were described in elsewhere[17].

In the below section, the abbreviations are used as follows:

DPM: Diphenylmethane
[Nucleus Exchange Reaction]
NEP: Nucleus exchange reaction products
NEP_g: Nucleus exchange reaction products from guaiacyl units.
NEP_s: Nucleus exchange reaction products from syringyl units.
NEP_g^{110} and NEP_s^{110}: Nucleus exchange reaction products from guaiacyl and syringyl at 110°C, respectively.
G: Guaiacol
C: Catechol
P-1, 3: Pyrogallol-1,3-dimethyl ether

P-1: Pyrogallol-1-methyl ether
P: Pyrogallol

[Nitrobenzene Oxidation]
NOP: Nitrobenzene oxidation products
NOP_g: Nitrobenzene oxidation products from guaiacyl units.
NOP_s: Nitrobenzene oxidation products from syringyl units.
V: Vanillin
VA: Vanillic acid
S: Syringaldehyde
SA: Syringic acid

The following equations summarize the quantitative calculations for various units in acid-catalyzed organosolv lignins[17].

Non-condensed guaiacyl units (Ga), mol%, $= NOP_g/0.78$ ………… (1)
DPM type guaiacyl units (Ga′, Gb′), mol%,
$= NEP_g -$ non-condensed guaiacyl units
$= NEP_g - (NOP_g/0.78)$ ………… (2)
Non-condensed syringyl units (Sa), mol%, $= NOP_s/0.77$ ………… (3)
DPM type syringyl units (Sa′, Sb′), mol%,
$= NEP_s -$ non-condensed syringyl units
$= NEP_s - (NOP_s/0.77)$ ………… (4)
Condensed guaiacyl and syringyl units (Gb, Sb), mol%,
$= 100 -$ non-condensed guaiacyl and syringyl units $(Ga + Sa)$
$-$ DPM type guaiacyl and syringyl units $(Ga' + Ga' + Sa' + Sb')$ ………… (5)

where 0.78 and 0.77 are NOP_g/NEP_g and NOP_s/NEP_s for aspen MWL, respectively.

Results and Discussion

The organosolv-treatment conditions and yields of isolated lignins and lignins remaining in the cellulosic

Table 1. Conditions of organosolv treatments and yields of isolated lignins

Cooking liquor pH	Catalyst	Catalyst concentration, M	Lignin yields (% of original lignin)	
			Water insoluble	In pulp
4.3*[1]	None	—	52	39
3.2	$NaHSO_4$	0.04	68	24
3.0*[2]	H_3PO_4	0.05	78	10
2.05	H_2SO_4	0.05	63	46
2.05*[2,3]	H_2SO_4	0.05	89	21

*[1] Acetic acid added to simulate xylan acetyl group hydrolysis.
*[2] Liquors neutralized prior to solvent evaporation.
*[3] 1 hour cooking.

residues are given in Table 1. In these experiments, the digester was allowed to cool to room temperature overnight, thus allowing some lignin reprecipitation onto the fibers which explains the relatively high residual lignin contents of some pulps. Total recovery of lignins in about 90% was observed for the less acidic pretreatments. The data suggest that a small amount of the low-molecular weight lignins were solubilized in this procedure. In the presence of sulfuric acid at a relatively high concentration, 0.05 M, the apparent recovery of lignins is about 110%, suggesting condensation of carbohydrate-derived materials onto the lignins (possibly to form highly condensed residual lignins).

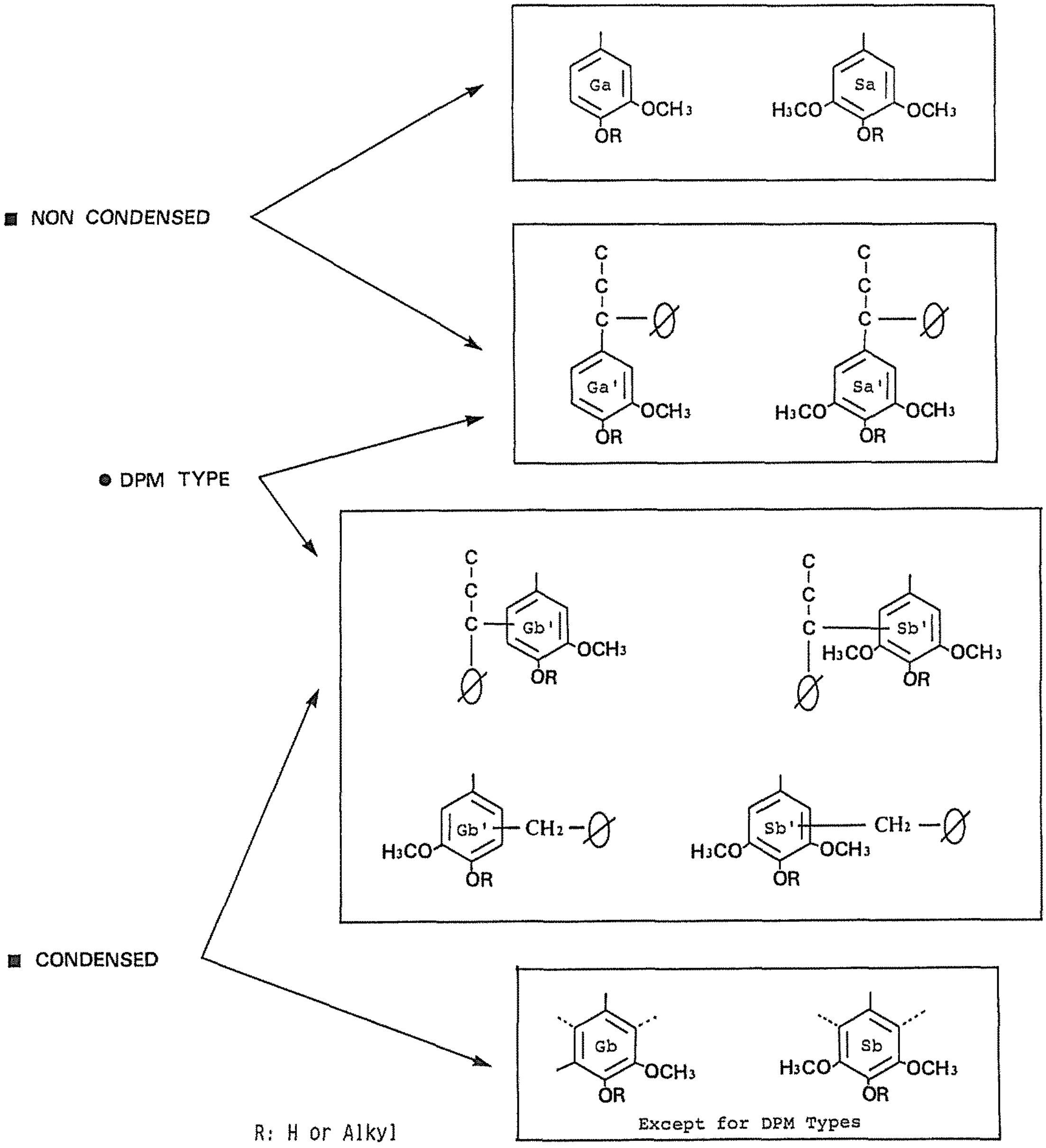

Fig. 1. Types of lignin phenyl nuclei.

Phenyl nuclei in hardwood protolignins can be classified into non-condensed guaiacyl (Type Ga), condensed guaiacyl (Type Gb) and non-condensed syringyl (Type Sa) units (Fig. 1). When treated in acidic media, these units undergo secondary condensations, mainly forming diphenylmethane type structures linked between benzylic carbons and aromatic nuclei. Consequently, in acid modified lignins, guaiacyl units can be of non-condensed (Ga), DPM (Ga′ and Gb′), and condensed (Gb) types. Similarly, syringyl units can be of non-condensed (Sa), DPM (Sa′ and Sb′), and condensed (Sb) types (Fig. 1).

Fig. 2 schematically illustrates the relationship betwee lignin structures and yields of NEP and NOP.

The NEP and NOP yields and various indexes calculated from them are shown in Tables 2, 3 and 4.

NOP originating structures are only non-condensed units (Ga, Sa)[18], whereas NEP originating structures are both of non-condensed (Ga, Sa) and DPM type (Ga′, Gb′, Sa′, Sb′) units[17,19]. Since there is no DPM unit in original MWL, NOP/NEP in MWL represents the maximum conversion of non-condensed units (Ga, Sa) into NOP. This value varies depending on the side chain structures. The NOP_g/NEP_g and NOP_s/NEP_s in aspen MWL were very close, indicating that guaiacyl and syringyl units have similar side chain structures. The NOP_g/NEP_g values at pH 4.3 and 3.2 were about the same, slightly lower than that in MWL, and the NOP_s/NEP_s at pH 3.2 was almost equal to that in MWL. This suggests that the secondary condensation of lignin did not occur to a large extent above pH 3.2. The lignin dissolved at pH 4.3 had higher NOP_s/NEP_s than MWL, indicating that this lignin had more amount of NOP high yielding structures such as aliphatic OH and conjugated double bonds in the side chains of syringyl units[18]. This structural change of side chains in syringyl units is likely due to the cleavage of syringyl β-O-4 linkages to a larger extent, because syringyl units originally have

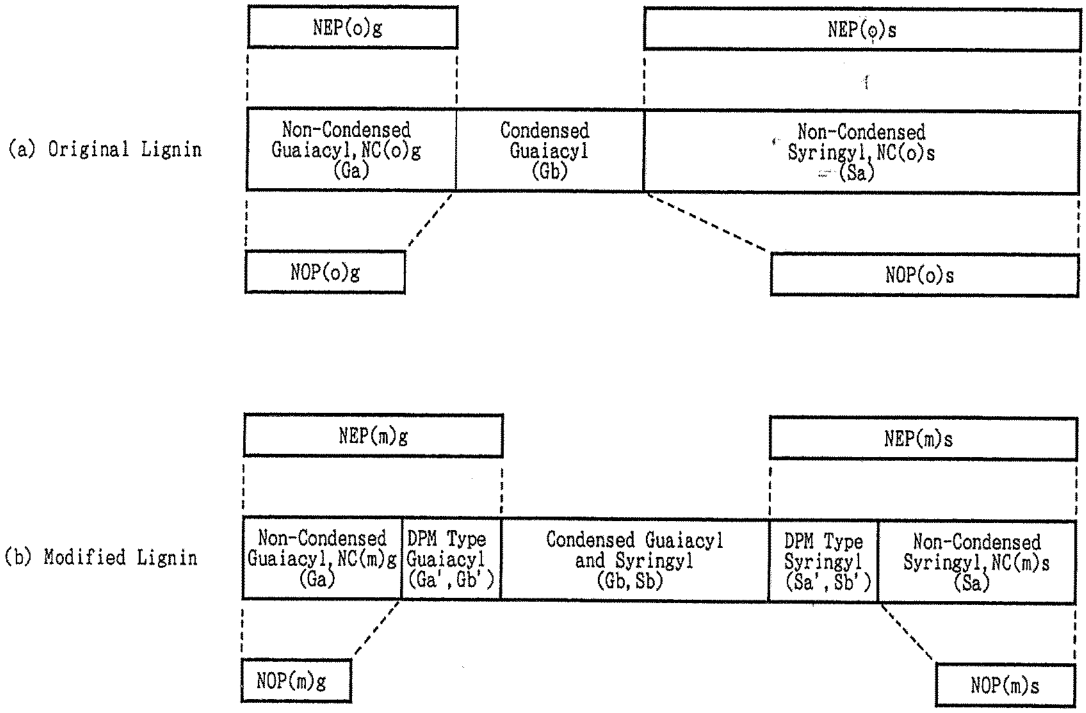

Fig. 2. Structural units of hardwood lignin and the yields of NEP and NOP.

Table 2. Nucleus exchange products from aspen milled wood and acid-catalyzed organosolv lignins (mole %)

Liquor pH	NEP_g^{110}			NEP_g			NEP_s^{110}				NEP_s*1
	G	C	Total	G	C	Total	P-1, 3	P-1	P	Total	
4.3	8.23	1.68	9.91	2.37	11.30	13.67	12.02	5.54	0.59	18.15	25.03
3.2	10.38	1.83	12.21	2.58	12.43	15.01	14.98	10.41	0.76	26.15	32.16
3.0	8.11	1.88	9.99	3.38	10.42	13.80	7.35	7.55	0.66	15.56	21.49
2.05*	6.29	1.17	7.46	2.30	8.73	11.03	5.65	3.87	0.37	9.89	14.63
2.05	5.99	1.64	7.63	2.10	8.63	10.73	5.02	4.93	0.56	10.51	14.78
MWL	10.11	1.04	11.15	2.66	14.46	17.12	18.34	6.04	+	24.38	37.45

*1 $NEP_s = NEP_s^{110} \times (NEP_g / NEP_g^{110})$
*2 1 hour cooking.

Table 3. Nitrobenzene oxidation products from aspen milled wood lignin and acid-catalyzed organosolv lignins (mole %)

Liquor pH	NOP_g			NOP_s		
	V	VA	Total	S	SA	Total
4.3	9.28	0.61	9.89	20.19	1.87	22.06
3.2	10.10	0.87	10.97	21.70	2.69	24.39
3.0	5.50	0.71	6.21	10.30	1.99	12.29
2.05*	2.24	0.87	3.11	3.95	1.57	5.52
2.05	0.85	0.73	2.58	3.40	1.31	4.71
MWL	12.30	1.12	13.42	24.99	3.74	28.73

*1 1 hour cooking.

Table 4. Various indexes bases on NEP and NOP

Liquor pH	$\frac{NOP_g}{NEP_g}$	$\frac{NOP_s}{NEP_s}$	$\frac{NEP_s}{NEP_g}$	$\frac{NOP_s}{NOP_g}$	$\frac{C}{G+C}$ *1	$\frac{P\text{-}1+P}{P\text{-}1,3+P\text{-}1+P}$ *2	$\frac{VA}{V+VA}$	$\frac{SA}{S+SA}$
4.3	0.72	0.88	1.83	2.23	0.17	0.34	0.06	0.08
3.2	0.73	0.76	2.14	2.22	0.15	0.43	0.08	0.11
3.0	0.45	0.57	1.56	1.98	0.19	0.53	0.11	0.16
2.05*3	0.28	0.38	1.33	1.78	0.16	0.43	0.28	0.28
2.05	0.24	0.32	1.38	1.83	0.22	0.52	0.28	0.28
MWL	0.78	0.77	2.19	2.14	0.09	0.25	0.08	0.13

*1 NEP_g^{110}
*2 NEP_s^{110}
*3 1 hour cooking.

larger amount of β-O-4 linkages. Below pH 3.0, the NOP/NEP decreased dramatically, indicating that DPM type structures were formed by the secondary condensation between benzylic carbons and phenyl nuclei.

In acid modified lignins, the NEP_s/NEP_g represents the ratio of non-condensed plus DPM type units between guaiacyl and syringyl, whereas the NOP_s/NOP_g (conventional S/V ratio) is the ratio of only the remaining non-condensed units. The NEP_s/NEP_g is more informative than conventional S/V, since DPM type units are formed from original non-condensed units. The NEP_s/NEP_g decreased only slightly above liquor pH 3.2, whereas it decreased dramatically below liquor pH 3.0, suggesting that the lignins dissolved below pH 3.0 were rich in guaiacyl units.

The lignin phenyl nuclei liberated as monomers by the nucleus exchange reaction (guaiacol from guaiacyl units, and pyrogallol-1,3-dimethyl ehter from syringyl units) are further demethylated by boron trifluoride to give catechol, pyrogallol-1-methyl ether and pyrogallol. Consequently, C/(G+C) and (P-1+P)/(P-1,3+P-1+P) represent the demethylation degree of methoxyl groups during the nucleus exchange reaction. The demethylation rate of methoxyl group is much slower[20,21], compared with the phenolation of side chains and the exchange of phenyl nuclei for phenol and varies depending on the activity of boron trifluoride. Boron trifluoride is sensitive to moisture and deactivated by water secondarily formed during the reaction. These indexes in both guaiacyl and syringyl were getting higher with decreasing liquor pH, indicating that the activity of boron trifluoride was higher in the nucleus exchange reaction of lignins dissolved at lower liquor pH, that is, less amount of water formed secondarily. The secondary formation of water during the nucleus exchange reaction is mainly due to (1) the reaction of aliphatic OH with phenol[20] and (2) the condensation between phenolic hydroxyl groups forming diphenylether structures[22]. Above result implies that lignins dissolved at lower pH have less amount of aliphatic hydroxyl groups in side chains that are reactive with phenol, because the influence of (2) can be regarded to be about the same between the lignins.

The ratio of acid in NOP [VA/(V+VA) and SA/(S+SA)] has a relatively good correlation with the amount of quinoid structures in lignins[23]. The higher value of VA/(V+VA) or SA/(S+SA) means larger amount of quinoid structures. Although this ratio was not so different between the lignins above liquor pH 3.2, it increased dramatically at pH 2.05. This would be due to the presence of more amount of mesomeric quinonemethides in the lignin at pH 2.05 that were derived from DPM type structures. The quinoid moieties in lignin form strong hydrogen bonds to adjacent hydroxyl groups, resulting in the rigidity of lignin molecule[24].

Quaiacyl and syringyl units were further divided into non-condensed (Ga, Sa), DPM type (Ga′, Gb′, Sa′, Sb′) and condensed (Gb, Sb) (Table 5). With decreasing liquor pH, especially below pH 3.0, non-condensed guaiacyl and syringyl units decreased rapidly, accompanied by the formation of DPM type units. This indicates that secondary condensation of lignin was accelerated below pH 3.0. It has been demonstrated by model experiments[25] and the nucleus exchange analysis[26,27] of acid-treated lignins that in the acidic media, benzylic

Table 5. Types of structural units in aspen milled wood lignin and acid-catalyzed organosolv lignins

(mole %)

Liquor pH	Non-Condensed Guaiacyl (Ga)	DPM Type Guaiacyl (Ga′, Gb′)	Condensed Guaiacyl and Syringyl (Gb, Sb)	Non-Condensed Syringyl (Sa)	DPM Type Syringyl (Sa′, Sb′)	C_9 Formula
4.3	13	1	57	29	—	—
3.2	14	1	53	32	Trace	$C_9H_{8.5}O_{2.6}(OCH_3)_{1.3}$
3.2	8	6	64	16	6	$C_9H_{8.2}O_{2.4}(OCH_3)_{1.2}$
2.05*	4	7	75	7	7	$C_9H_{7.6}O_{2.4}(OCH_3)_{1.1}$
2.05	3	7	75	6	9	$C_9H_{7.6}O_{2.1}(OCH_3)_{1.2}$
MWL	17	—	45	38	—	$C_9H_{8.5}O_{3.5}(OCH_3)_{1.4}$

* 1 hour cooking.

carbons of lignin are readily attacked by nucleophiles, forming DPM type structures. However, the total quantity of DPM type units (12–16 mol%) in acid catalyzed organosolv lignins is not very much. This is possibly due not only to the prevention of secondary condensation by alcohol but to the retention of highly condensed units in pulp.

The total of non-condensed (Sa) and DPM type (Sa′, Sb′) units in syringyl has a correlation with the syringyl content calculated from the C_9 formula. This means that the condensation of syringyl units were mostly of DPM types. Below pH 3.0, a less amount of syringyl units was involved in the isolated black liquor lignins. This is partly due to the degradation of syringyl units to smaller fractions that are water-soluble. However, this would be probably due mainly to the more preferential participation of syringyl units in the secondary condensation reactions since these units are more flexible than guaiacyl, due to the absence of the condensed structures. Consequently, a higher amount of syringyl units might be retained in the pulps in the form of condensed moieties. To confirm this proposition, the characterization of the residual pulp lignins is required.

Concluding Remarks

The structures of organosolv lignins dissolved at various liquor pH were analyzed by the combination of nucleus exchange reaction and nitrobenzene oxidation.

Generlly, with decreasing liquor pH, reactive aliphatic hydroxyl groups decreased and the secondary condensation occurred to a larger extent. That is, above pH 3.2, the compositions of dissolved lignins were similar to that of original lignin and the condensation reaction did not occur extensively, whereas below pH 3.0, the condensation occurred dramatically, forming DPM type structures. The dissolved lignins were rich in guaiacyl units which were mainly of type Gb.

These informations are important for the utilization of organosolv lignins. For example, the lignin dissolved at pH 2.05 is less reactive because of less amount of aliphatic hydroxyl groups and the high condensation degree of phenyl nuclei. However, dissolved lignins do not represent whole modified lignins, and some parts of lignins are still in the pulp. Based on the current study, residual pulp lignins are presumed to have more amount of secondarily formed condensed units. Consequently, in order to elucidate the overall structural change of lignin during acid-catalyzed organosolv treatment, the analysis of residual lignins in pulp will also be required in the future.

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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，Cα–アリール縮合構造が形成された。低 pH で流出するリグニンは，グアイアイアイアシル単位にリッチであった。