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**ALKALINE OXYGEN OXIDATION OF DIOXANE LIGNIN AND
CREOSOL IN AQUEOUS ETHANOL**

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ABSTRACT

The degradation of dioxane lignin with oxygen in alkaline aqueous ethanol was studied. An increase in the ethanol concentration resulted in an accelerated degradation of lignin. Separate experiments with creosol (2-methoxy-4-methylphenol) indicated that this effect can at least partly be ascribed to the inhibition of the coupling of phenoxy radicals, which prevents the recondensation of the lignin fragments.

INTRODUCTION

It has been shown that the rate of alkaline delignification of pine wood increases markedly

if the chips are first pretreated under mild conditions with oxygen in alkaline aqueous alcohol¹. Further studies have shown that lignin is to some extent degraded and the content of hydrophilic groups is increased^{2,3}. In this paper further attempts are made to explain the effect of alcohol on the degradation and oxidation of lignin. To avoid the complexity caused by physical and morphological factors such as the diffusion of oxygen into the wood structure, the experiments were carried out with dioxane lignin and with creosol (2-methoxy- 4-methylphenol).

RESULTS AND DISCUSSION

Table 1 shows the data obtained for the molecular weight distribution of dioxane lignin after 2 hours'

TABLE 1

Molecular Weight Distributions of Dioxane Lignin Samples After Two Hours of Oxygen Oxidation in Alkaline Liquors Containing Various Amounts of Ethanol.

Sample	Ethanol, % w/w	M >			
		10 000	5 000	3 000	1 000
DL	-	14	36	51	80
DLOX-0	0	14	36	49	76
DLOX-20	20	11	30	43	72
DLOX-50	50	9	26	39	69
DLOX-80	80	7	24	36	65

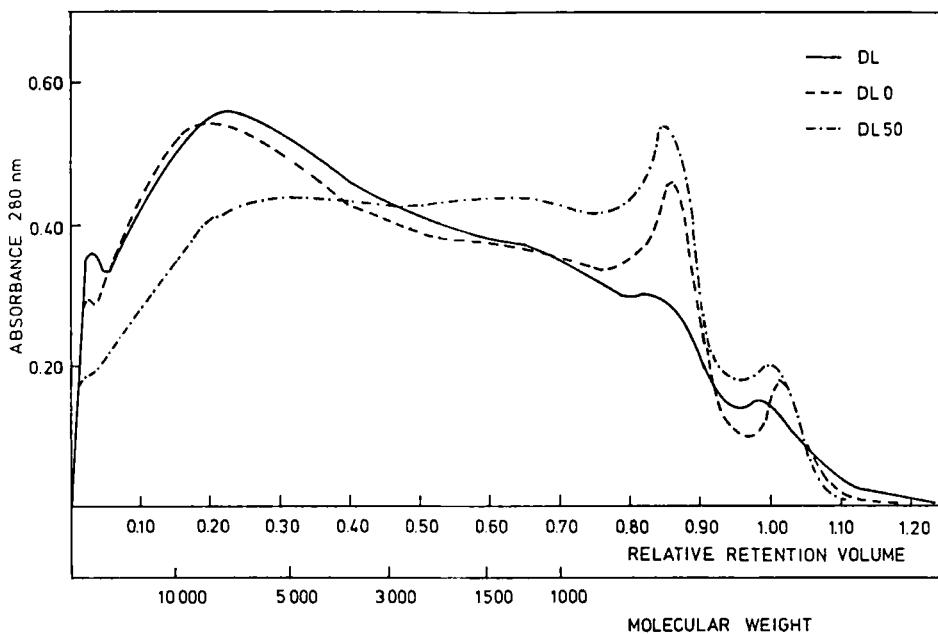


FIGURE 1. Gel permeation chromatogram (Sephadex G-50, 0.5 M NaOH) of the untreated dioxane lignin (DL), and the dioxane lignin sample after 2 hours of oxygen treatment (700 kPa, 60°C) in 0.2 M NaOH, containing 0 (DL-0) or 50 % (w/w) ethanol (DL-50).

treatment at various ethanol concentrations and Fig. 1 gives an example of the molecular weight distribution curve for two of the cases (pure water and 50 % ethanol-water solution). A further illustration is given in Fig. 2, in which the average molecular weight is plotted against the ethanol concentration in the oxidation solution. The results clearly show that the degradation of lignin accelerated markedly with

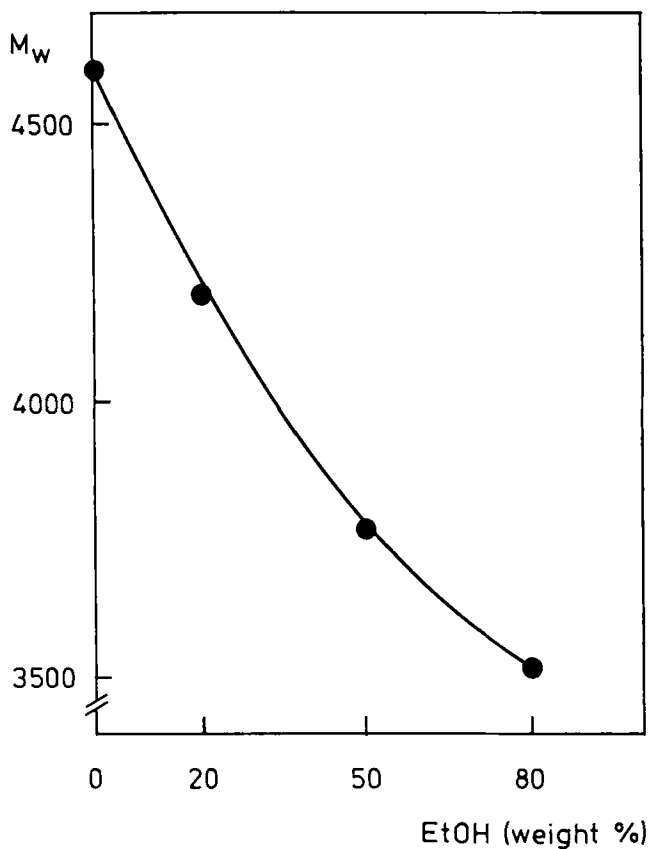


FIGURE 2. The calculated average molecular weight (M_w) of dioxane lignin after oxygen treatment in alkaline aqueous ethanol (0.2 M NaOH, O_2 pressure 700 kPa, 60°C , 2 hours).

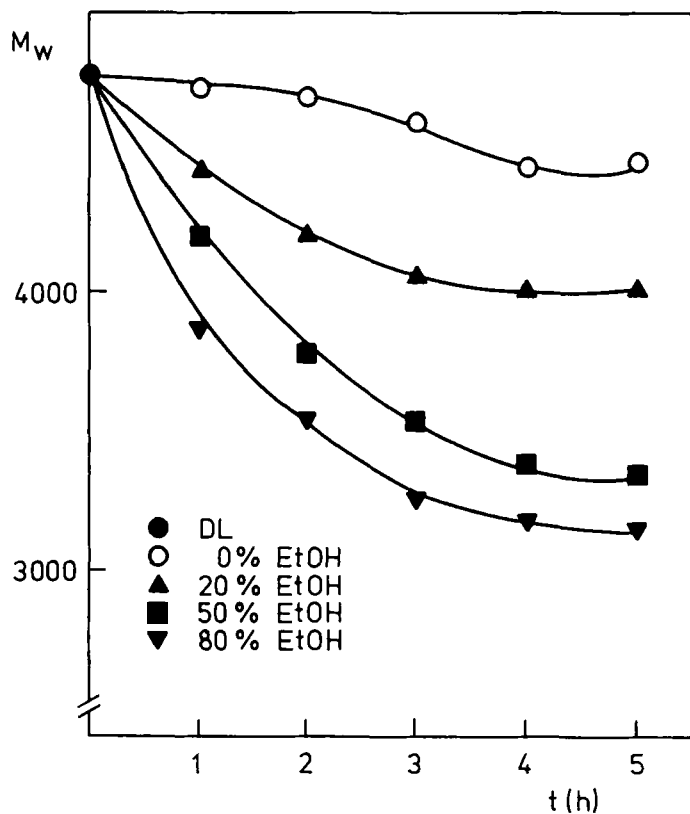


FIGURE 3. The calculated average molecular weight of oxidized dioxane lignin (M_w) as a function of treatment time. For treatment conditions, see Figure 3.

increasing ethanol concentration. When the reaction time was increased to five hours the lignin degradation practically levelled off (Fig. 3). This cannot be due to lack of alkali⁴, because an excess of it was charged.

Some preliminary experiments were made using ultraviolet ionization difference absorption spectra to

study the effect of ethanol on the generation of phenolic hydroxyl groups and α -carbonyl groups in the dioxane lignin during oxidation. The differential absorbance at 300 nm, reflecting the content of unconjugated phenolic hydroxyl groups, first decreased for all the oxidized dioxane lignin samples, but later increased to reach a maximum that was close to the initial value. However, the rate at which the maximum was reached was dependent on the ethanol concentration in the solution. The behaviour of the 350 nm differential absorbance, which is associated with the content of α -carbonyl groups conjugated with free phenolic hydroxyl groups, did not show any clear correlation with the ethanol concentration in the solution.

In the oxidation of lignin, ethanol seems either to influence the degradation of less reactive lignin units^{5,6} or, more likely, to retard the polymerization reactions^{7,8}. In order to clarify the latter possibility, a simple monomeric model compound, creosol, which is known to undergo coupling during alkaline autoxidation^{9,10}, was oxidized using various ethanol concentrations. Samples of the reaction mixture were withdrawn after specified times and analysed for the starting material and for the corresponding dimeric coupling products using ultraviolet difference spectroscopy and gas chromatography. As can be seen from Fig. 4, the stability of creosol towards alkaline

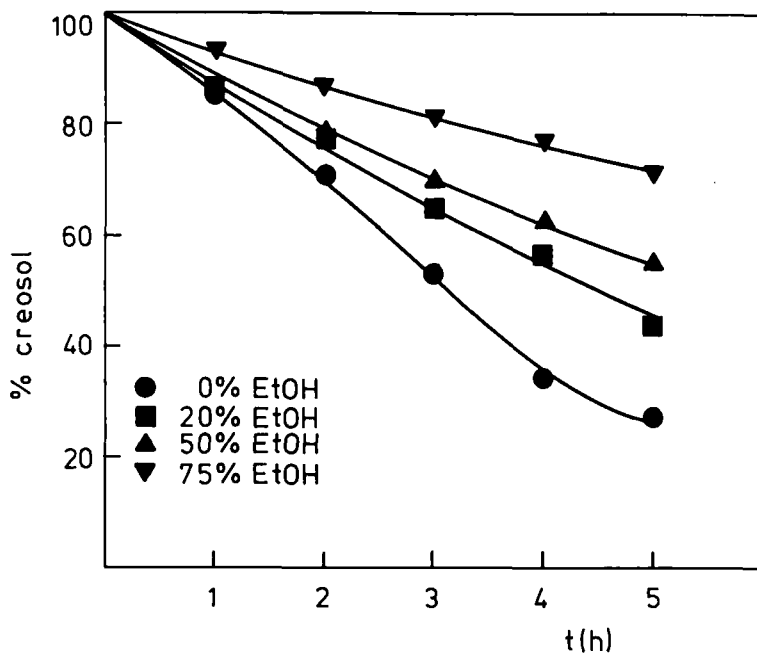


FIGURE 4. The disappearance of creosol during oxygen treatment (0.2 M NaOH, 200 kPa O_2 , 60°C).

oxygen oxidation increased with increasing ethanol concentration. Simultaneously, the tendency for 5-5 coupling decreased with increasing ethanol concentration (Fig. 5). One explanation is that the radicals possibly formed from ethanol in this system participate in the coupling reactions with phenoxy radicals, causing a decrease in the formation of dimers.

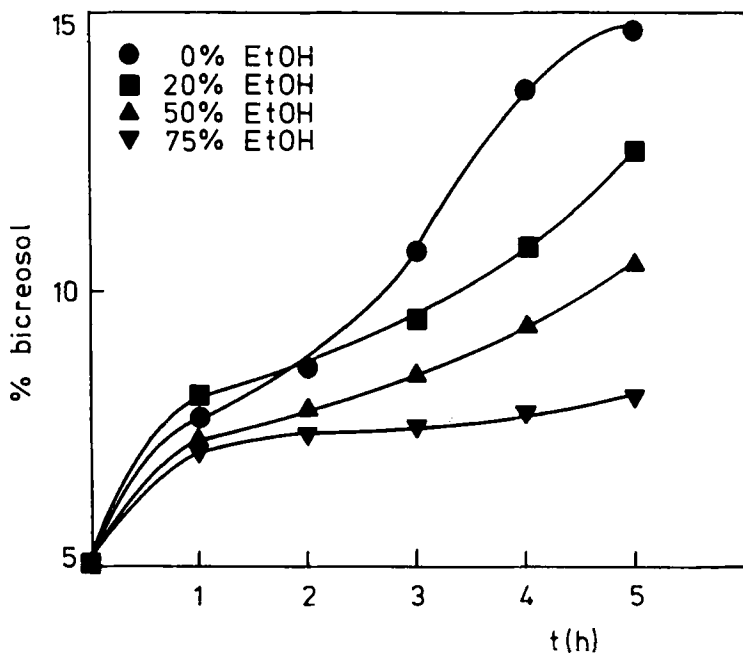


FIGURE 5. The formation of bicrosol during alkaline oxygen treatment (0.2 M NaOH, 200 kPa O₂, 60°C) of creosol.

CONCLUSIONS

The presence of an organic solvent (ethanol) in the solution used for mild oxygen-alkali treatment of dioxane lignin facilitates its depolymerization as shown by the measurements of the molecular weight distributions. One explanation for this is that the solvent retards the oxidative coupling reactions and in this way inhibits repolymerization of the lignin fragments. Although many questions still remain

unanswered, the observations made in this study partly explain why the conditions used are beneficial in the pretreatment of wood prior to alkaline pulping.

EXPERIMENTAL

Materials

Wood meal, made from Scots pine (Pinus sylvestris) was first extracted in a Soxhlet thimble for 48 hours with acetone. Dioxane lignin was then prepared from the extractive-free wood according to the method described by Rezanowich et al.¹¹.

Creosol (2-methoxy-4-methylphenol) was a commercial sample obtained from Ventron and it was shown by gas chromatography to be pure (as its TMS derivative). The dimer 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-methylbiphenyl (bicrosol) was prepared through oxidative coupling of creosol with potassium ferricyanide according to the procedure described by Haynes et al.¹².

Oxidation of Dioxane Lignin

Oxidation of dioxane lignin was carried out in a 500 mL teflon-lined autoclave equipped with a stirrer

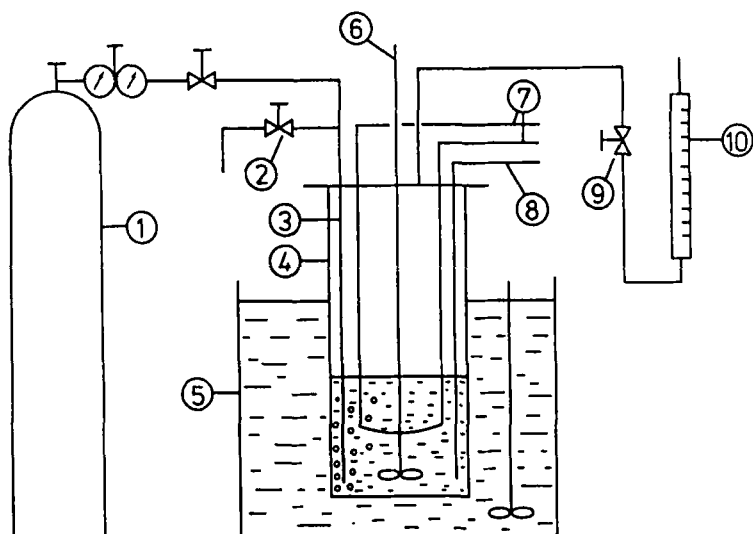


FIGURE 6. Treatment and sampling system. 1. Oxygen cylinder, 2. sampling valve, 3. oxygen inlet tube/sampling tube, 4. PTFE-lined autoclave, 5. thermostated water bath, 6. stirrer, 7. cooling/heating coil, 8. thermocouple for temperature measurements, 9. oxygen outlet valve, 10. rotameter.

and a sampling system as shown in Fig. 6. The reactor, containing 180 mL of 0.2 M NaOH in aqueous ethanol (the concentration of ethanol was varied), was thermostated to 60°C after which the dioxane lignin sample (200 mg) dissolved in the same alkaline solution (20 mL) was introduced. The reactor was closed and oxygen was bubbled through the solution for 2 minutes (8 mL/min). The oxygen pressure was then adjusted to 700 kPa and the oxygen flow to 1 mL/min. The reaction mixture was

stirred at constant speed (800 r/min). Samples withdrawn from the reaction mixture were analysed immediately or stored after neutralization with 0.2 M H_2SO_4 under nitrogen in a refrigerator.

Gel Filtration

After oxidation the ethanol was evaporated from the sample solutions in a Rotavapor. For gel filtration a column, 150 cm x 1 cm (i.d.), filled with Sephadex G-50 was used. The samples (0.5 mg dissolved in 0.5 M NaOH) were introduced to the top of the column and eluted with 0.5 M NaOH. The fractionation was monitored with a UV-detector at 280 nm. Calibration was carried out according to Forss et al.¹³.

Ultraviolet Characterization of the Oxidized Dioxane Lignin

The content of unconjugated free phenolic hydroxyl groups in the dioxane lignin after oxidation was determined from the absorption maximum at 300 nm in the ionization difference spectra¹⁴. The content of α -carbonyl groups was estimated from the maximum absorbance at 350 nm¹⁵.

Oxidation of Creosol

The alkaline reaction solution, 0.2 M NaOH (20 mL) in aqueous ethanol (the concentration of ethanol was

varied), was placed in vials sealed with septa. The air was removed by evacuation and replaced with oxygen (200 kPa). After thermostating to 60°C, 310 μ L of creosol solution was introduced by injection. The vial was shaken for 10 seconds, after which a sample was withdrawn for determination of the initial creosol concentration. The vials were agitated with magnetic stirrers. Each sample withdrawn from the vial was diluted (1:250) with buffer solutions to pH 3 and 13. These solutions were used to determine the UV ionization difference spectra. Above 280 nm, these spectra were composites of that of creosol (max. $\epsilon_{298} = 3683 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ and $\epsilon_{315} = 0 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$) and that of its biphenyl dimer (max. $\epsilon_{298} = 1846 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$ and $\epsilon_{315} = 6806 \text{ L}\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$). Thus, the concentrations of the two components could be determined. The degradation of creosol and the formation of bicrosols were also studied by gas chromatography of their TMS derivatives using the TMS ether of syringol as internal standard. The gas chromatographic analyses were carried out with a Hewlett Packard 5880 A instrument equipped with a fused-silica capillary column, OV-101 (25 m * 0.32 mm i.d.) and a flame-ionization detector. The temperature program was 2 min at 100°C, 20°C/min to 230°C, and 20 min at 230°C. The temperature of both the injection port and the detector was 260°C. Hydrogen was used as carrier gas at a flow rate of 2 mL/min and the split ratio was 20:1.

REFERENCES

1. Hagström, C. and E. Sjöström, J. Wood Chem. Technol. 2 (4), 431 (1982).

2. Hagström-Näsi, C. and E. Sjöström, *Holzforschung* 40 (Suppl.), 133 (1986).
3. Hagström-Näsi, C. and E. Sjöström, *Holzforschung*, 41 (1), 39 (1987).
4. Gratzl, J. S., H.-M. Chang and W. T. McKean, The 4th Canadian Wood Chem. Symp. Quebec, July 4-6, 1973, 63.
5. Reeves, R. H. and I. A. Pearl, *Tappi* 48 (2), 121 (1965).
6. Bailey, C. W. and C. W. Dence, *Tappi* 52, 491 (1969).
7. Clare, S. I. and C. Steelink, *Tappi* 56, 119 (1973).
8. Katuscak, S., K. Horsky and M. Mahdalik, *Paperi ja Puu* 53, 197 (1971).
9. Kratzl, K., J. Gratzl and P. Claus, *Adv. Chem. Series* 59, 157 (1966).
10. Kratzl, K., P. Claus, W. Lonsky and J. Gratzl, *Wood Sci. Technol.* 8, 35 (1974).
11. Rezanowich, A., W. Q. Yean and D. A. I. Goring, *Svensk Papperstid.* 66, 141 (1963).
12. Haynes, G. G., A. H. Turner and W. A. Waters, *J. Chem. Soc.*, 2823 (1956).
13. Forss, K. G., B. G. Stenlund and P.-E. Sångfors, *Appl. Polym. Symp.* 28, 1185 (1976).
14. Goldschmid, O., *Anal. Chem.* 26, 1421 (1954).
15. Goldschmid, O., In: K. V. Sarkanen & C. H. Ludwig (Eds.) *Lignin, occurrence, formation, structure and reactions.* Wiley Intersci. New York, 1971. p. 241.