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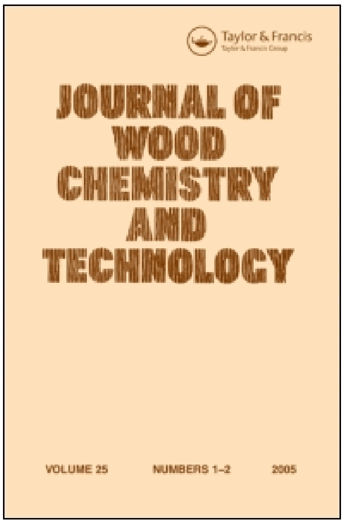

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CHANGES OF MOLECULAR CHARACTERISTICS OF RESIDUAL PULP LIGNIN IN TWO-STEP SODA-OXYGEN PULPING

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ABSTRACT

In order to explain the behavior of soda pulp in the following next oxygen stage, the molecular characteristics of the residual lignins isolated from spruce and pine wood pulps cooked to yields between 71.8 and 49.8% in the soda pretreatment step were examined. The revealed differences in the cross-linking density and degree of condensation correlated with the effectiveness of lignin removal from soda pulps in the oxygen stage.

INTRODUCTION

The concept that lignins exist in wood as polymers with tetrafunctional branching points provides plausible quantitative characteristics of the differences among lignins derived from the various species of wood using the diffferent pulping methods[1,2]. The influence of various additives on the number- and weight-average molecular weights and other related parameters of the residual pulp lignin from soda pulping of pine wood was shown in our previous paper[3].

The soda pulping of wood involves fragmentation reactions causing the dissolving of lignin and also condensation reactions which contribute to difficulties in the removal of residual lignin during pulping[4,5]. It is known that in two-step soda and oxygen pulping the conditions of soda wood pretreatment have a significant influences on the oxygen pulp yield, the bleachability, the brightness and the strength properties of oxygen pulps[6-9].

From the viewpoint of explanation the influence of soda pretreatment in two-stage pulping on delignification by oxygen, the reactivity changes of wood polymers in both pulping steps were studied in our previous paper[10]. A stepwise extraction of a series of pine soda and soda-O_2 pulps in neutral, acid and alkaline medium has been used to determine extractability changes of lignin and polysaccharides during soda-O_2 delignification[10]. The objective of present paper was to identify the differences in molecular characteristics between the residual lignin of soda pulps cooked to different degrees of delignification. Moreover, we describe here our efforts to create a relationship between the macromolecular properties of soda pulp lignin and the effectiveness of lignin removal in the following O_2-NaOH step.

EXPERIMENTAL

A series of pine wood pulps, cooked to yields between 72.2% and 53.9% in the soda pretreatment step and to an almost constant level of yield ($\sim$ 50 %) and residual lignin content ($\sim$ 10%) in the O_2-stage, was prepared using principally the some conditions as reported earlier[10].

Residual pulp lignins were isolated by 8 h acidolysis of pulp in dioxane-water (9:1) containing 0.1 M HCl.

Gel permeation chromatography analysis (GPC), viscosimetric measurements, CuO/OH^- oxidative degradation as well as calculation of macromolecular parameters and condensation factors were described in the preceding paper[3].

RESULTS AND DISCUSSION

To determine the changes of the macromolecular properties of lignin in the first stage of soda-oxygen pulping, the partial delignification of spruce and/or pine was performed under conditions which yielded the soda spruce pulps in 71.6%, 63.5% and 55.5% yields as well as the soda pine pulps in 72.4%, 60.6% and 53.9% yields. The latter were delignified in a second stage by oxygen to about 50% yield on wood. The empirical formulas and mean molecular weight of C_9 structural units of the residual soda and soda-O_2 pulp lignins isolated by acidolysis in dioxane are summarized in Table 1 and Table 2. For all lignin pulp samples the molecular weights, $\overline{Mn}$ and $\overline{Mw}$, and related parameters were determined and are shown in Table 3 and Table 4. In terms of degradation theory the used method of pulp residual lignin isolation is continuing the degelation reaction begun by the alkali. It can be suggested, that this method has constant effect on lignin degradation and that the isolated dioxane lignins are suitable preparations for a relative comparison of the molecular characteristic changes of the residual lignin during pulping.

A comparison of the molecular weight profiles of the spruce wood and pulp dioxane lignins as well as soda lignin precipitated from the corresponding spent liquor (yield of pulp 55.5%) is illustrated on Fig. 1. The residual dioxane pulp lignin has higher molecular weight ($\overline{Mw}$ = 11400) than the wood dioxane lignin ($\overline{Mw}$ = 5200).

TABLE 1

Characterization of Spruce Soda Pulp Residual Dioxane Lignins.

Pulping method	Yield of dioxane lignin %*	Empirical formula	$\overline{Mw}_{C_9}$
Soda /71.6%/	61.2	$C_9H_{7.57}O_{2.77}/OCH_3/_{0.82}$	185.4
Soda /63.5%/	69.3	$C_9H_{7.20}O_{2.77}/OCH_3/_{0.89}$	187.2
Soda /55.5%/	77.0	$C_9H_{7.20}O_{3.16}/OCH_3/_{0.60}$	184.5
Spruce wood	90.7	$C_9H_{7.50}O_{3.02}/OCH_3/_{0.84}$	191.6

*% based on the pulp residual lignin

TABLE 2

Characterization of Pine Soda Pulp Residual Dioxane Lignins

Pulping method	Yield of dioxane lignin %*	Empirical formula	$\overline{Mw}_{C_9}$
Soda /72.4%/	83.0	$C_9H_{7.26}O_{2.82}/OCH_3/_{0.86}$	187.3
Soda /60.6%/	63.7	$C_9H_{7.44}O_{3.03}/OCH_3/_{0.82}$	189.5
Soda /53.9%/	75.6	$C_9H_{8.31}O_{2.65}/OCH_3/_{0.73}$	181.5
O_2-Soda /49.8%/	74.0	$C_9H_{7.71}O_{3.13}/OCH_3/_{0.99}$	196.5
O_2-Soda /49.5%/	78.2	$C_9H_{7.75}O_{3.25}/OCH_3/_{0.70}$	189.6
O_2-Soda /50.2%/	89.7	$C_9H_{7.47}O_{3.15}/OCH_3/_{0.74}$	189.0
Pine wood	90.2	$C_9H_{8.19}O_{2.85}/OCH_3/_{0.93}$	190.9

*% based on the pulp residual lignin

TABLE 3

Some Molecular Parameters of Spruce Soda Pulp Residual Dioxane Lignins

Pulping method	$\overline{Mw}$	$\overline{Mn}$	D	MWD /%/			η /cm^3g^{-1}/	ρ
				$< 10^3$	10^3-10^4	$> 10^4$		
Soda /71.6%/	5964	2550	2.3	7.9	85.4	6.8	5.40	0.3981
Soda /63.5%/	7093	2742	2.6	7.0	81.7	11.3	5.74	0.3353
Soda /55.5%/	11402	3150	3.6	9.3	71.9	19.1	6.66	0.4536
Spruce wood	5260	2840	1.85	2.1	89.6	8.3	5.20	0.4265

TABLE 4

Some Molecular Parameters of Pine Soda and Soda-O_2 Pulp Residual Dioxane Lignins

Pulping method	$\overline{Mw}$	$\overline{Mn}$	D	MWD /%/			η /cm^3g^{-1}/	ρ
				$< 10^3$	10^3-10^4	$> 10^4$		
Soda /72.4%/	7202	1726	4.2	21.7	65.3	13.0	5.71	0.4127
Soda /60.6%/	9219	2068	4.4	12.2	61.9	25.9	6.16	0.3874
Soda /53.9%/	10800	2571	4.2	16.7	62.5	20.5	6.25	0.3614
Soda-O_2 /49.8%/	8922	2500	3.6	10.2	73.1	16.7	6.72	0.3557
Soda-O_2 /49.5%/	8972	2514	3.6	12.9	64.4	22.7	6.36	0.3381
Soda-O_2 /50.2%/	7278	2030	3.6	16.1	68.2	15.7	6.02	0.3431
Pine wood	5630	2740	2.0	0.4	96.2	3.4	5.27	0.4555

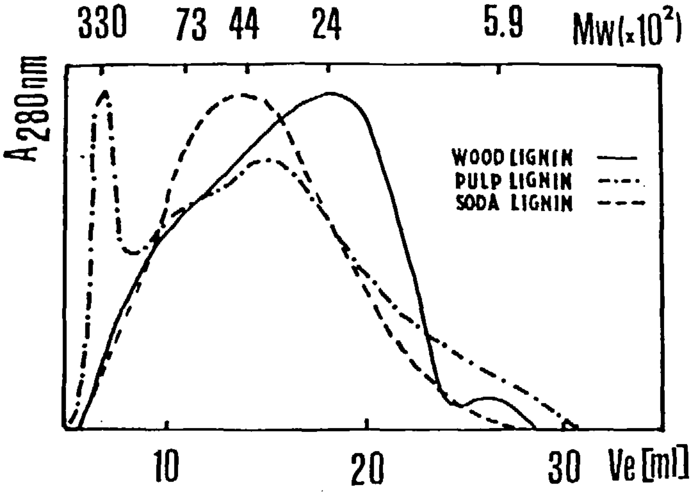

Fig. 1. The molecular weight distribution changes of in soda pulping of spruce wood.

The soda lignin ($\overline{Mw}$ = 5700) was considerably more degraded compared to the residual lignin.

As can be seen in Table 3, the lower yield of pulp, the more high-molecular weight lignin fraction ($\overline{Mw}$> 10000) is obtained by dioxane/water/HCl extraction of the pulps. This fact results in increasing the molecular weights Mw and Mn and polydispersity D with increasing degrees of delignification. In contrast, the degree of branching and cross-linking density, ρ, ρ', decreases as delignification proceeds (Fig. 2). The molecular characteristics soda pine pulp lignins (Table 4, Fig. 2) show the same tendency.

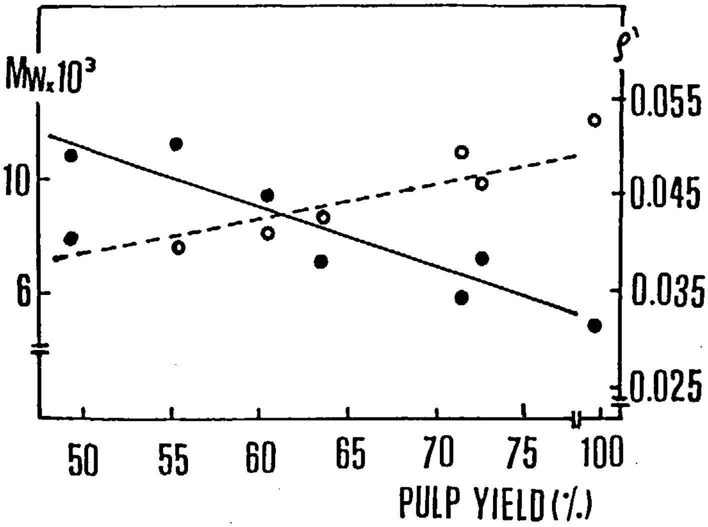

Fig. 2. Cross-linking density of the residual soda and soda-oxygen pulps lignins (ρ').

Summarizing of the $\overline{Mw}$ and ρ' values calculated for both spruce and pine soda pulp lignins in Fig. 3 shows the negative correlation of soda pulp yields with average molecular weight, $\overline{Mw}$, and positive correlation with cross-linking density, ρ' .

To explain the reactions leading to the increase of molecular weight of residual lignin during soda pulping, the condensation factors K_1 and K_2 of all investigated lignin preparations were evaluated, K_1 is defined as the ratio of biphenyl and diaryl structures to hydrolyzable alkyl ethers, K_2 is the ratio of alkyl aryl C-C structures to hydrolyzable alkyl aryl ethers[3]. The

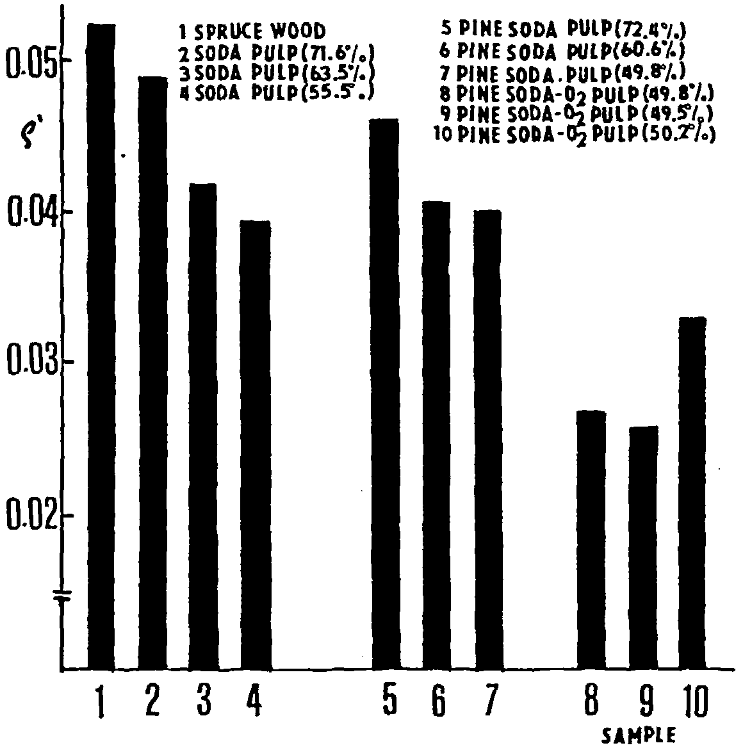

Fig. 3. The average molecular weight ($\overline{M}w$) and cross-linking density (ϱ') as a function of soda pulp yield.

values obtained (Table 5 and Table 6, Fig. 4 and Fig. 5) indicate that the alkaline partial delignification of both soft woods is accompanied with formation of alkyl aryl C-C linkages as well as diaryl and biphenyl structures in lignin remained in the pulps. Their content increases with decreasing of soda pulp yield.

TABLE 5

Distribution of Degradation Products Between Monomeric Monocarboxylic Acids /Region A/, Monomeric di- and Multicarboxylic Acids /Region B/ and Dimeric Acids /Region C/ of Soda Spruce Pulp Residual Dioxane Lignins /in % of weight/

Pulping method	Yield*	A	B	C
Soda /71.6%/	54.5	59.7	15.9	24.4
Soda /63.5%/	62.6	57.1	16.8	26.1
Soda /55.5%/	72.2	42.3	18.4	39.3
Spruce wood	87.1	79.1	12.0	8.9

*degradation products yield /% of original lignin sample weight/

TABLE 6

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

Pulping method	Yield*	A	B	C
Soda /72.4%/	82.8	51.6	16.3	32.1
Soda /60.6%/	71.4	44.3	16.6	39.1
Soda /53.9%/	71.0	40.8	16.5	42.7
Soda-O_2 /49.8%/	68.2	59.9	18.1	22.0
Soda-O_2 /49.5%/	59.6	50.3	26.8	22.9
Soda-O_2 /50.2%/	64.7	61.8	24.5	13.7
Pine wood	69.4	82.7	5.5	11.8

*degradation products yield /% of original lignin ple weight/

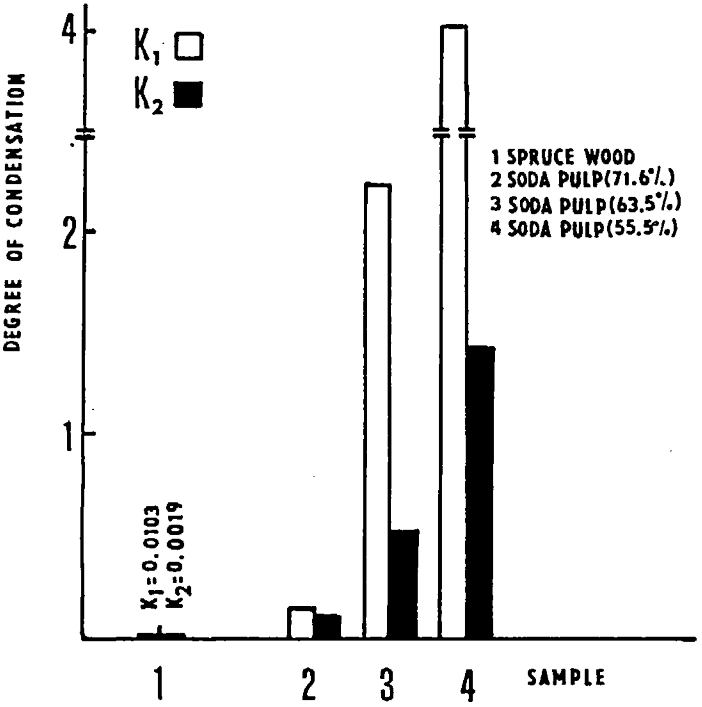

Fig. 4 Condensation factors of dioxane wood lignins and soda pulp spruce residual lignins.

The observed differences of the pulp lignin condensation factors, in comparison with those of the native wood, were substantial. A significant higher degree of condensation of the pulp lignin is in agreement with the determined lignin reactivity changes in alkaline pulping described in our previous paper[11].

The revealed correlations between some molecular parameters and soda pulp yield allow the suggestion that

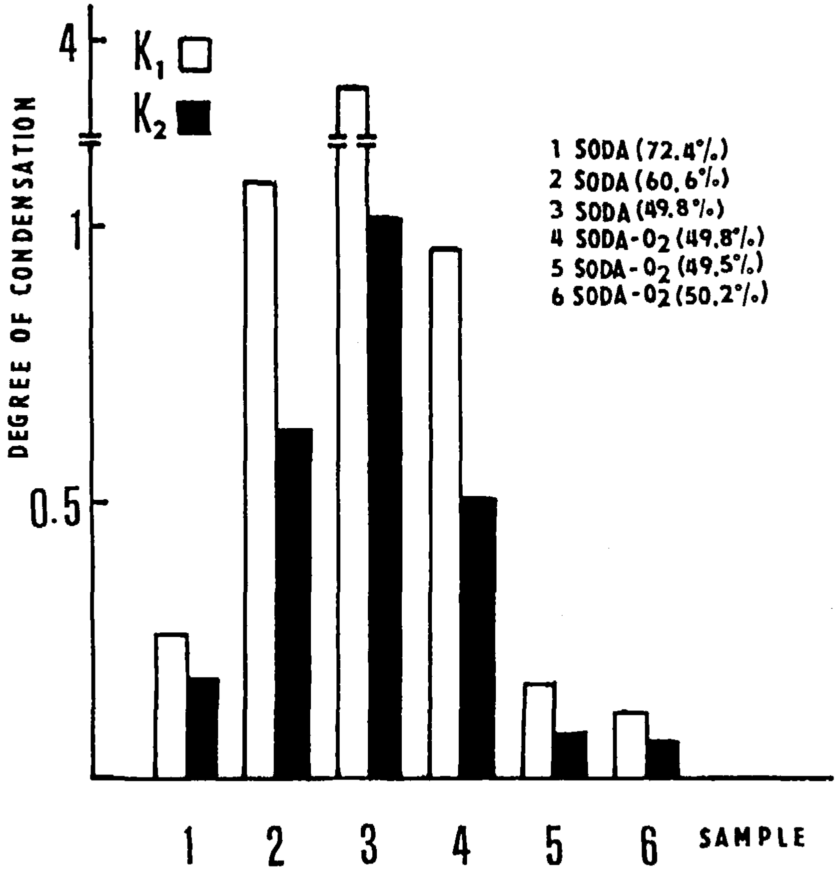

Fig. 5. Condensation factors of the residual soda and O_2-soda pulp pine lignins.

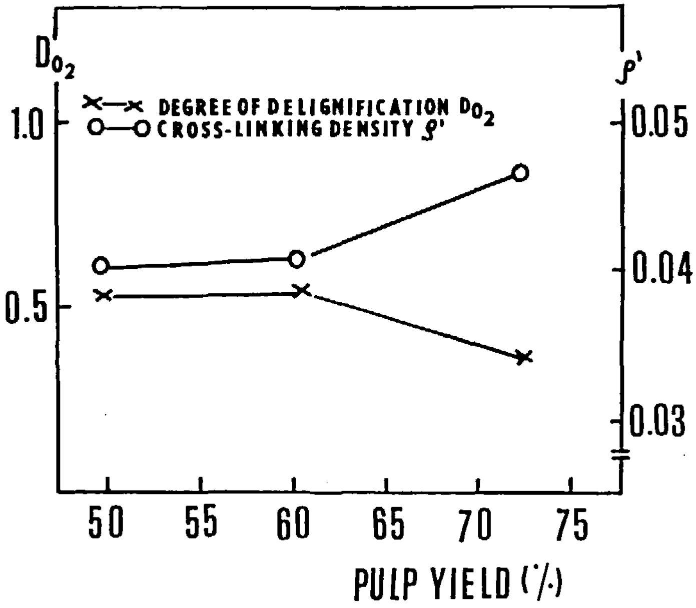

Fig. 6. Degree O_2-delignification (DO_2) and cross-linking density (ρ') of the residual lignins as a function of soda pine pulp yield.

lignin present in the soda pulps cooked to 60-65% yield has the optimal macromolecular properties with respect to its removal in the following oxygen treatment.

This suggestion is in accord with the behaviour of soda pine pulps under investigation in the following constant oxygen stage (49%) described in our previous paper[10]. Degree of O_2-delignification as a function of soda pulp yield is illustrated in Fig. 6. It is evident, that soda pulp corresponding to yield over 70% has the lowest degree of delignification and the highest degree of cross-linking density. From 70 to 60% yield the degree of delignification increases and then remains almost constant level between 60 and 48% yields. The progressive nature of this phenomenon can be explained in the terms of the progressive changes of cross-linking density, ρ', of the soda pulp lignin with the decreasing pulp yield. A decrease of ρ' was observed in the case of soda pulp prepared in 60.6% yield. This value was changed negligibly in soda pulping to lower yield (53.9%). The results obtained indicate that O_2-delignification in second stage is affected by extent to which lignin cross-links are broken in soda pretreatment.

The molecular characteristics of lignins isolated from the soda-oxygen pulps (Tab. 4, Fig. 2) indicate that oxygen treatment causes a considerable decrease of the cross-linking density ρ without significantly decreasing of molecular weight Mw and degree of branching ς . The quantitative changes of the condensation factors of pulp lignin in the oxygen step of cooking (Fig. 5) show very effective degradation of condensed structures in soda pulp lignin. This observation is in agreement with the theory of O_2-NaOH pulping proposed by Gierer[12]. O_2-oxygen pulps prepared from lower yield soda pulp ($<$ 60) can be expected suitable for bleaching due to their low values of condensation factors.

CONCLUSIONS

1. The determined macromolecular parameters including weight- and number average molecular weights, $\overline{Mw}$ and $\overline{Mn}$, molecular weight distribution MWD, polydispersity D, degree of branching ρ and cross-linking ρ' density provide a useful basis for characterization of the nature of changes introduced in the residual lignin as a result of the alkali-pretreatment conditions with the respect to its case of removal in the next stage of soda oxygen pulping.

2. The condensation factors allowed quantification of the extent of condensation reactions which accompanied degradation of lignin in soda-oxygen pulping.

3. The correlation between the effectiveness of lignin removal from soda pulps in oxygen pulping and the extent of splitting of residual lignin cross-links in soda pretreatment of pine wood was revealed.

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