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CHANGES IN A SOUTHERN PINE DIOXANE LIGNIN ON OXIDATION
WITH OXYGEN IN SODIUM CARBONATE MEDIA

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Changes in a southern pine dioxane lignin on oxidation with oxygen in sodium carbonate media.

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Abstract

Loblolly pine dioxane lignin was oxidized with oxygen (618 kPa) in 0.5 and 0.13$\underline{N}$ sodium carbonate for varying lengths of time. Chemical characterization indicated that the amounts of phenolic hydroxyl and carbonyl groups decreased rapidly, whereas carboxyl groups increased substantially during oxidation. Molecular weight distributions of the oxidized lignins indicated extensive cross-linking occurred during the initial stage of oxidation, followed by degradation to smaller molecules. Mild preoxidation of the lignin with peroxyacetic acid before reaction with oxygen did not appear to inhibit cross-linking during subsequent reactions with oxygen.

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The goal of developing a commercially viable oxygen-based pulping process has encouraged several efforts to improve the selectivity of delignification with oxygen. Marton and Leopold (1) found that a first-stage cook of conifer chips in the presence of a small amount of oxygen gave a modified pulp which was more readily delignified during the second-stage oxygen/alkali (O/A) cook than was the unmodified pulp. Johnson, et al.(2) observed that treatment of fiberized red maple with peroxyacetic acid (but not fiberized loblolly pine) prior to O/A pulping led to faster and more selective delignification.

This investigation was concerned with changes in functional groups and molecular weight of an isolated lignin under O/A pulping conditions, as a function of time of oxidation. A sample of lignin was modified by peroxyacetic acid (PAA) in order to investigate the effect of such a preoxidation on the reactivity of the lignin toward degradation with O/A.

RESULTS AND DISCUSSION

Characterization of the Loblolly Pine Dioxane Lignin

A loblolly pine (Pinus taeda L.) dioxane acidolysis lignin (DL) was prepared according to the procedure of Pepper, et al.(3,4). Analyses: yield, 20.5% of the Klason lignin; carbohydrate content, 1.4%; ash content, 3.1%; ε 280 nm, 20.6 $Lg^{-1}cm^{-1}$; $\overline{M}_w$, 11,000; elemental and

methoxyl analysis gave the empirical formula $C_9 H_{7.81} O_{2.67} (OCH_3)_{0.97}$; phenolic hydroxyl, 0.27 per C_9 unit; carbonyl, 0.18 per C_9 unit; carboxyl, 0.02 per C_9 unit.

The analytical data for the DL showed that it was very similar to other softwood lignins. The phenolic hydroxyl content was nearly identical with that reported for a spruce dioxane lignin (5), while somewhat lower values were found (6) (0.202 and 0.190 $PhOH/C_9$) for a spruce cellulolytic enzyme lignin (CEL), and a milled wood lignin (MWL), respectively. The degree of aromatic condensation as estimated from the PMR integral of the acetylated DL was 65% which was typically higher than that generally found for MWL samples (40-50%) (7). The weight average molecular weight ($\overline{M}_w$) of the DL (11,000) was identical with that reported for spruce MWL (8), but slightly lower than a different spruce MWL (15,000) (9).

The infrared spectrum of the DL was similar to reported spectra of spruce MWC and CEL (6) with the exception of a weak band at 1715 cm^{-1}. This band has previously been attributed (10) to increased β-ketone content due to the acidic conditions employed in isolating the DL. However, persistence of the band in the spectra of DL samples either subjected to sodium borohydride reduction, or freeze-dried from media of pH 3 and 9 suggested that the band may be due to aromatic ester groups.

The carbon-13 NMR spectrum of the DL contained all of the signals assigned by Ludemann and Nimz (11) in spruce MWL, and it was not possible

to assign the slight differences between the spectra to either the isolation procedure or to species differences.

Oxidation in Sodium Carbonate Media

Changes in selected properties of the DL as a function of time of oxidation were characterized for oxidations carried out in 0.13$\underline{N}$ (OX.13) and 0.50$\underline{N}$ (OX.50) Na_2CO_3 at an initial oxygen pressure of 618 kPa and 120°C. After suitable intervals, the reaction was terminated and the final pH of the liquor determined (see Table 1). The pH was adjusted first to 3 to remove carbonate as CO_2, then to pH 9 and freeze-dried. The sample number for a given oxidation series corresponds to the time, in hours, of oxidation.

Starting material (SM) was isolated by suspending the DL in the appropriate alkaline medium and recovering the sample. The 0.0-hour sample was prepared by placing a sample of DL in the reactor in 50 ml of distilled water, heating the reactor to temperature, cooling, adding the appropriate amount of alkali, and freeze drying.

As expected, methoxyl contents decreased while the oxygen content increased for both oxidation series with increasing time of oxidation (Table 1). Comparison of the OX.13 series data with the OX.50 series data indicated that, for a given time of oxidation, the lignin was more extensively degraded at the higher alkali concentration. The more gradual decline in pH for the OX.50 series coupled with the faster development of carboxyl groups also illustrates the importance of alkali concentration to lignin reactivity with oxygen. The higher alkali level

should provide a higher concentration of phenolic anions, which are believed to play an important role in lignin-oxygen reactions (12-15).

Infrared spectra of the oxidized lignins (freeze-dried at pH 9.0) were characterized by increased absorption at 1600 and 1400 cm^{-1} indicating formation of carboxylate groups with increasing time of oxidation.

Both oxidation series were characterized by rapid loss of phenolic hydroxyls in the first hour of reaction after which the phenolic hydroxyl content appeared to level off at a low value (Table 1). This result suggested the formation, and/or the initial presence of relatively stable phenolic hydroxyl-containing structures. There was an apparent decrease in phenolic hydroxyl content associated with bringing the reactor to temperature, indicated by the decrease in phenolic hydroxyl from 2.4% to 1.9%. Since the only difference in the preparation of these samples was bringing the 0.0-hour sample up to reaction temperature in the reactor, this decrease may be attributed to thermal degradation of the lignin.

Ultraviolet spectra of the OX.50 samples are compared in Fig. 1. With the exception of the 8.0-hour sample, spectra were characterized by increased absorptivity at about 260 and 300 nm with little change in absorptivity at 280 nm. Free and etherified phenolic hydroxyl groups are major contributors to the band at 280 nm (16). In view of the significant decrease in methoxyl and phenolic hydroxyl contents of the lignin with time of oxidation, one would predict that the 280 nm band should decrease in intensity with time of oxidation. The relatively

constant absorptivity at 280 nm and the increasing absorptivity with time of oxidation at 260 and 300 nm may be interpreted to indicate formation of biphenyl linkages in the lignin. Pew (17) studied the ultraviolet absorption of 5,5'-linked biphenyl structures related to lignin and observed a similar pattern of absorbance. Increased absorbance at 260 nm has also been assigned to formation of α-carboxylic acids in spruce MWL oxidized by fungi and these groups may also contribute to absorbance in this region (9). The different spectrum exhibited by the 8.0-hour sample suggests the destruction of these biphenyl structures and other aromatic rings at longer oxidation times.

Carbonyl contents of the OX.13 and OX.50 samples, are compared in Table 1. Carbonyl contents at both carbonate concentrations decreased rapidly in the early stages of oxidation. The loss of all α-carbonyl structures from the lignin would eliminate the possibility for lignin degradation by proton abstraction from the β-carbon of the side chain, as discussed by Aoyagi, et al. (18) and Gierer and Imsgard (19,20). That this latter route is not a dominant mechanism of lignin degradation is suggested by noting the continuing degradation of OX.50 samples beyond two hours where the α-carbonyl content is nil.

Carboxyl contents of the OX.13 and OX.50 samples were estimated by potentiometric titration (Table 1). Both series were characterized by a rapid initial increase in carboxyl with a slower increase at longer oxidation times. For a given time of oxidation the OX.50 series samples were more oxidized as shown by their consistently higher carboxyl content.

The molecular weight distributions of the OX.13 samples, determined by column chromatography on Sephadex G-50 with formamide as eluant (21), are compared in Fig. 2. Elution was monitored by monochromatic light absorption at 280 nm. Interpretation of molecular weight distribution curves based on UV absorption must be qualified since absorption depends on the extinction coefficient as well as the concentration of the solute. However, from a qualitative point of view the absorbance provides a useful basis for comparison of changes in molecular weight as a function of time of oxidation.

The low molecular weight region of the elution curve was calibrated using vanillic acid (MW = 168) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-methyl-phenoxy)-1-propanone (MW = 330).

Elution curves were bimodal, exhibiting both a low molecular weight fraction and a high molecular weight fraction containing material too large to be resolved by the column. There was a general decrease in absorbance of the oxidized samples in the intermediate molecular weight region relative to the SM sample. These results indicate that there was rapid cross-linking of the lignin in the initial stages of oxidation. The low molecular weight peak at an elution volume of 380 ml indicated formation of degradation products with a molecular weight close to that of vanillic acid (MW = 168). A similar molecular weight distribution pattern was observed for the OX.50 samples (not shown).

The evidence for rapid cross-linking in the initial stages of oxidation followed by degradation to smaller molecules, is in general accord with

expectations based on studies of the oxidation of lignin-related phenols[12-14] including the relative ease (lower critical oxidation potential) of oxidation of biphenyl systems compared with their phenolic precursors.

Molecular weight distributions of the 8.0-hour samples from the OX.13 and OX.50 runs are compared in Fig. 3, using Sephadex G-75. The results indicated that, for a given time of oxidation, lignin oxidized at the higher alkali concentration was more extensively degraded.

A sample of DL and one of the OX.50-2.0 lignin were also separated on a column of Sephadex G-100 in order to obtain a measure of the molecular weight of the high molecular weight fraction. Elution curves for the two samples are compared in Fig. 4. A small amount of the DL was still excluded from the column. There was again a large high molecular weight peak in the oxidized sample, indicating the presence of material too large to be resolved with the column. The high molecular weight fraction of the OX.50-2.0 sample was isolated, freeze-dried (freeze-dry weight = 14% of total sample weight) and analyzed for weight average molecular weight by the meniscus depletion method with an ultracentrifuge (22). The weight average molecular weight was 78,000 and the number average molecular weight was 64,000 for the high molecular weight fraction.

Effect of Peroxyacetic Acid Pretreatment of Dioxane Lignin on its Reaction with Oxygen/Alkali

Johnson, et al. (2) observed that treatment of fiberized red maple with PAA prior to O/A pulping led to faster and more selective delignification

than a control. The nature of changes introduced in the lignin as a result of the pretreatment was not known. PAA had been shown in model compound studies to lead to formation of hydroxylated intermediates (23,24) and α-carbonyl containing intermediates (25,26). In view of proposed mechanisms of lignin degradation which proceed either through radical initiation at the phenolic anion or by β-proton abstraction in structures containing an α-carbonyl, an increase in either phenolic hydroxyl content or α-carbonyl content would be expected to increase the reactivity of the lignin toward degradation with O/A.

A sample of the DL was treated with PAA (0.50 mole PAA/equivalent weight of DL, 188.9). Major structural changes in the DL as a result of the treatment included a slight increase in phenolic hydroxyl (2.42 to 2.52%), a large increase in carboxyl content (0.81 to 7.38%), formation of some low molecular weight material (based on comparison of the molecular weight distributions), and destruction of α-carbonyl groups (based on the disappearance of α-carbonyl related signals in the carbon-13 NMR spectrum). The destruction of α-carbonyls and the failure to increase phenolic hydroxyl contents was probably due to preferential oxidation of these structural moieties by the PAA to acidic products.

Oxidation of the PAA-modified lignin with oxygen in 0.13$\underline{N}$ Na_2CO_3 and isolation of the oxidized lignin at different periods of time indicated that the modified lignin was, with one exception, no more reactive than unmodified DL. The one instance where there appeared to be a significant difference in reactivity is shown in Fig. 3, which compares the

molecular weight distributions of the 8.0-hour oxidation samples from the modified and unmodified lignins. The larger high molecular weight fraction in the PAA-modified lignin indicated more extensive cross-linking of the modified lignin on charging the reactor with oxygen and alkali.

CONCLUSIONS

Lignin degradation under oxygen/alkali pulping conditions may be initiated either by a single electron transfer from a phenolic anion to oxygen[12-14] or by proton abstraction from the β-carbon when the phenolic group is etherified and there is an α-carbonyl in the side chain (16,17). Results from this investigation indicated that phenolic hydroxyls and carbonyls were consumed in the early stages of oxidation with oxygen in sodium carbonate solutions. Molecular weight distributions of the oxidized lignins indicated that the DL first underwent extensive cross-linking by reaction with O/A. Ultraviolet spectra provided support for the formation of biphenyl linkages in the cross-linked lignin. The loss of phenolic hydroxyl, together with simultaneous formation of a high molecular weight fraction followed by degradation to acidic products suggests that the degradation pattern observed in this study was similar to the pattern expected on the basis of model compound studies by Kratzl, et al.[12-14]

Attempts to modify the DL by treatment with PAA prior to oxidation with O/A failed to increase lignin reactivity. Results indicated that the formation of lower molecular weight fragments from PAA oxidation led to

more extensive cross-linking of the lignin on charging the reactor with oxygen and alkali. Although the α-carbonyl content was eliminated by the PAA pretreatment, the modified DL was nevertheless degraded to an extent comparable with the unmodified DL. It thus appears that the presence of α-carbonyl groups does not exert a major impact on degradation of lignin by oxygen.

EXPERIMENTAL

Materials

Water used in this study was triply distilled to remove metal ions. 1,4-Dioxane was purified according to the method of Fieser (27). Peroxyacetic acid was prepared according to the FMC procedure (28) described by Farrand (21). Loblolly pine dioxane lignin was prepared according to the method of Pepper, et al. (3,4), from acetone extracted wood meal prepared from loblolly pine (Pinus taeda L.). The DL was stored under vacuum (P_2O_5) in the dark at $5^{\circ}C$.

Oxidation Procedure

Lignin oxidations were carried out in a 150 ml Teflon-lined reactor fitted with an alkali injection device, an internal thermocouple, an oxygen charging line, and a gas sampling line (22). Prior to addition of lignin and alkali, the reactor was preheated in a water bath at $80^{\circ}C$ for 1 hour. The lignin sample (1.0 g) and triply distilled water (50 ml) were placed in the bottom of the reactor. A weighed amount of alkali

(0.6841 g or 2.6498 g Na_2CO_3, corresponding to 0.13$\underline{N}$ or 0.50$\underline{N}$, respectively) was placed in the Teflon injector tube which was attached to the lid of the reactor on the oxygen charging line. The reactor was then flushed with nitrogen, sealed, and brought to temperature (120°C) in 75 minutes in an oil bath. Once at temperature, oxygen was introduced to the reactor for 1 min at a pressure of 618 kPa (calculated at 120°). The initial oxygen concentration of the saturated solution was 73 ppm in 0.13$\underline{N}$ Na_2CO_3 and 61 ppm in 0.50$\underline{N}$ Na_2CO_3 (22).

The plug in the bottom of the injection tube was blown out by the oxygen which introduced the alkali to the reactor with the oxygen. Reaction was terminated after the desired period of time by reducing the pressure to atmospheric and immersing the reactor in cold water. After measuring, pH was adjusted to 3.0 by addition of 1.0$\underline{N}$ HCl and the solution bubbled with nitrogen and stirred for 3 hours to remove carbonate. Finally, the pH was adjusted to 9.0 by addition of 1.0$\underline{N}$ NaOH and the sample freeze-dried.

The peroxyacetic acid modified lignin was prepared by oxidizing 10 g of DL in 100 ml of acetic acid/water (9/1) to which was added sufficient PAA to give a molar ratio of 0.50 PAA on lignin (lignin formula weight = 188.9). The total volume was adjusted to 200 ml with acetic acid/water (9/1) and the solution reacted at 25°C until PAA could no longer be detected (29) (52 hours). The reacted lignin was freeze-dried and stored under vacuum over P_2O_5.

Analytical Procedures

Carbohydrate content was determined by gas chromatographic analysis of the alditol acetates prepared from the hydrolyzed lignin (30). Carbon-hydrogen analyses were performed by Chemalytics, Inc. of Tempe AR. Oxygen content was computed by difference. The ash content of the DL was determined as the oxide ash at $550^{o}C$. Methoxyl content was determined by TAPPI Standard Method T 209. Carbon-13 and proton magnetic resonance spectra were obtained using a JEOL Model FX-100 FT-NMR spectrometer, and infrared spectra were obtained on a Perkin Elmer Model 700 spectrometer. Ultraviolet spectra were determined (Cary Model 15) according to the procedure of Arseneau and Pepper (5). Phenolic hydroxyl content was obtained by UV difference spectroscopy (31). Carbonyl content was determined by the oximation procedure of Gierer and Soderberg (32). Carboxyl contents were estimated by potentiometric titration of the acidified sample with a Corning Model 12 Research pH Meter. Molecular weight distributions were determined by column chromatography on Sephadex G-50, G-75, or G-100 (superfine grade), using formamide as eluant. Columns were prepared as described by Brown, et al. (21). Molecular weight distributions were determined by the sedimentation equilibrium technique with a Beckman Model E Analytical Ultracentrifuge. Determinations were made in reagent grade formamide (Fisher Scientific) at $25^{o}C$.

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Table 1. Analyses[a] of Dioxane Lignin after Reaction with Oxygen in 0.13N (OX.13) and 0.5N (OX.50) Sodium Carbonate Solutions

Sample Number	Time of Reactions, hrs.	C, %	H, %	O, %	OCH_3, %	Final, pH	Phenolic, %	Carboxyl, %	Carbonyl, %
OX.13	SM[b]	58.51	4.45	21.39	15.65	10.965	2.42	0.81	2.63
	0.0	53.41	4.77	26.99	14.83	10.970	1.97	0.46	2.06
	0.5	Not determined		28.50	13.47	10.079	0.79	4.6	0.40
	1.0	54.30	4.13	28.50	13.07	9.669	0.19	7.7	0.17
	2.0	51.46	3.64	32.16	12.75	9.486	0.24	9.5	0.74
	4.0	47.13	3.24	38.32	11.31	9.433	0.0	10.9	0.40
	8.0	48.24	3.59	38.69	9.49	9.322	0.11	14.5	0.0
OX.50	SM[b]	57.58	4.13	23.02	15.26	11.128	2.43	0.0	---
	0.0	59.43	4.81	21.34	14.42	11.155	1.93	0.60	1.71
	0.5	54.16	4.08	27.32	14.44	10.639	0.74	8.0	0.54
	1.0	57.12	4.04	25.51	13.32	10.485	0.55	9.2	---
	2.0	47.86	4.32	36.13	11.71	9.912	0.33	14.1	0.0
	4.0	49.30	3.00	39.49	8.22	9.738	0.29	17.8	0.0
	8.0	46.23	3.33	44.25	6.19	9.538	0.28	18.9	---

[a]Based on moisture-free weight (dried over P_2O_5 under vacuum), corrected for ash and carbohydrate.

[b]SM = Starting material.
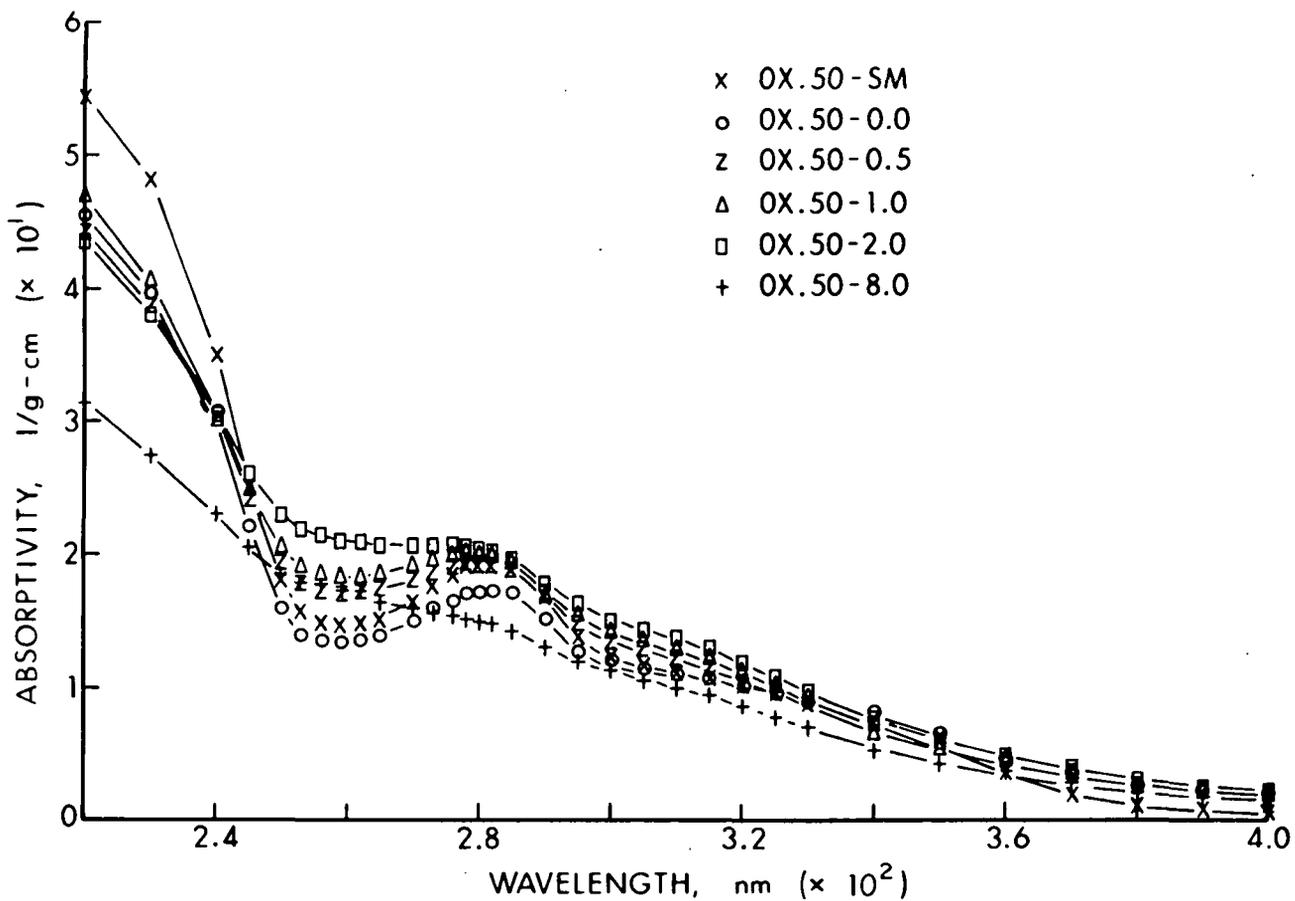
Fig. 1.   Comparison of ultraviolet spectra of dioxane lignin oxidized

in 0.5N Na$_2$CO$_3$ and 618 kPa oxygen.
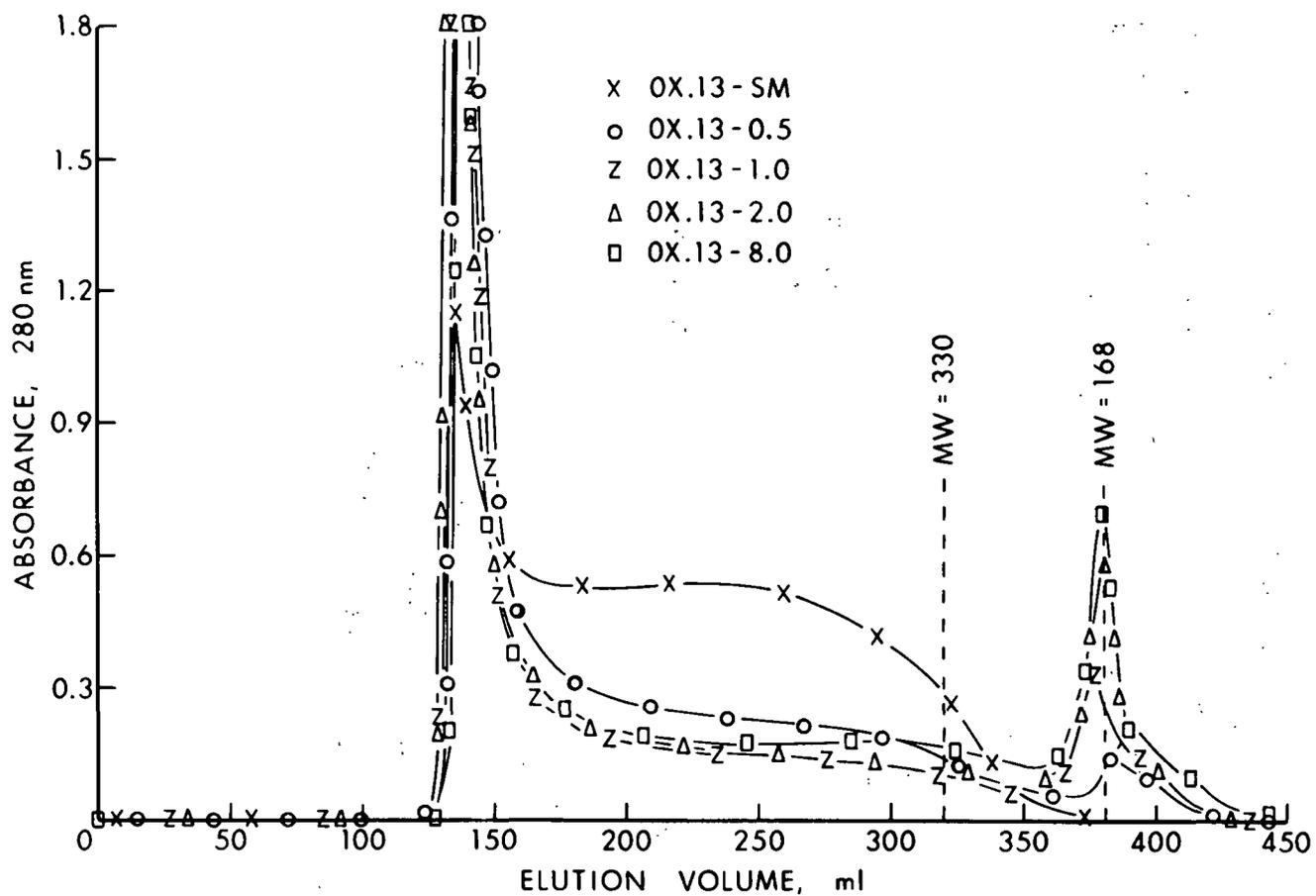
Fig. 2. Comparison of molecular weight distribution of dioxane lignin oxidized in 0.13N Na$_2$CO$_3$ and 618 kPa oxygen.
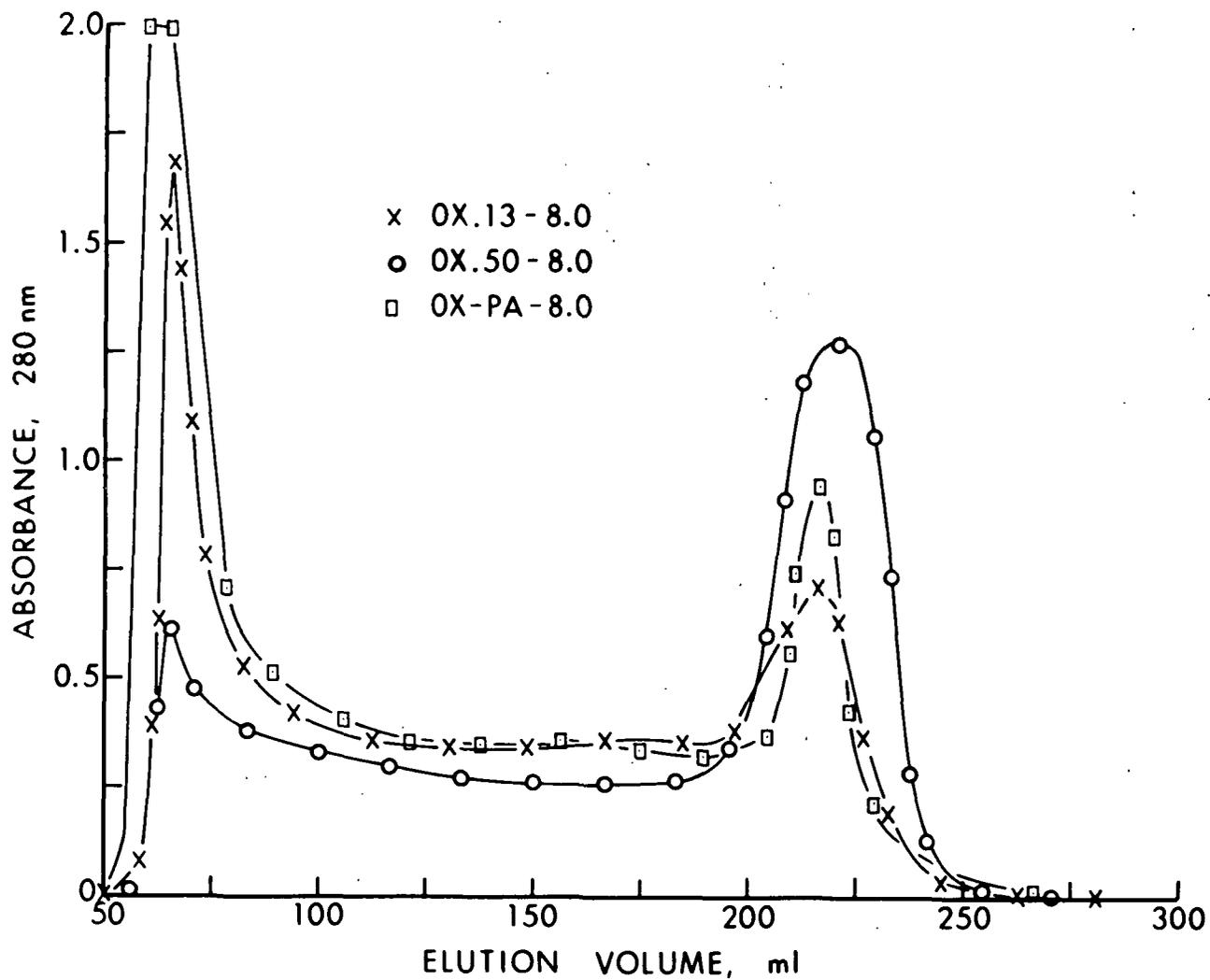
Fig. 3.   Comparison of molecular weight distributions of dioxane

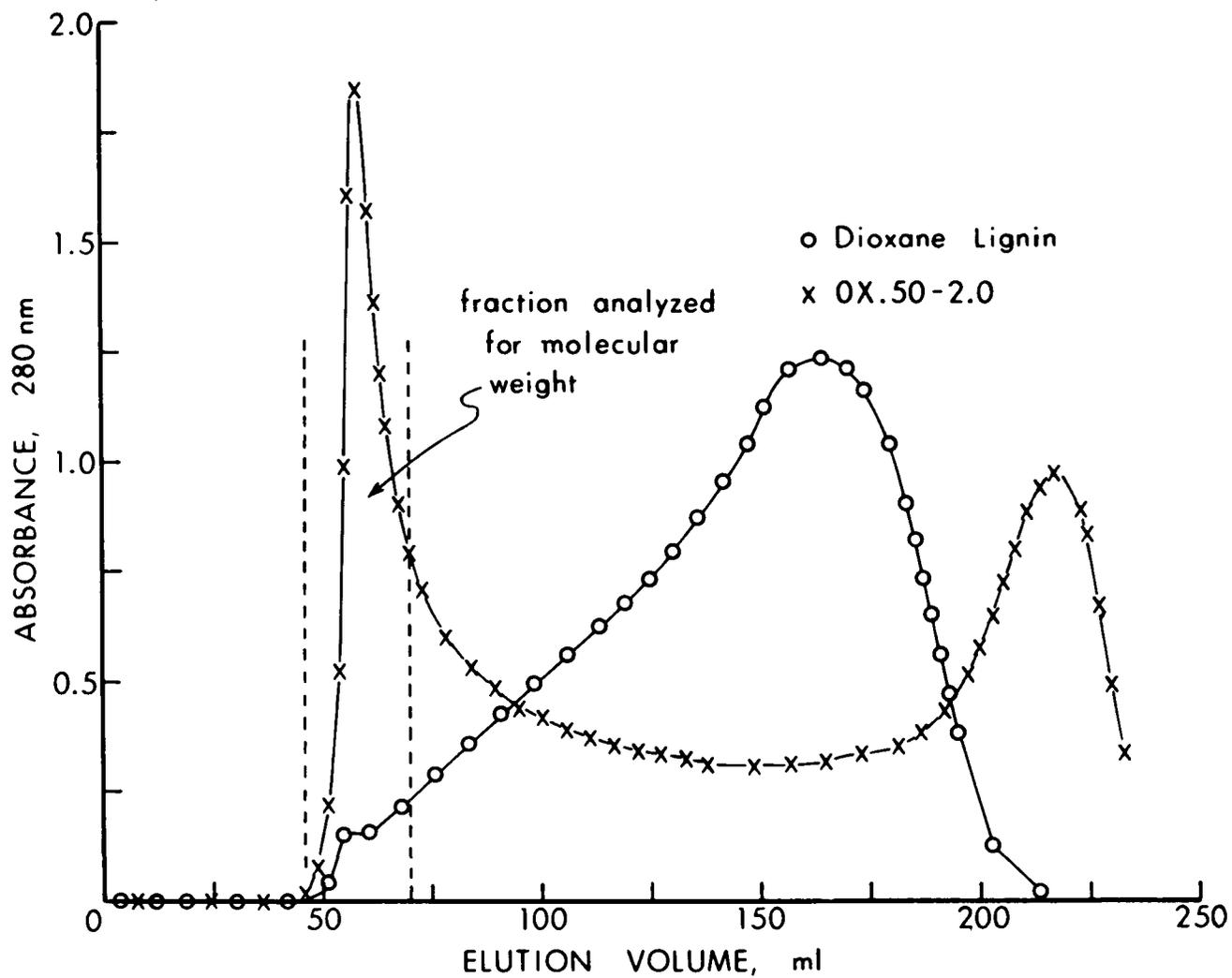lignins oxidized for 8 hours under different conditions.

Fig. 4. Comparison of molecular weight distributions of dioxane lignin and OX.50-2.0 samples determined on Sephadex G-100.