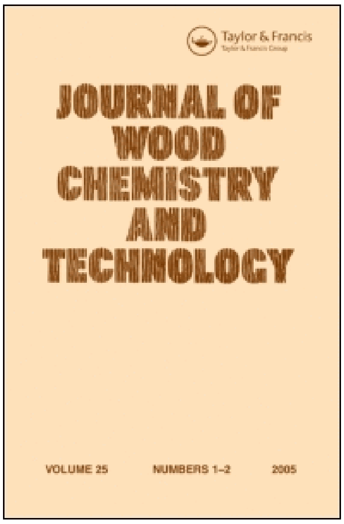

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Košíková, Božena and Mlynár, Juraj(1992) 'Effect of Soda-Additive Pulping on Molecular Characteristics of Residual Pulp Lignin', Journal of Wood Chemistry and Technology, 12: 3, 243 — 259

To link to this Article: DOI: 10.1080/02773819208545233

URL: http://dx.doi.org/10.1080/02773819208545233

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 12(3), 243-259 (1992)

EFFECT OF SODA-ADDITIVE PULPING ON MOLECULAR CHARACTERISTICS OF RESIDUAL PULP LIGNIN

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ABSTRACT

The soda-additive pulps of pine wood were compared to corresponding soda and kraft pulps in respect to the macromolecular properties of the residual pulp lignins. Results of measurements of number and weight-average molecular weights as well as branching parameters show that the presence of additives such as anthraquinone, methanol and O_2-pretreatment significantly causes the breaking of cross-links in the pulp lignin. On the other hand, ethylenediamine and hydrosulfide ion contribute mainly to extensive lignin degradation. The influence of used additives on the condensation reactions of the residual lignin has also been studied.

INTRODUCTION

Soda-additive pulping belongs to prospective sulphur-free cooking processes. The role of additives especially of anthraquinone (AQ) in alkaline cooking has been studied for several years by various authors[1,2]. Anthrahydroquinone (AHQ), which is formed by reactions with wood polysaccharides in the pulping process has been shown by several number workers to promote fragmentation reactions of lignin model compounds[3,4,5].

Although it has been well recognized that lignin in its natural or degraded state is a branched polymer, and that delignification is analogous to degelation where specific linkages are cleaved[6], the lignin macromolecular characteristics have been reported for soda pulping in the presence of additives only to a limited extent[7,8].

The soda pulping and its various modifications was examined with respect to the reactivity of lignin and polysaccharides as well as to the paper properties of pulps in our previous papers[9]. The purpose of the present paper is to characterize the influence of anthrahydroquinone (AHQ), hydrosulfide ion (SH^-), ethylenediamine (EDA), methanol (CH_3OH) and O_2 pretreatment on the macromolecular properties of the residual soda pulp lignins as well as on the extent of condensations reaction.

EXPERIMENTAL

The pulps with yields between 46.0 and 53.8 % and an almost constant residual lignin ($\sim$ 11 %) were prepared from pine chips (Pinus sylvestris L.) in 15 l rotating autoclaves using principally the same conditions as reported earlier[9,10]. The cooking time at 170°C was 90 min, but in the soda-AQ cook 30 min. After the cooks the pulps were washed and then defibrated in a disc refiner with 0.5 mm clearance.

Residual pulp lignins were isolated by 8 h acidolysis (90°C) in dioxane-water (9:1) containing 0.1M HCl[11].

GPC Analysis

The lignin preparations were analysed by gel permeation chromatography (GPC) on a column (53x0.8 cm) of Sephadex LH 60 using a mixture of dioxane and water containing 0.005 M aqueous NaOH and 0.001 M LiCl (7:3) as the eluant[12]. The column was calibrated using a series of lignin fractions the molecular weights of which had been determined by ultracentrifugation[13]. The average molecular weights ($\overline{Mw}$) of the samples were calculated from molecular weight distribution.

Viscosimetric Measurements

Viscosities of dioxane lignins were performed on a viscomatics MS FICA viscosimeter in a Θ solvent (dioxane-ethanol 10: 24.5) according to Pla and Robert[14].

Oxidative Degradation

Lignin samples were subjected to sequential ethylation (Et_2SO_4), depolymerization (CuO/OH^-), methylation (Me_2SO_4) and oxidative degradation by alkaline permangate and subsequently by H_2O_2. Mono- and dimeric degradation products were separated quantitatively by gas chromatography as methyl esters[15].

RESULTS AND DISCUSSION

The soda pulps were subjected to the dioxane-water-HCl extraction with intention to obtain pulp lignin as quantitatively as possible, though in a chemically altered form. Dioxane lignins have been used also in work Pla and Robert[12] in the studies of lignin macromolecular properties.

The lignin fractions obtained by precipitation of the dioxane-water HCl extracts of wood and soda-additive pulps were subjected to elemental and GPC analysis as well as to viscosimetric measurements to determine macromolecular parameters of the residual pulp lignins. The empirical formulas of all lignin preparations are shown in Table 1. The mean molecular weight of the C_9 structural unit was 189.4 ± 1.3.

TABLE 1

Characterization of Soda-Additive Pine Pulp Residual Dioxane Lignins

Pulping method	Yield of dioxane lignin %*	Empirical formula	$\overline{Mw}_{C_9}$
Soda /49.2%/	63.5	$C_9H_{7.24}O_{2.87}/OCH_3/_{0.89}$	188.9
Kraft /50.6%/	54.9	$C_9H_{7.15}O_{3.04}/OCH_3/_{0.88}$	191.3
Soda-AQ /53.8%/	80.0	$C_9H_{7.14}O_{2.89}/OCH_3/_{0.85}$	187.8
Soda-EDA /47.0%/	40.7	$C_9H_{7.48}O_{2.92}/OCH_3/_{0.83}N_{0.29}$	188.1
O_2-Soda /46.0%/	60.0	$C_9H_{7.10}O_{2.93}/OCH_3/_{0.90}$	190.1
Soda-MeOH /49.0%/	71.4	$C_9H_{6.91}O_{3.06}/OCH_3/_{0.81}$	189.1
Pine wood	90.1	$C_9H_{8.19}O_{2.85}/OCH_3/_{0.93}$	190.8

*% based on the pulp residual lignin

A comparison of the dioxane extracted residual lignins from soda-additive pulps and pine wood including average molecular weight $\overline{M}w$, number molecular weight $\overline{M}n$, polydispersity D, molecular weight distribution MWD (Table 2) shows the differences in the molecular characteristics. This means, that although all used soda cooking modification have been equally effective in lignin removal, they affected the macromolecular parameters of the residual lignin to a different extent.

As indicated, the determined $\overline{M}w$, $\overline{M}n$ and D values for all modifications of soda pulping at a given degree of delignification caused a decrease of molecular weight and polydispersity of the residual lignins in the following order:

$$AQ < SH^- < O_2 + NAOH < CH_3OH < EDA.$$

The molecular weight distributions of the lignins under investigation indicates that lignin fragmentation efficiency of AHQ is far below that of the SH^- ion and/or EDA although the same type of delignification reactions are proposed to be involved in the kraft pulping and soda pulping with additives like anthraquinones or amines[1,2]. Similar conclusions were drawn from a study of the molecular weight distribution of lignin fractions dissolved during soda-AQ and kraft pulping of pine wood by Forss et al.[16].

TABLE 2

Some Molecular Parameters of Soda-Additive Pine Pulp Residual Dioxane Lignins

Pulping method	$\overline{Mw}$	$\overline{Mn}$	D	MWD /%/			η /cm^{3}g^{-1}/	ρ
				$< 10^3$	10^3-10^4	$> 10^4$		
Soda /49.2%/	10800	2571	4.2	16.7	62.5	20.8	6.25	0.3614
Kraft /50.6%/	7216	1925	3.7	17,9	66.9	15.2	6.05	0.3382
Soda-AQ /53.8%/	9247	2360	3.9	15.0	68.8	16.4	6.58	0.3033
Soda-EDA /47.0%/	1176	1300	1.4	22.4	76.8	0.8	4.04	0.3149
O_2-Soda /46.0%/	6624	2100	3.1	15.6	71.6	12.8	4.53	0.3264
Soda-MeOH /49.0%/	5213	1760	3.0	18.5	73.8	7.7	5.46	0.3634
Pine wood	5630	2740	2.0	0.4	96.2	3.4	5.27	0.4555

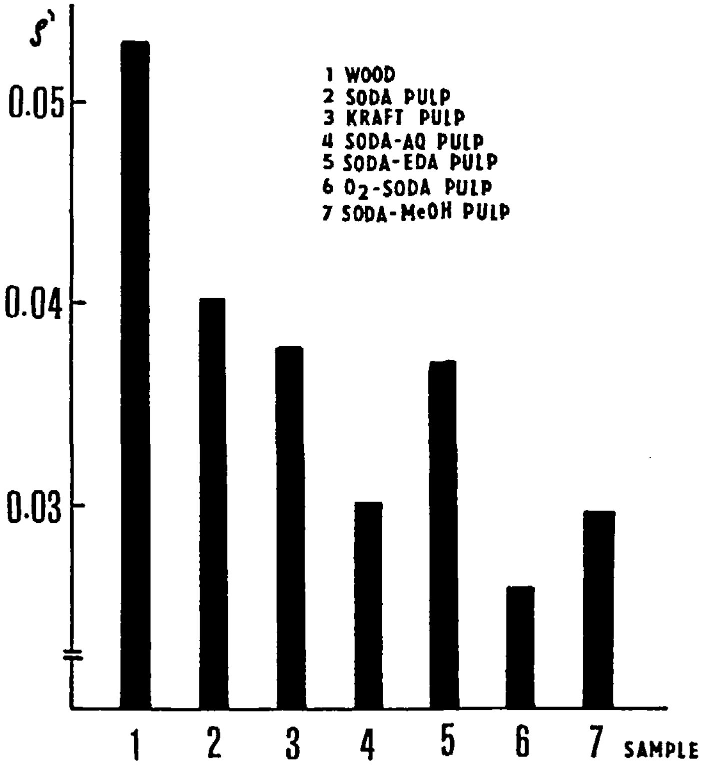


Fig. 1. Cross-linking density of the residual soda-additive pulp dioxane lignins.

As follows from the data in Table 2 and Fig. 1 soda-additive pulping has some effect on the branching characteristics of the residual lignins ϱ and ϱ', e.g. number of trifunctional and tetrafunctional phenylpropane units, respectively. Degree of branching ϱ and cross-linking density ϱ' were calculated according to the equations described by Pla and Robert[14] and Dolk et al.[17]:

$$\rho^{\cdot} = \frac{\bar{n}_w}{\overline{DP}w}$$

$$g_3 = \frac{6}{\bar{n}_w} \cdot \left[\frac{1}{2} \cdot \left(\frac{2+\bar{n}_w}{\bar{n}_w} \right)^{1/2} . \ln \frac{(2+\bar{n}_w)^{1/2}+\bar{n}_w{}^{1/2}}{(2+\bar{n}_w)^{1,2}-\bar{n}_w{}^{1/2}} -1 \right]$$

$\bar{n}_w$ - average number of branching points

$$\rho` = 2\ (1-P'-1/\overline{DP}n)$$

$$p` = (\overline{DP}w-\rho`-1)/(\overline{DP}w+1+\rho`(1+2\ \overline{DP}w))$$

The pulp lignins are significantly less branched and cross-linked in comparison with wood lignin. All modifications of soda pulping reduced cross-linked density of the residual pulp lignins. Mutual differences in this parameter show, in part, the effectiveness of used additives in soda pulping.

The determined molecular characteristics indicate that AHQ improves the selectivity of cooking, probably by reducing the cross-linking density, resulted in "linearization" of lignin without significant degradation of lignin macromolecule into low molecular weight fragments. This conclusion is in agreement with our previous reported experiments concerning the NSSC delignification of beech wood in the presence or absence of oxidized lignin derivative and anthraquinone[18].

Sundquist[19] proposed the differentiated model for residual lignin in unbleached chemical pulp. In this model the cross-linked lignin and the lignin chemically bonded to polysaccharides account for a considerable proportion of the kraft pulp residual lignin (45-75%). In agreement with this fragment model it can be suggested that soda-AQ and soda-CH_3OH pulps which contain relatively low cross-linked lignin are more suitable with respect to bleaching in comparison with other modifications of soda cooking.

In condensation reactions involved in soda pulping, lignin and/or lignin fragments combine to form high molecular weight material containing new types of bonds[7] which may contribute to the reactivity changes of residual pulp lignin. In an attempt to investigate the influence of additives on condensation reaction in soda pulping the condensation factors of the isolated residual lignin were determined by CuO/OH^- degradation according to Glasser[15]. Monomeric and dimeric degradation products were quantitatively determined by integrating individual peaks on the gas chromatographs

TABLE 3

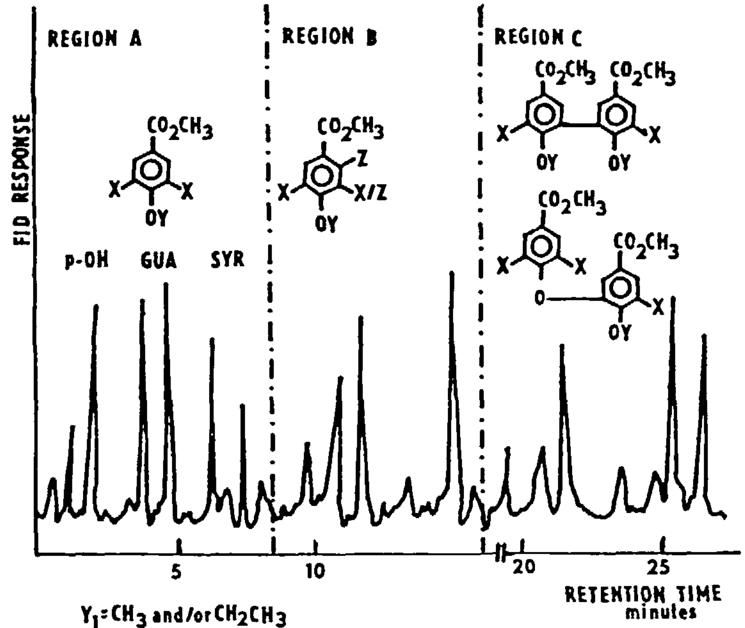
Distibution of Degradation Products Between Monomeric Monocarboxylic Acids /Region A/, Monomeric di- and Multicarboxylic Acids /Region B/ and Dimeric Acids /Region C/ of Soda-Additive Pine Pulp Residual Dioxane Lignin /in % of weight/

Pulping method	Yield*	A	B	C
Soda /49.2%/	71.0	40.8	16.5	42.7
Kraft /50.6%/	56.9	57.6	19.0	23.4
Soda-AQ /53.8/	58.7	60.0	25.5	14.5
Soda-EDA /47.0%/	62.9	76.5	16.9	6.6
O_2-Soda /46.0%/	77.3	42.1	33.1	24.8
Soda-MeOH /49.0%/	76.2	53.8	27.7	18.5
Pine wood	69.4	82.7	5.5	11.8

degradation products yield /% of original lignin sample weight/

of the product mixtures obtained from the dioxane-extracted residual lignins (Table 3). The typical gas chromatogram of lignin permanganate oxidation product mixtures is shown in Fig. 2. The condensation factors were calculated as follows:

$$K_1 = \frac{\sum \text{biphenyl and diaryl structures}}{\sum \text{hydrolyzable alkyl aryl ethers}}$$



$Y_1 = CH_3$ and/or CH_2CH_3
$Y_2 = CH_3$
$Y_3 = CH_2CH_3$
$Y_4 = CH_3$ or CH_2CH_3
$X = H$ or OCH_3
$Z = CO_2CH_3$ or H

$$KF_1 = \frac{\Sigma\, C_{Y_1,X}}{\Sigma\, A_{Y_2,X}} \qquad KF_2 = \frac{\Sigma\, B_{X,Y_1,Z}}{\Sigma\, A_{Y_2,X}}$$

Fig. 2. Typical gas chromatogram of a permangate oxidation product mixture of lignin.

$$K_2 = \frac{\sum \text{alkyl aryl C-C structures}}{\sum \text{hydrolyzable alkyl aryl ethers}}$$

The values obtained (Fig. 3) illustrate the contribution of the individual additives to lignin stabilization towards formation of condensation

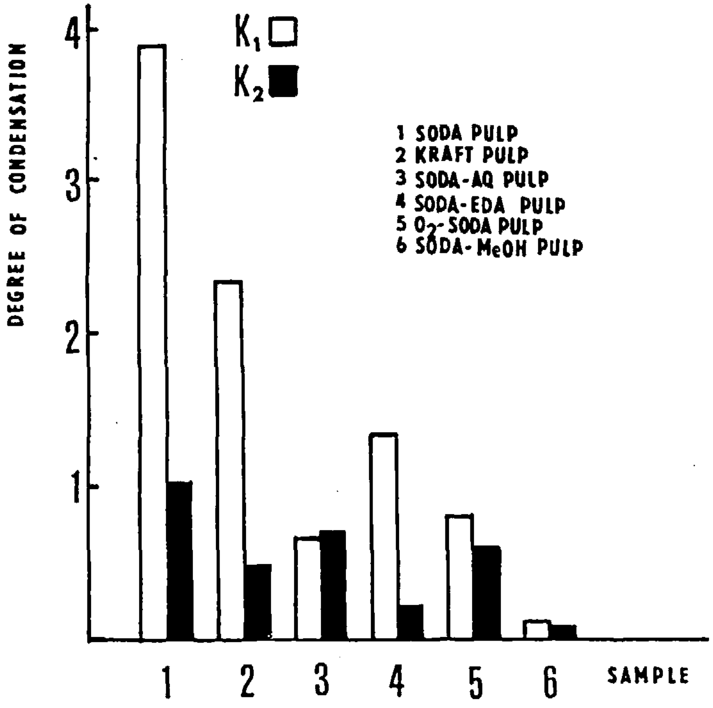
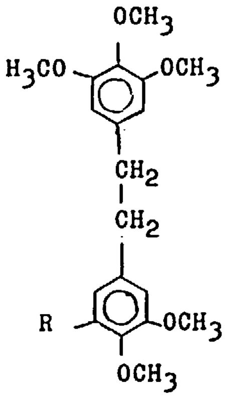


Fig. 3. Condensation factors of the residual soda-additive pulp dioxane lignins.

structures. AHQ and CH_3OH were shown to be the most effective in retarding condensation reactions.

The effect of anthraquinone on lignin stabilization were confirmed also by Bogomolov et al.[20] by the results of electrophoresis, gel chromatographic and polarographic analysis of soda lignins when AQ was added in higher quantity than 0.1% on wood. In contrast, the addition of AQ in kraft pulping contributed to more extensive cleavage of β-aryl ether.

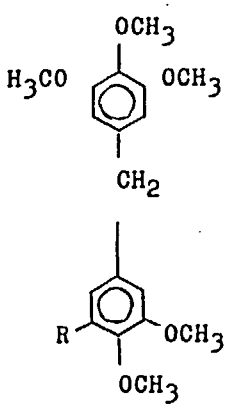
The retardation of vanillyl alcohol and syringyl alcohol condensation reactions in the presence of AHQ was described in our previous study[21]. GPC and GC/MS analysis of reaction products indicated, about 85% conversion of both models to dimers 1 and 2 at the beginning of soda-AQ cook. These structures manifest rather high stability towards further condensation in contrast to diphenylmethane structures 3 and 4 formed in the absence of AHQ. Based on the results obtained in agreement with the observation of Dimmel et al.[7], we assumed that lignin condensation includes the formation of benzyl radicals through quinone methide intermediates which recombine to give dimers 1 and 2.



R = H

R = OCH_3

Structure 1 and 2



R = H

R = OCH_3

Structure 3 and 4

CONCLUSIONS

1. In the investigated series of soda pine pulps, all tested additives contributed to decreases in the weight- and number average molecular weights, polydispersity and cross-linking density of the residual lignins to a different extents.

2. A comparison of the molecular characteristics and condensation factors of soda-additives pulp lignins indicates, that anthrahydroquinone, methanol as well as O_2-pretreatment significantly reduced lignin condensation reactions, while ethylene diamine and hydrogen sulphide ion contributed mainly to extensive lignin degradation in alkaline delignification.

3. The improved selectivity of soda-AQ pulping can be explained by combined effect of anthraquinone on the promotion of breaking lignin cross-links as well as the stabilization of both polysaccharides and lignin, the latter towards condensation.

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