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Molecular Weight Distributions of Effluents from Chlorine Dioxide Delignification

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MOLECULAR WEIGHT DISTRIBUTIONS OF EFFLUENTS FROM CHLORINE DIOXIDE DELIGNIFICATION

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ABSTRACT

The amount of low molecular weight chlorinated organic material formed during bleaching is a concern because this material has the potential to adversely affect the environment. To study the extent of the formation of low molecular weight material during elemental chlorine free (ECF) bleaching, a method of aqueous gel permeation chromatography (GPC) was developed for the determination of bleaching effluent molecular weight distributions. It employs Sephadex gels, aqueous LiCl eluents, and total organic carbon (TOC) detection.

Softwood kraft pulp was delignified with ClO_2 , NaOH, and O_2 and the molecular weight distributions for both the D and (EO) stage effluents were determined. Complete substitution of ClO_2 for Cl_2 decreased the proportion of low (< 960) molecular weight material in the bleaching effluents by 14-18%. Smaller effects result from changes in D stage initial pH and reaction time. Oxygen delignification prior to 100% chlorine dioxide bleaching slightly decreased the proportion of low molecular weight material in the (EO) stage effluent.

INTRODUCTION

The molecular weight distribution of bleaching effluents is important from an environmental perspective, because high molecular weight material is not biologically active and may therefore be innocuous. High (> 1000) molecular weight effluent material has been shown to be either non-toxic (1) or less toxic (2) than the low molecular weight fraction, which contains the majority of the effluent's acute toxicity (3). However, low molecular weight material is more readily degraded in biological treatment systems than high molecular weight material (4, 5).

Molecular weight distributions of bleaching effluents have been determined by both ultrafiltration (6-11) and gel permeation chromatography (GPC) (1, 11, 12). The two methods give widely differing results, with GPC detecting more low molecular weight material than ultrafiltration (11). Both methods indicate considerably more high molecular weight material in E stage effluents than in C or D stage effluents (1, 6-9, 12). Several studies have determined the effect of bleaching variables, such as chlorine dioxide substitution (7, 13) or oxygen bleaching (8, 9, 14) on the molecular weight distributions of effluents. It is difficult to draw conclusions from these limited results however, due to the lack of reliability of ultrafiltration which has most often been used in such studies. Ultrafiltration may indicate more high molecular weight material than GPC because of the concentration dependent association that occurs in ultrafiltration (11). Such association can be controlled with GPC. However, GPC has not often been used to investigate the effects of bleaching process variables on the molecular weight distribution of effluents.

A method of aqueous GPC was developed in this laboratory, as described elsewhere (12). The method employs Sephadex gels, aqueous LiCl eluent, and total organic carbon (TOC) detection. This method has several advantages over other GPC methods, including greater resolution, control of association, and a universal detection system. TOC detection is more appropriate than ultraviolet (UV) detection for GPC of bleaching effluents, since effluents may contain carbohydrates and other materials, not detected by UV.

In the present investigation, this method was used to determine the molecular weight distributions of bleaching effluents produced in the laboratory under well controlled bleaching conditions. The effects of 100% ClO_2 substitution, oxygen bleaching, D stage initial pH, and D stage reaction time were studied.

EXPERIMENTAL APPROACH

Distributions of D and (EO) stage effluents were determined individually. Gel permeation was done using 2 Sephadex columns in series. The first contained G-50 gel and the second contained G-15 gel. The 2-column system was used to achieve improved low molecular weight separation (12). Polyethylene glycol standards of known molecular weight were used to calibrate the system, and all distributions were transformed to a relative retention volume scale based on high and low molecular weight standards

(12). Relative retention volume is calculated as follows:

$$\text{Relative Retention Volume} = R_s - R_h / R_l - R_h$$

where

R_s = retention volume of sample.

R_l = retention volume of low molecular weight standard.

R_h = retention volume of high molecular weight standard.

TOC Detection

The eluent passes from the columns through a 1 ml flow cell, from which TOC samples are drawn. At each sampling interval, the instrument draws 5 250 μ l samples and injects them to the waste stream. This essentially empties the flow cell, and allows it to fill with fresh column eluent containing a new sample. Immediately after the injections to waste, the sample for TOC determination is drawn and analyzed. This process is automatically repeated as often as the TOC instrument can achieve a baseline after TOC measurement (usually every 3-4 minutes). The eluent flow rate was 0.6 ml/minute and total column volume was 200 ml or less. Therefore, a typical experiment lasted 300 minutes or more and consisted of more than 85 individual TOC determinations.

Molecular Weight Distributions

The GPC chromatograms, as originally collected, consist of pairs of time and TOC data. The data were transformed to the relative retention volume scale, the baseline corrected to zero TOC, the chromatograms integrated to determine eluted TOC, the curves normalized to 1000 μ g TOC, and the area between the mean elution values of the standards determined.

This information was used to construct cumulative molecular weight distributions. Such distributions provide an approximate numerical measure of the percentage of effluent TOC below a given molecular weight level. All standards exhibit retention volumes with approximately normal distributions and the center of the distribution was used in determining the cumulative distributions of the effluents. Therefore it is not strictly correct to state that these curves indicate the percentage of material with a molecular weight less than the corresponding molecular weight, since material of a particular molecular weight actu-

ally elutes both before and after the mean retention volume of the standard. However, these cumulative distribution curves remain valuable for comparing effluent distributions. They allow quantitative analysis rather than the purely qualitative analysis usually done with this type of data.

Statistical Analysis

Quantitative results allow statistical analysis and determination of significant differences between effluents. A total of 32 samples were analyzed. The D and (EO) stage effluents were produced under 8 different sets of bleaching conditions. Each bleaching sequence was performed twice. In one case, a replicate effluent sample was not available. In this case, the identical sample was run twice. The variation was not distinguishable from that attained with the replicate effluent samples and therefore this replicate chromatogram of the identical sample was used in the analysis. A 2-way analysis of variance was performed on the percentage of material with a molecular weight of less than 960 for each set of bleaching conditions and for both stages. Duncan's multiple range test (15) was used to determine which differences were statistically significant.

RESULTS AND DISCUSSION

The reproducibility of both the bleaching experiments and GPC runs was very good as illustrated in Figure 1. This shows the normalized D and (EO) stage effluent distributions for the OD(EO) bleaching sequence. The D stage distributions represent the 2 replicate chromatograms for the identical effluent, while the (EO) stage distributions represent a single GPC chromatogram for each of 2 replicate effluents.

The relative retention volume scale, which serves as the x-axis for the chromatograms, was determined using high and low molecular weight standards. The relative retention volumes for all molecular weight standards are given in Table I, and the corresponding calibration curve is shown in Figure 2.

The cumulative molecular weight distribution curves given here are based on the mean results of the 2 replicates per set of bleaching conditions. Figure 3 shows replicate cumulative D stage molecular weight distribution data for 5 minute and 3 second D stage reaction times. This figure makes clear how reproducible the cumulative data are, particularly at molecular weight levels of greater than 300. The fig-

ure shows that small significant differences can be detected, due to precise data.

The cumulative molecular weight distributions were interpreted principally in terms of the proportion of material with a molecular weight of less than 960, since this is the environmentally significant portion of the effluent. Throughout this paper, the material with a molecular weight of less than 960 will be referred to as "low" molecular weight material.

The Effect of 100% ClO_2 and O_2 Bleaching

Effluents from OC(EO), OD(EO), and D(EO) bleaching of softwood kraft pulps were previously generated (16). The cumulative molecular weight distributions for D or C, and for (EO) stage bleaching effluents from these partial sequences are shown in Figures 4 and 5.

For all 3 sequences, the D or C stage effluents contained a significantly greater proportion of low molecular weight material than the (EO) stage effluents. For example, within the OC(EO) sequence, about 94% of the C stage material was low molecular weight, while only 85% of the (EO) stage material was low molecular weight.

Use of chlorine dioxide to completely replace chlorine decreased the proportion of low molecular weight material in the effluents from both stages. Use of 100% chlorine resulted in about 94% low molecular weight material in the D or C stage compared to about 81% when chlorine dioxide was used. Similarly within the (EO) stage, use of 100% chlorine dioxide decreased the proportion of low molecular weight material from about 85% to 70%. On the basis of these molecular weight distributions, it may be concluded that the environmental benefits of ClO_2 delignification include formation of a decreased proportion of low molecular weight material.

The effect of oxygen bleaching on the effluent molecular weight distribution was not nearly as large but was nevertheless statistically significant. Oxygen delignification preceding 100% chlorine dioxide bleaching increased the proportion of low molecular weight material in the (EO) stage effluent (70 vs. 67%). Although a greater proportion of low molecular weight material was formed in the OD(EO) sequence, on an absolute basis the D(EO) sequence produced more low molecular weight material since about half of the lignin was removed during oxygen bleaching.

The Effect of D Stage pH

Cumulative molecular weight distributions for effluents from the OD(EO) bleaching sequence utilizing 2 initial D stage pH levels (17), are presented in Figures 6 and 7. As previously observed for different bleaching sequences, the D stage effluents contained an increased proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents, the D stage begun at pH 2 resulted in 81% low molecular weight material, while the D stage begun at pH 4 resulted in 78% low molecular weight material. However, in the (EO) stage effluents the trend was reversed, with the D stage begun at pH 2 resulting in 70% low molecular weight material and the D stage begun at pH 4 resulting in 74% low molecular weight material. Overall, changing the D stage initial pH over the range of 2 to 4 had little effect on effluent molecular weight distribution.

The Effect of D Stage Reaction Time

Using a specially designed D stage bleaching reactor, effluents were produced by using the OD(EO) bleaching sequence, with D stage reaction times of between 3 seconds and 30 minutes (18). The cumulative molecular weight distributions for the effluents are presented in Figures 8 and 9. Like D stage pH level, D stage reaction time has little effect. Again, the D stage effluents consist of a greater proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents (Figure 8), 30 minute and 3 second D stage bleaching times resulted in a significantly greater proportion of low molecular weight material than D stage bleaching times of 5 minutes and 1 minute. The 30 minute and 3 second D stages resulted in about 80% low molecular weight material. The 5 minute and 1 minute D stages resulted in about 75% low molecular weight material. It is reasonable to suppose that in the first 3 seconds of bleaching the most accessible lignin end units are preferentially affected, resulting in an increased proportion of low molecular weight material. Subsequently, higher molecular weight material is removed, while the removed material is simultaneously degraded in solution.

In the case of the (EO) stage effluents (Figure 9), no simple time trend is observed. Although a 30 minute D stage significantly increased the level of low

molecular weight material compared to 5 minutes or 3 seconds, it was not significantly different from the proportion of low molecular weight material produced in the 1 minute D stage. The absence of a time trend suggests that the process of making lignin alkali soluble occurs within the first 3 seconds of the D stage. This is consistent with work (18) that showed that the entire amount of TOC that could be released during caustic extraction, was released after only a 3 second D stage.

Recovery of Effluent TOC

An advantage of GPC with TOC detection is that it allows a determination of effluent recovery from the columns, by comparison of the integrated chromatogram TOC level with the actual measured TOC of the effluent. Any additional TOC due to column degradation or loss of TOC due to adsorption are apparent using TOC detection but would be unnoticed with other types of detection. Table II presents the average recovery for each bleaching sequence and for each stage. TOC losses were generally less than 25%.

EXPERIMENTAL METHODS

Sample Preparation

Effluent samples were stored in the dark, under highly acidic conditions ($< \text{pH } 2$), and at 4°C . Prior to storage, samples were sparged under acidic conditions to remove carbonates. LiCl was added to the samples to adjust its concentration to 0.1 M and the pH was adjusted to 5.0-5.5 prior to chromatography.

Gel Preparation and Column Packing

Sephadex G-type gels, made of crosslinked dextran, were used for GPC work. The gels were purchased in a powdered state and were swelled in 0.1 M LiCl before column packing. Pharmacia HR 16/50 columns were used for GPC work, and a HR 16 column packing reservoir used during the packing process. Each column was packed individually. The swelled gel was added to the column and the packing reservoir and the gel was packed into the column using flow rates and pressures in excess of those used during chromatography experiments. At least 2 column volumes of eluent (200 ml) was passed through the columns under these conditions to stabilize the gel bed. Once the bed was stable, the column top adapter was attached, and the columns used for chromatography.

Gel Permeation Chromatography

Chromatography was done using a Sephadex G-50 column followed by a G-15 column. Eluent flow was maintained through the chromatography system with an Alltech Model 300 LC pump and an attached pulse dampener. Total organic carbon (TOC) detection was done using a Shimadzu Model TOC-5050 total organic carbon analyzer.

SUMMARY AND CONCLUSIONS

Gel permeation chromatography, utilizing aqueous LiCl eluent, Sephadex G-type gels, and TOC detection was used to determine the molecular weight distributions of a series of laboratory produced effluents.

Use of 100% chlorine dioxide rather than 100% chlorine to bleach oxygen delignified pulp, decreased the proportion of low molecular weight material in the bleaching effluents by 14-18%. The decreased proportion of low molecular weight material formed by ClO_2 is significant from an environmental viewpoint, particularly since this material is also much less chlorinated.

Oxygen delignification before 100% ClO_2 bleaching had a significant effect on the proportion of low molecular weight material formed only in the case of the (EO) stage effluent. However, the effect was much smaller, with only about 3% more low molecular weight material formed when oxygen bleaching preceded chlorine dioxide. Although the OD(EO) sequence resulted in a larger proportion of (EO) stage low molecular weight material, on an absolute basis it still produced about half the low molecular weight material as the D(EO) sequence because oxygen bleaching achieved about 50% delignification prior to the D stage.

D stage initial pH had only a small effect on the proportion of low molecular weight material formed. An initial D stage pH of 2 increased the proportion of low molecular weight D stage material, but decreased the proportion of low molecular weight (EO) stage material, compared to a D stage begun at pH 4.

The D stage reaction time also had only a small effect on the proportion of low molecular weight material. Within the D stage, low molecular weight material was removed at short reaction times, followed by the removal of higher molecular weight material. At longer times, the material was possibly degraded, resulting again in a greater proportion of low molecu-

lar weight material. On the other hand, the (EO) stage effluent distribution was independent of D stage reaction time.

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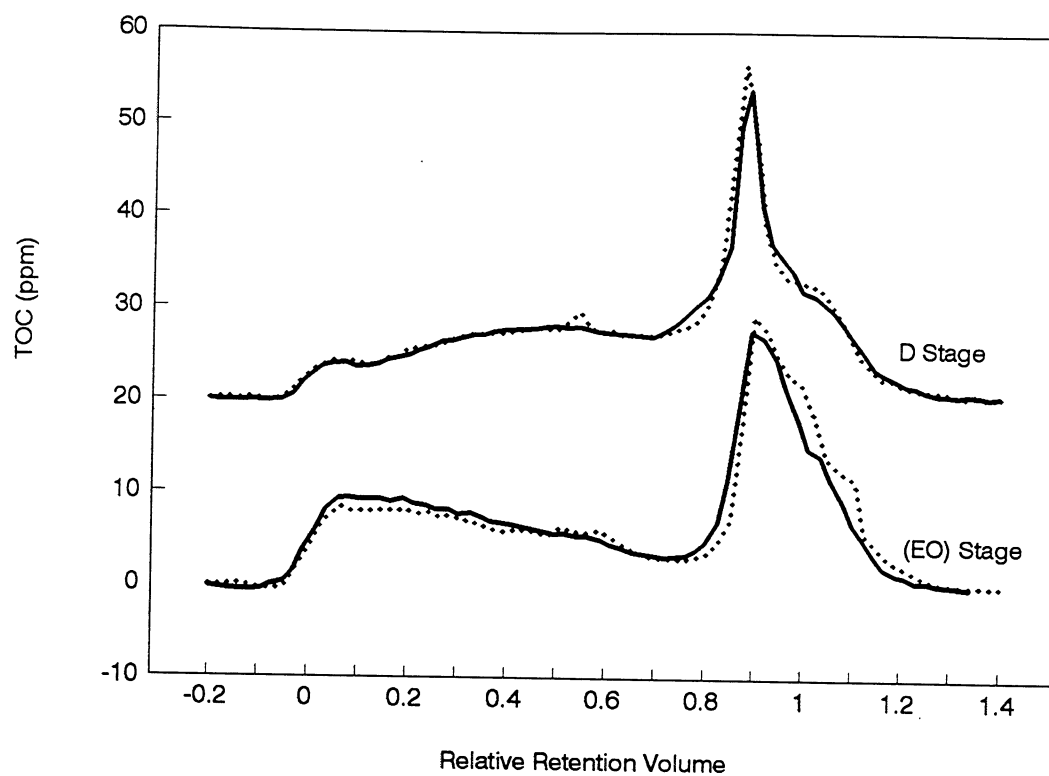


Figure 1. Reproducibility of Chromatograms.

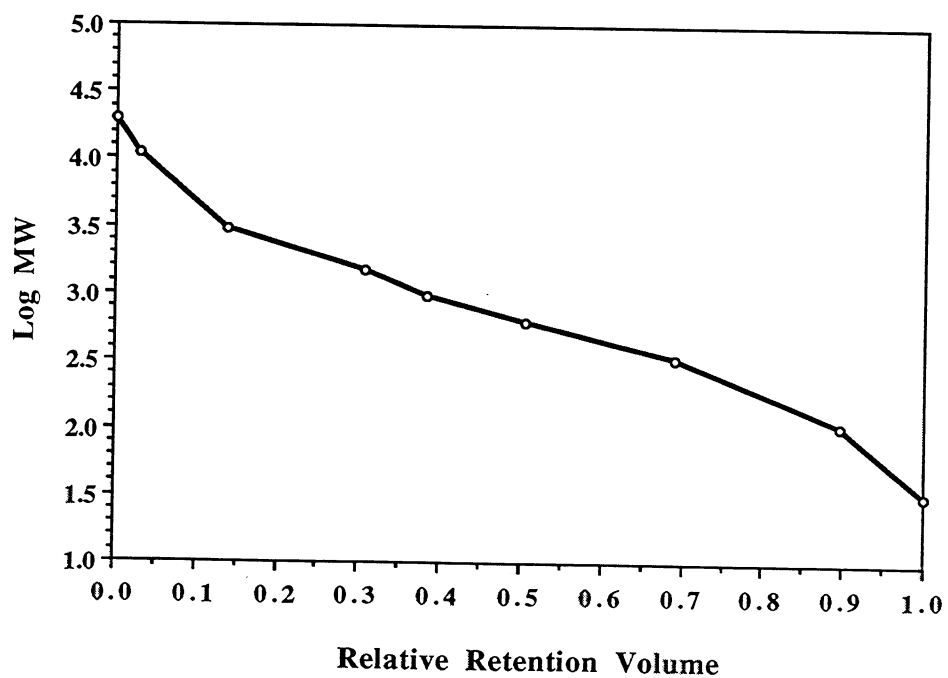


Figure 2. GPC Calibration Curve.

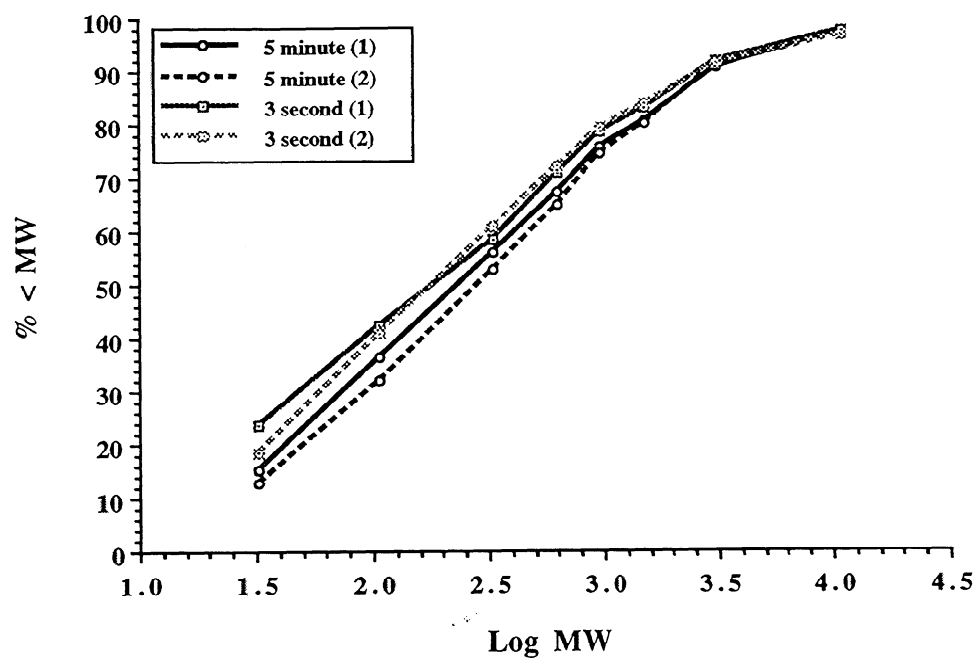


Figure 3. Reproducibility of D Stage Cumulative Molecular Weight Distributions.

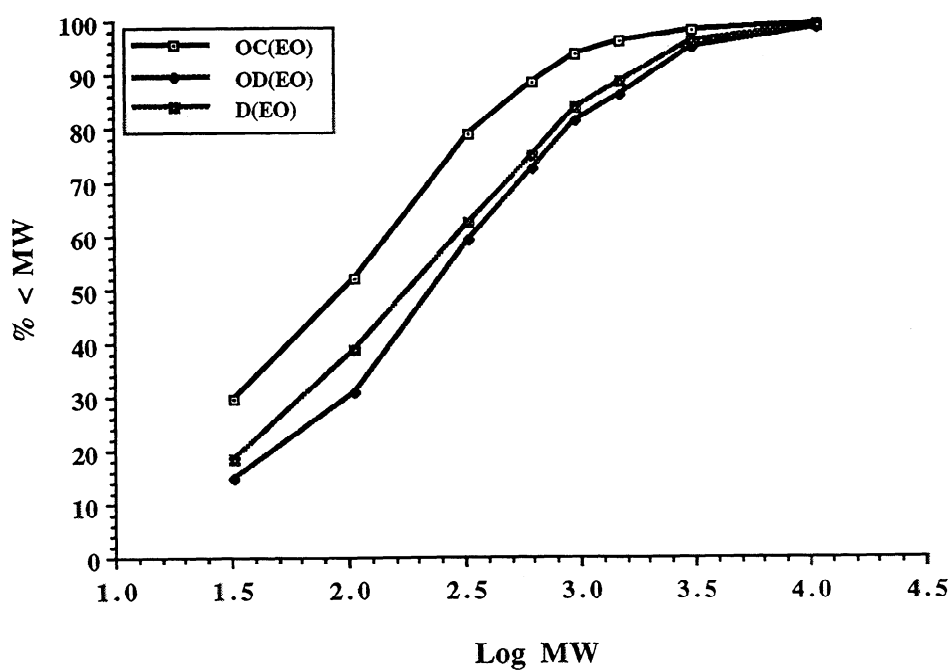


Figure 4. D or C Stage Effluent Cumulative Molecular Weight Distributions.

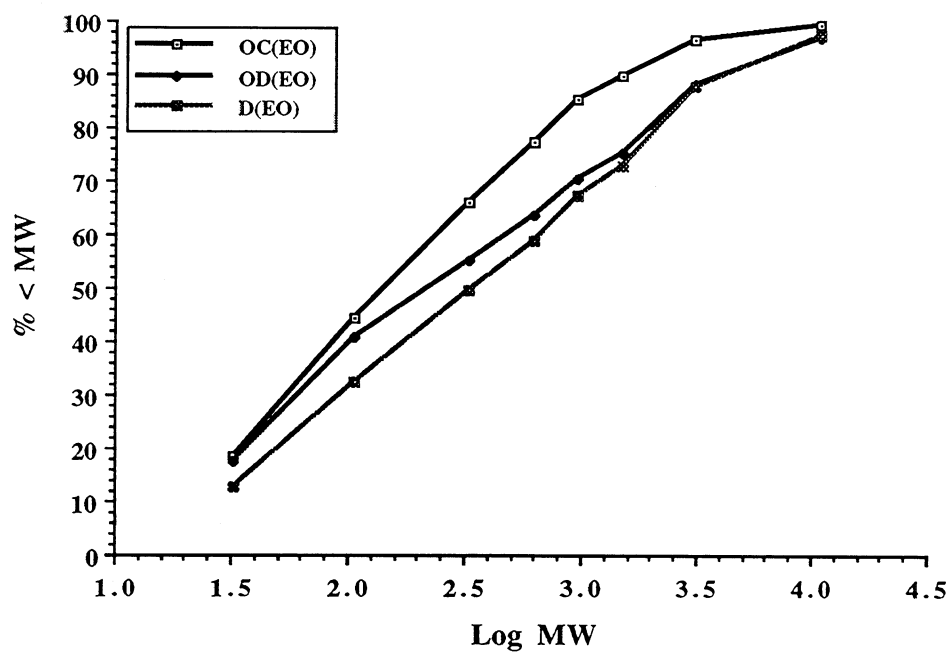


Figure 5. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

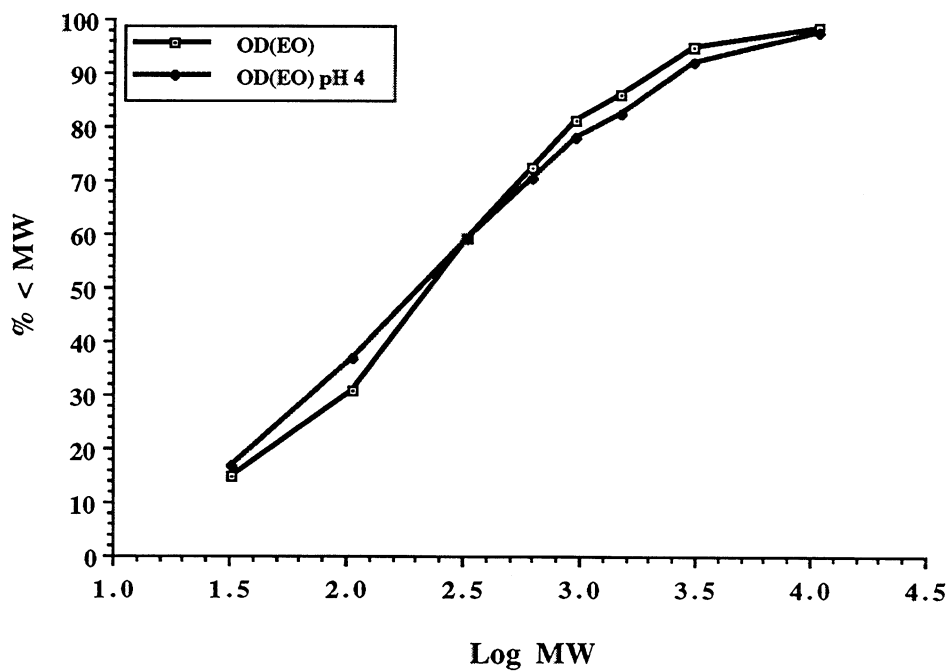


Figure 6. D Stage Effluent Cumulative Molecular Weight Distributions.

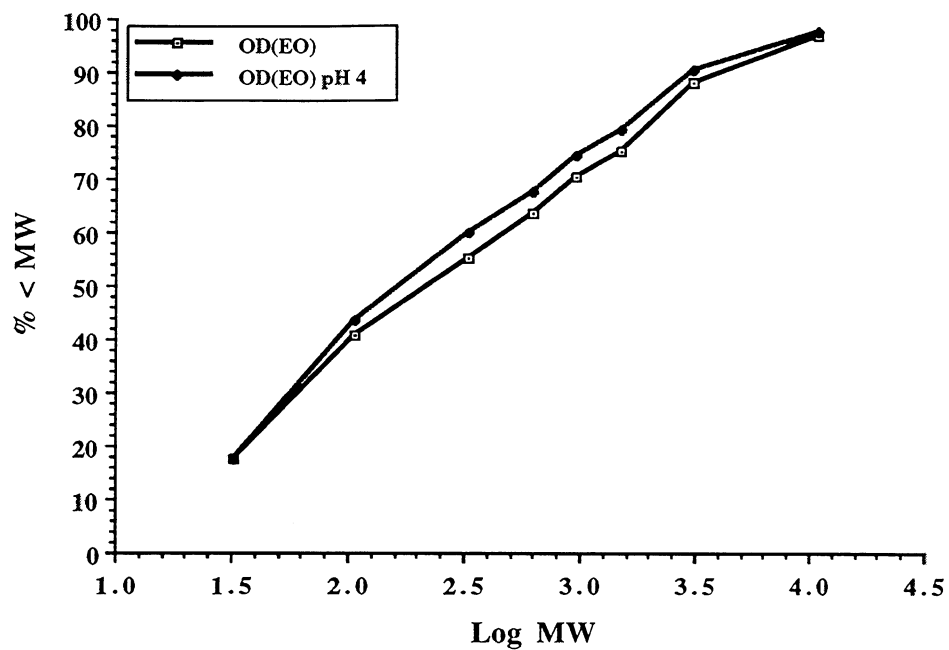


Figure 7. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

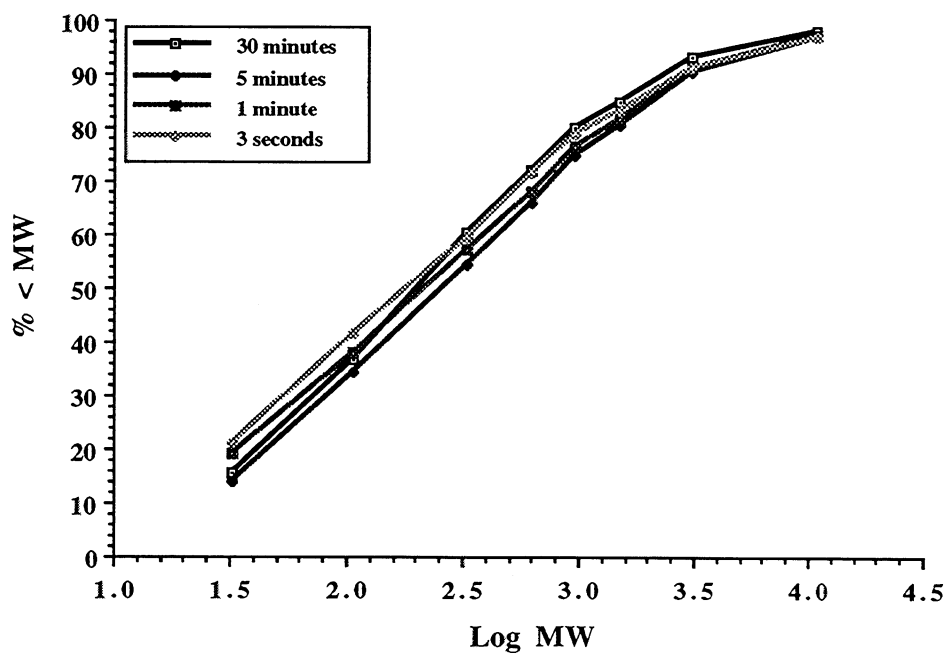


Figure 8. D Stage Effluent Cumulative Molecular Weight Distributions.

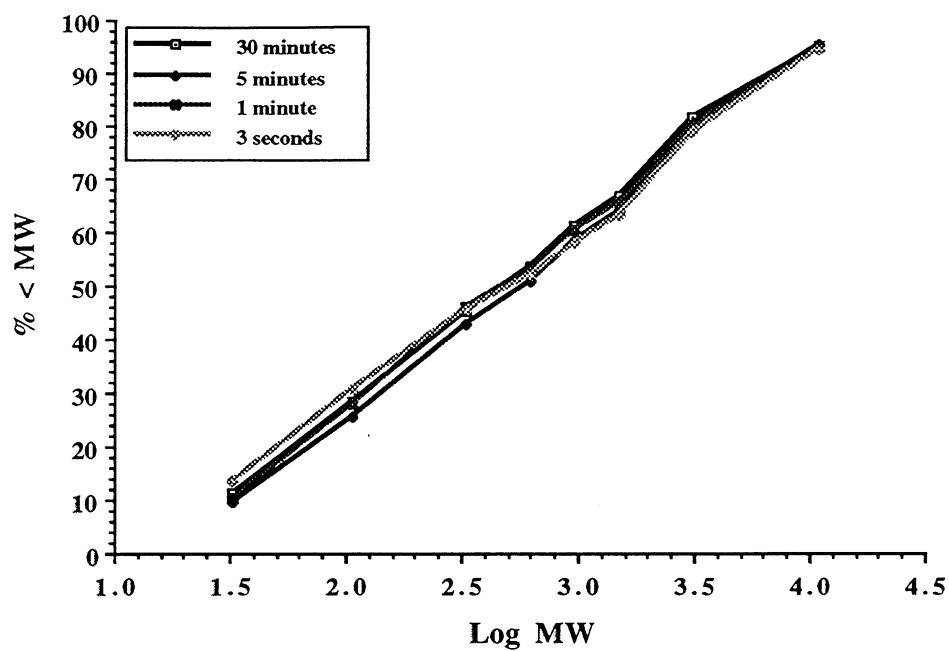


Figure 9. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

Table I. Relative Retention Volume of PEG Standards and Methanol.

Molecular Weight	Relative Retention Volume
19,700	0.000
10,900	0.028
3,070	0.138
1,490	0.308
960	0.383
629	0.506
331	0.691
106	0.897
32	1.000

Table II. Recovery of Effluent TOC.

Bleaching Sequence	D or C Stage Recovery (%)	(EO) Stage Recovery (%)
OC(EO)	75.6	75.7
OD(EO)	85.2	71.7
D(EO)	81.9	76.1
OD(EO)-pH 4 D Stage	78.0	70.3
OD(EO)-30 min D Stage	96.8	77.1
OD(EO)-5 min D Stage	111.8	76.3
OD(EO)-1 min D Stage	98.1	76.6
OD(EO)-3 sec D Stage	104.8	79.0

