

## REACTIONS OF LIGNIN DURING PULPING

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The main feature of the process of chemical pulping is removal of lignin from intercellular area and cell wall. This is achieved by degradation of lignin macromolecule by the action of cooking chemicals into soluble fragments which are small enough for removal by diffusion through the cell wall.

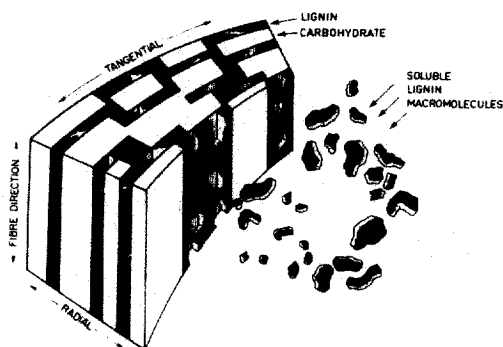


Fig. 1. Schematic of the breakdown and solution of lignin during chemical pulping.<sup>1)</sup>

Fig. 1 is the schematic representation of dissolution of lignin fragments from the cell wall.<sup>1)</sup> The physical properties of the lignin fragments are conveniently interpreted by assuming that they are dissolved as various size of membranes of about 2nm thick. Thus each fraction of lignin as it is released from the wood is widely polydisperse, and the average molecular weight of lignin fragments increases as the delignification proceeds (Fig. 2).<sup>2)</sup> The average molecular weight of liginosulfonic acid dissolved in the cooking liquor is higher than that of kraft lignin.

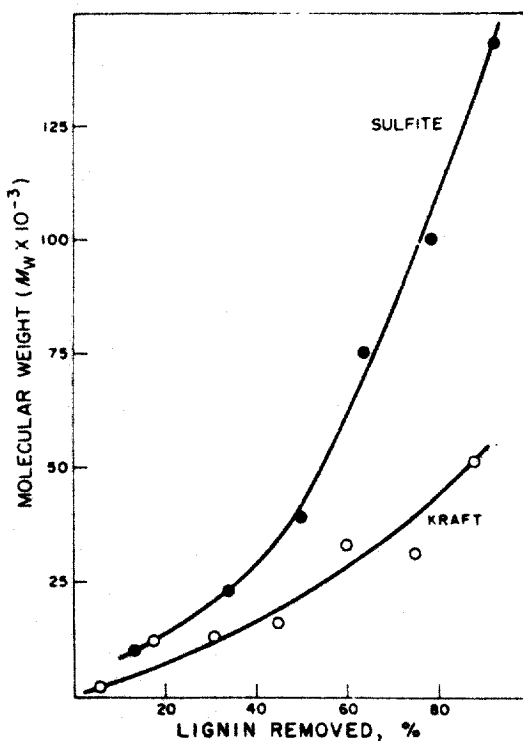


Fig. 2. Comparison of the molecular weights of kraft and sulfite lignins as the delignification proceeds.<sup>2)</sup>

In kraft pulping process, breaking up of lignin macromolecule is achieved by the action of sodium hydroxide and sodium sulfide. The latter chemical plays an important role in promoting dissolution of lignin as shown in Fig. 3.<sup>3)</sup> This effect is interpreted in various ways, and the fact that sodium sulfide promotes cleavage of bond between lignin building stones is shown by a model experiment (Fig. 4)<sup>4)</sup> in which the most abundant bond type in

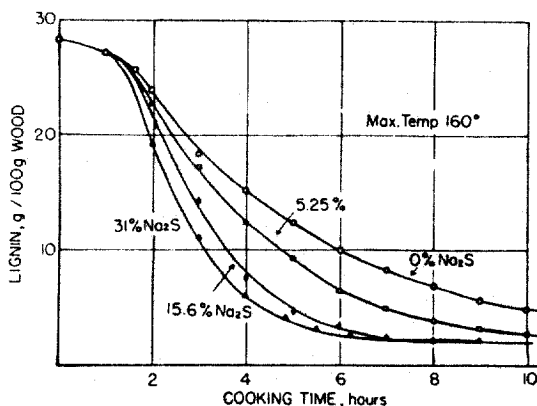


Fig. 3. Effect of sulfidity on delignification.<sup>3)</sup>

lignin - arylglycerol- $\beta$ -aryl ether - is easily cleaved to liberate guaiacol in presence of sodium sulfide, while the bond is hardly cleaved by sodium hydroxide only.

Reaction of  $\beta$ -aryl ether structure ① are summarized in Fig. 5, where ①  $\rightarrow$  ②  $\rightarrow$  ③  $\rightarrow$  ④  $\rightarrow$  ⑤  $\rightarrow$  will be main path way in presence of sodium sulfide, while ①  $\rightarrow$  ⑥ will be the major one in absence of sulfide.

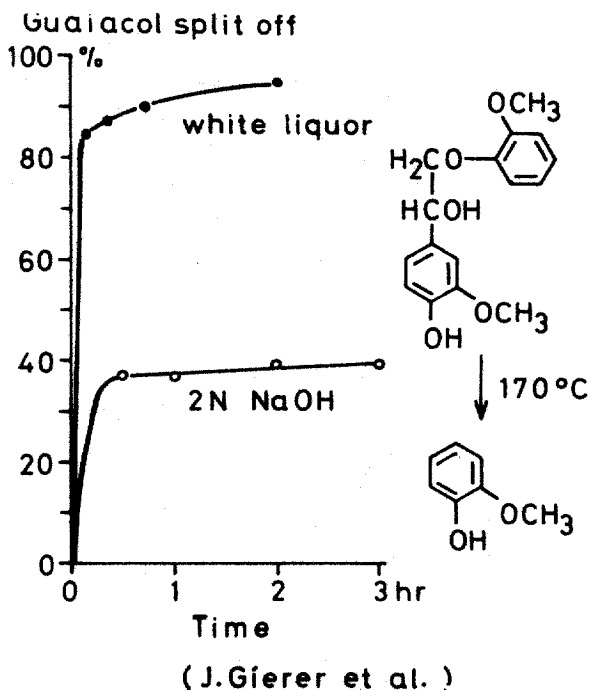


Fig. 4. Effect of sodium sulfide on cleavage of  $\beta$ -aryl ether.<sup>4)</sup>

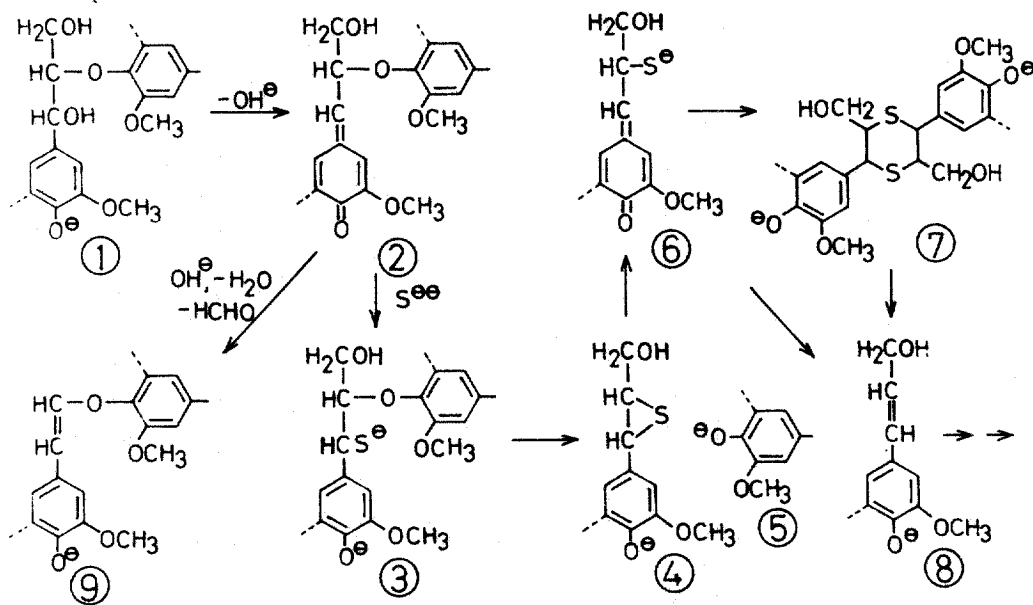


Fig. 5. Reaction of guaiacylglycerol  $\beta$ -aryl ether during soda and kraft pulping.

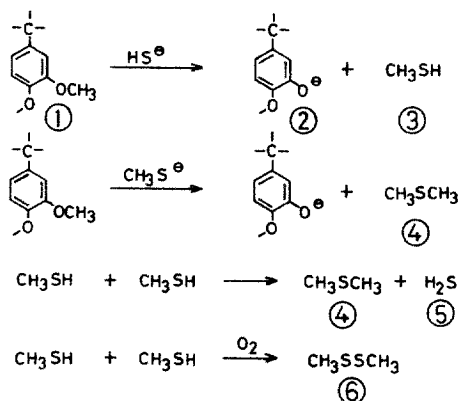


Fig. 6. Reaction of methoxyl group during kraft pulping.

Degradation mechanisms of another structural units have been also investigated. Effects of sulfide are considered to be not only promotion of cleavage of lignin macromolecule but also prevention of recombination of lignin with carbohydrate during the cooking.<sup>5)</sup>

However the use of this excellent chemical, sodium sulfide has serious disadvantages that strongly smelling kraft odor substances such as methylmercaptan and dimethyl sulfide are produced as shown in Fig. 6. To avoid environmental problems due to kraft odor, non-sulfur pulping methods such as oxygen-alkali, anthraquinone-alkali and methanol-alkali pulping methods have been actively investigated.

Kraft pulp and those alkali pulps are generally of excellent quality for paper making except that they are brown colored and resistant to bleaching. As the main part of the coloring materials in pulps are derived from lignin, reaction of lignin during pulping to form chromophoric structure have been intensively studied. Chromophoric structures responsible for the color of lignosulfonic acid have been largely elucidated,<sup>6)</sup> while for kraft lignin only about half of the visible light absorption is explained by known chromophores.

Tracer techniques using radioactive isotope or stable isotope are useful method for investigation of

complicated sequence of lignin reactions during pulping.

When ferulic acid or sinapic acid specifically labelled by <sup>3</sup>H or <sup>14</sup>C are administered to living plant, these lignin precursors are metabolized via the biosynthetic pathway and newly formed lignin is specifically labeled according to the specific labeling of precursors.<sup>7)</sup>

Five kinds of radioactive pine woods were prepared in which lignins were specifically labeled with <sup>14</sup>C at  $\alpha$ -,  $\beta$ -,  $\gamma$ -carbons of side chain, methoxyl or ring carbons respectively. Treatment of the woods under pulping condition and tracing the radioactivity incorporated into dissolved lignin or lignin remaining in pulps afforded useful information on structural changes during pulping.<sup>8)</sup>

Table 1. Relative Incorporation Ratio and Number of Carbon Atoms in Purified Kraft Lignin

	Labeled position				
	$\alpha$	$\beta$	$\gamma$	MeO	Ring
Relative incorporation ratio %	79.4	84.0	69.4	76.2	100.0
Number of carbon atoms per one monomer unit	0.79	0.84	0.69	0.76	6.00

Table 1 shows specific incorporation of side chain carbons, methoxyl carbon and ring carbons into kraft lignin. Methoxyl carbon and  $\gamma$ -carbon are more easily removed than other carbons from lignin macromolecule, and average number of side chain carbon is estimated at 2.32 per 6 ring carbons. Elementary analysis and molecular weight determination affords

Table 2. Molecular Formula of Kraft Lignin

Elementary composition %	C: 62.98	H: 5.81	O: 29.33	S: 1.88
Methoxyl %	13.60			
Mol. weight	1560			
Mol. formula	[C <sub>8.32</sub> H <sub>7.89</sub> O <sub>2.40</sub> S <sub>0.1</sub> (OCH <sub>3</sub> ) <sub>0.76</sub> ] <sub>n</sub>			

molecular formula of kraft lignin as shown in Table 2.<sup>8)</sup>

It was shown from the result of similar experiment on sulfite pulping that the average number of side chain carbon is 2.78 in lignosulfonic acid and change of carbon skeleton in lignosulfonic acid is milder than that in kraft lignin (Table 3).<sup>9)</sup>

Table 3. Molecular Formula of Lignosulfonic Acid

Number of carbon atoms per one monomer unit	Labeled position				
	$\alpha$	$\beta$	$\gamma$	MeO	Ring
	0.89	1.01	0.87	1.01	6.00
Elementary composition %	C: 50.50 O: 39.66 H: 5.16 S: 5.53				
Methoxyl %	12.23				
Size of monomer unit	$C_6 - C_{2.78}$				
Molecular formula	$[C_{8.78}H_{9.14}O_{3.56}(OCH_3)_{0.92}(SO_3H)_{0.41}]_n$				

Table 4. Relative Number of Carbon Atoms in Residual Lignin in Kraft Pulp Prepared under Various Conditions

Cooking condition	Degree of delignification %	Labeled position				
		$\alpha$	$\beta$	$\gamma$	MeO	Ring
No. 1 (0-120°C)	13	89	88	89	79	100
No. 2 (0-170°C)	43	82	80	78	79	100
No. 3 (170°C 1h)	83	77	77	55	81	100
No. 4 (170°C 2h)	91	56	75	38	73	100

Table 4 shows relative number of carbons in lignin remaining in kraft pulp.<sup>10)</sup> Side chain carbon, especially  $\gamma$ -carbon is split off to greater extent with the progress of cooking.

Splitting off of low molecular fragments was examined by radiotracer method.<sup>11)</sup> Fig. 7 shows gas chromatogram of volatile compounds distilled by bubbling nitrogen gas through kraft black liquor. Relative incorporation of radioactivity into these

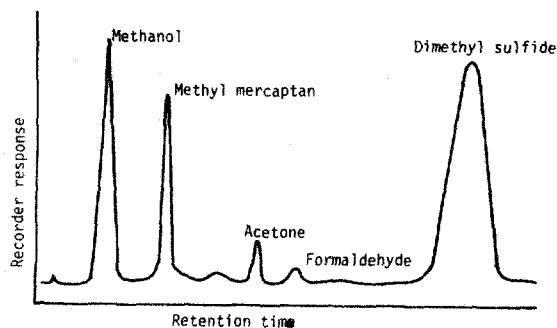


Fig. 7. Gas chromatogram of volatile compounds in black liquor.

Table 5. Corrected Index of Specific Incorporation of Radioactivity\*

Volatile product	$\alpha$	$\beta$	$\gamma$	MeO	Ring
Methyl mercaptan	1	3	2	793	4
Dimethyl sulfide	7	2	1	1334	1
Methanol	1	2	1	40	1
Acetone	10	10	2	1	8
Formaldehyde	12	13	213	1	17

$$*\text{Sp. incorp. ratio} = \frac{\text{sp. activity of product}}{\text{sp. activity of MWL}} \times 100$$

volatile compounds shown in Table 5 indicates that methyl mercaptan, dimethyl sulfide and methanol mainly originate from methoxyl group in lignin. Approximately 90% of total formaldehyde originates from  $\gamma$ -carbon atoms and remaining part originates from  $\alpha$  and  $\beta$ -carbon atoms. The origins of carbon atoms of acetone are combinations of  $\alpha$ -,  $\beta$ - and aromatic ring carbon atoms, or  $\alpha$ -,  $\beta$ - and  $\gamma$ -carbon atoms.

Fig. 8 shows that formaldehyde derived from  $\gamma$ -carbon of side chain plays an important role in recondensation of lignin.<sup>12)</sup> A model compound ① specifically labeled with  $^{14}\text{C}$  at  $\alpha$ -,  $\beta$ - or  $\gamma$ -carbon of side chain were treated under kraft cooking condition. The product was methylated and oxidized to yield acids ② ~ ⑥. High incorporation of radio-

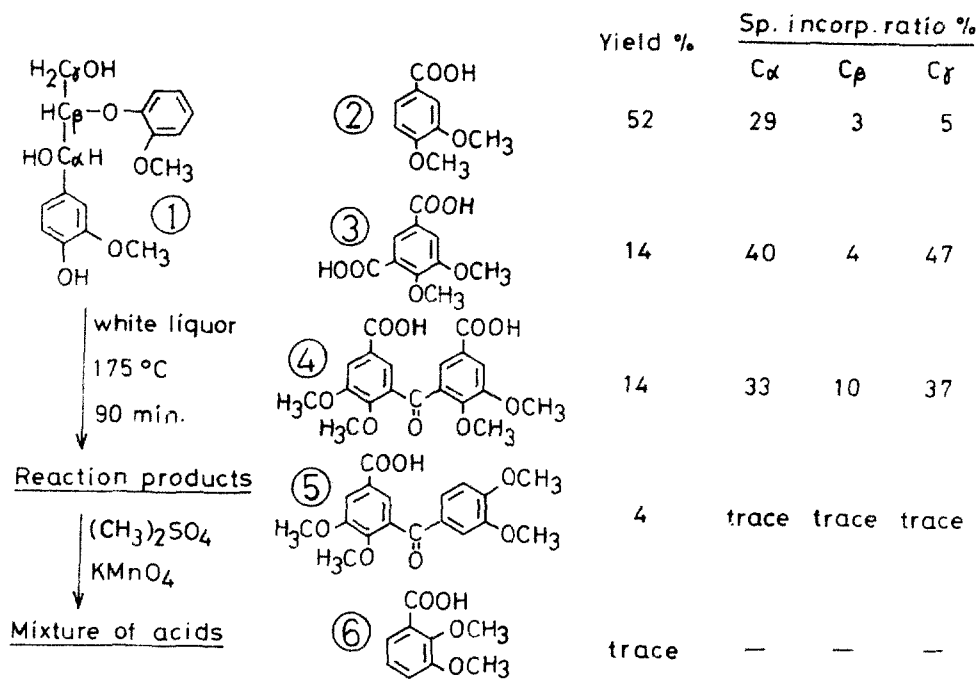


Fig. 8. Behavior of the specific side chain carbon of compound ①

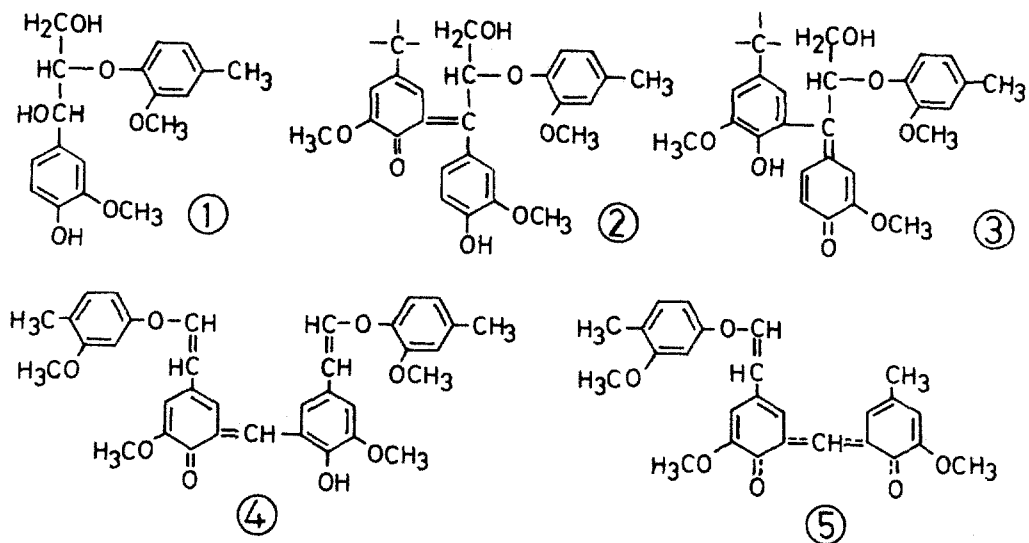


Fig. 9. A representative lignin model compound ① and some chromophoric structures derived from it.

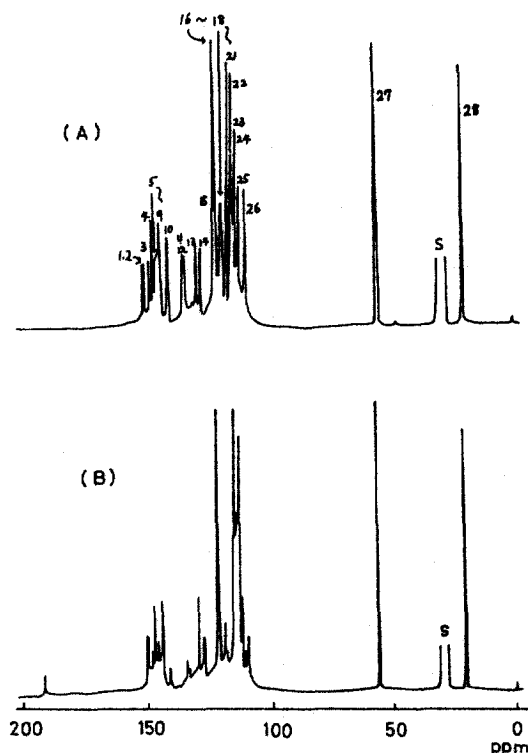


Fig. 10. <sup>13</sup>C-NMR spectra of alkali treated product (A) and its colored oxidation product (B) from compound ① in Fig. 9.

activity into ③ and ④ from  $\gamma$ -<sup>14</sup>C indicates that COOH or C = O is derived from the terminal carbon. Condensation of formaldehyde with lignin fragments to form chromophoric structure has been shown in other experiments.

Labeling with stable isotope at specific position is also useful method for investigation of chromophoric structure.<sup>13) 14)</sup> On treatment on lignin model compound ① (Fig. 9) with hot alkali, followed by air oxidation, many compounds such as ②, ③ ... are formed and <sup>13</sup>C-NMR spectra of the reaction mixtures are very complex (Fig. 10), while on treatment of ① labeled at  $\alpha$ -carbon with <sup>13</sup>C (about 90% <sup>13</sup>C content) gave mixtures whose <sup>13</sup>C-NMR spectra

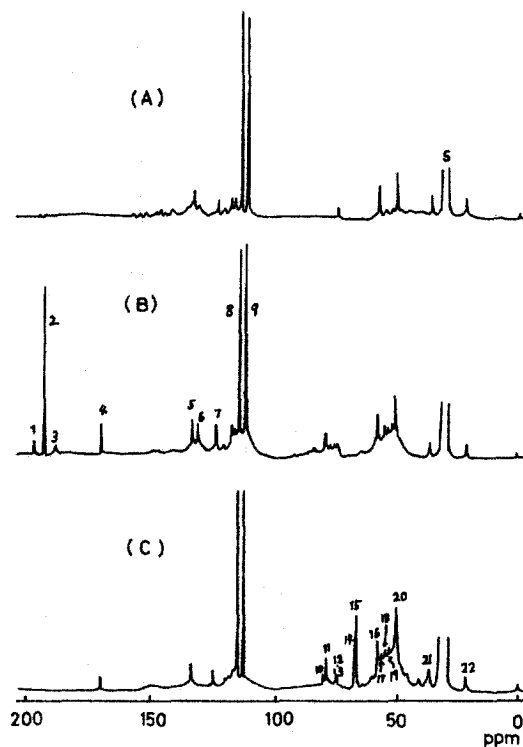


Fig. 11. <sup>13</sup>C-NMR spectra of alkali treated product (A), its colored oxidation product (B) and NaBH<sub>4</sub> reduced product (C) from compound ① labeled by <sup>13</sup>C at  $\alpha$  position of side chain.

(Fig. 11) are very simple to assign the signals<sup>15)</sup> Some chromophoric structures are shown in Fig. 9. Demethylation to afford catechols and *o*-quinones are also important reaction for formation of chromophore, and combination of many types of chromophores may be responsible for brown color of alkali lignin.

The reaction of lignin under pulping condition is thus a very complex one involving degradation and condensation reactions and still open to future investigation. Elucidation of true nature of lignin reaction during pulping will provide a valuable knowledge not only for better pulping method but for more efficient utilization of industrial lignin.

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