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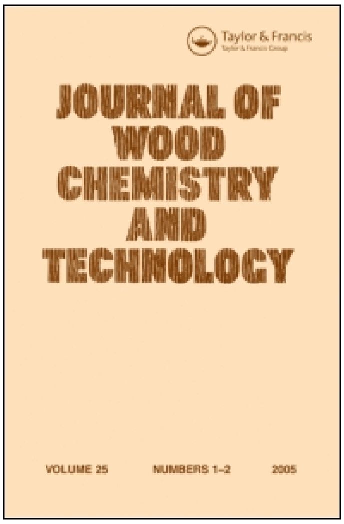

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INFLUENCE OF LIGNINS ON THE DEGRADATION OF CELLULOSE DURING OZONE TREATMENT

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ABSTRACT

Three lignin-carbohydrate model systems were studied to determine the mechanism of the effect of lignin on cellulose degradation during ozone bleaching. The three model systems are: methyl ß-D-glucopyranoside, dextran and fully-bleached kraft pulps in the presence of various lignin model compounds. It was found that the lignin models can both promote and suppress the degradation of the carbohydrate during ozone treatment. The presence of the lignin models can exhibit a protective effect by competing with the carbohydrates for the ozone available in the system. On the other hand, the ozone-lignin reactions give rise to the formation of hydroxyl radicals which promote the carbohydrate degradation.

It is suggested that much more hydroxyl radicals are formed via the ozone-lignin reaction route than via ozone self-decomposition. Among the lignin model compounds studied, the phenolic lignin structures have a more pronounced effect on carbohydrate degradation. This is explained by the easier formation of hydroxyl radicals from phenolic lignin models than from non-phenolic models.

INTRODUCTION

In order to reduce the environmental impact associated with chlorine-based pulp bleaching, a large development effort has been devoted to incorporate ozone bleaching in totally chlorine-free (TCF) and elemental chlorine-free (ECF) bleaching sequences for the production of fully bleached chemical pulps. However, industrial implementation of ozone pulp bleaching is still limited by the severe cellulose degradation which occurs during this stage.

The cellulose degradation during ozone bleaching is influenced by several factors. One of these factors is the amount and structure of the residual lignin of the pulp entering the ozone bleaching stage. The effect of lignin on cellulose degradation during ozone bleaching is quite complicated, and both a protective and a degrading effect have been reported in the literature. Jacobson et al. [1] found that, at the same ozone charge, fully bleached pulp showed a greater viscosity loss than unbleached pulps with a relatively high residual lignin content (kappa number 18 and 26), suggesting a protective effect of lignin. However, the biggest viscosity loss was obtained, not by the fully bleached pulp, but when pulp had a kappa number of 3, which indicates a degrading effect of lignin. A similar result was also obtained by Chirat and Lachenal [2] who showed that pulps with a low lignin content (kappa number 7.4 and 5.2) exhibits a higher viscosity loss than the corresponding fully bleached pulps.

The present study is undertaken to clarify the role of residual lignin during ozone bleaching. The approach taken was to study the effect of various lignin model compounds on the degradation of two carbohydrate model compounds and on that of fully bleached kraft pulp. The results should also help to identify which residual lignin structures in particular promote cellulose degradation. This information is not only useful in designing appropriate TCF bleaching sequences which include an ozone bleaching stage, but also is important for the understanding of the effect of bleach spent liquor recirculation on the cellulose degradation during ozone bleaching stage.

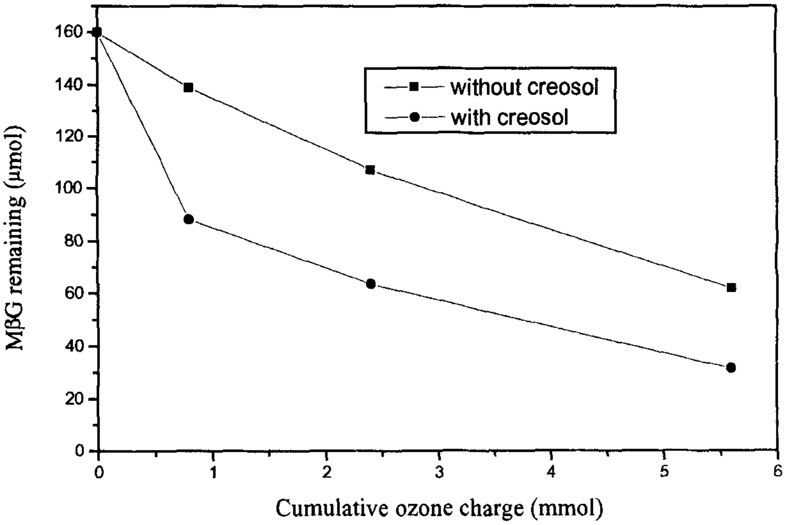


FIGURE 1. Effect of the creosol addition on the degradation of MßG during ozone treatment in water.

RESULTS AND DISCUSSION

Ozonation of Methyl-ß-D-Glucopyranoside in the Presence of Lignin Model Compounds

Effect of creosol

The reaction of methyl ß-D-glucopyranoside(MßG) during ozonation in water with and without the presence of a phenolic lignin monomer, creosol, is shown in Fig. 1. The initial pH was not adjusted and the end pH after the ozone treatment was 3.10 and 2.87 respectively. It can be seen that the reaction of MßG is enhanced by the presence of creosol. Furthermore, the promoting effect occurs mostly in the initial phase of the ozonation when creosol is still present in the system. After an ozone charge of 0.8 m mol, when creosol is totally

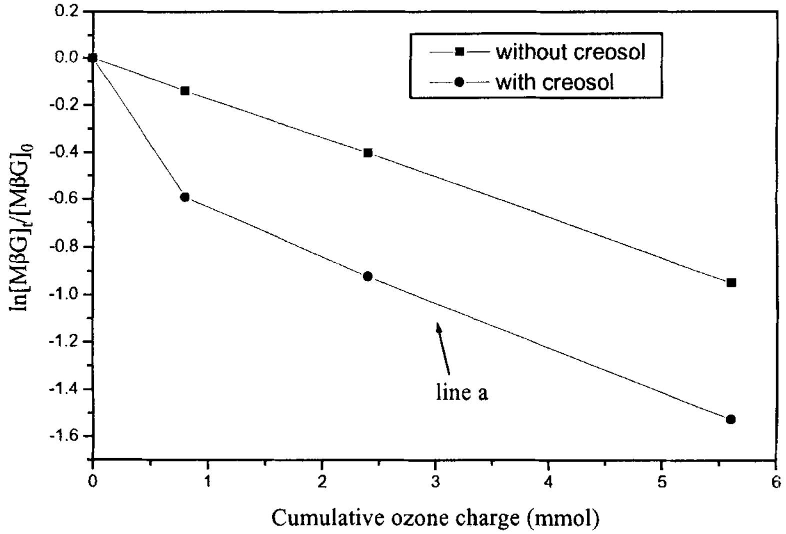
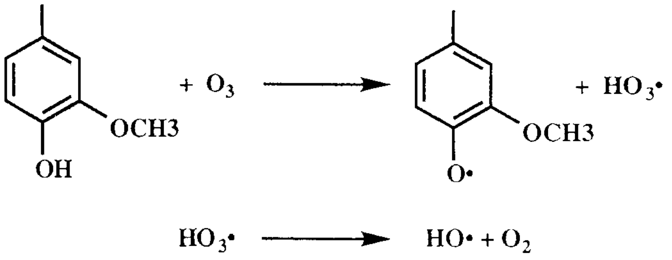


FIGURE 2. Quantitative determination of the MßG degradation due to the creosol addition during ozone treatment in water.

consumed by reaction with ozone, the reaction of MßG slows down and proceeds approximately at the same rate as in the experiment without creosol addition.

In order to evaluate quantitatively the reaction of MßG caused by the presence of creosol, the data in Fig. 1 were plotted as $\ln[\text{MßG}]_t/[\text{MßG}]_0$ versus ozone charge (Fig. 2). It can be seen that, for the MßG/creosol system, a straight line (line a) can be drawn through the three data points where creosol is no longer present in the system. The slope of this line is slightly steeper than that without creosol addition. The straight lines produced suggest that the reaction of MßG is a pseudo first order reaction. By extrapolating line a to zero ozone charge, an extrapolated value of $\ln[\text{MßG}]_t/[\text{MßG}]_0 = -0.43$ is obtained. This corresponds to the reaction of MßG by 35% due to the presence of creosol, i.e. the presence of creosol enhances the reaction of MßG by 35%.

It is known that the reaction of MßG in water is caused by both in-situ generated hydroxyl radicals, and ozone direct attack though the former is more

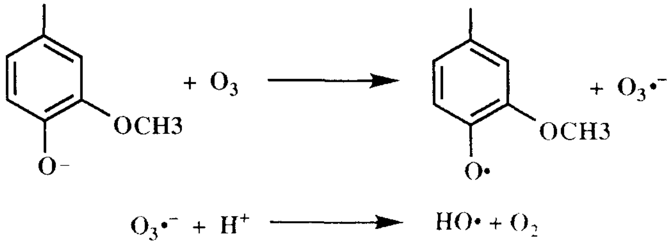


SCHEME 1. Formation of hydroxyl radicals via hydrogen abstraction from a phenolic compound

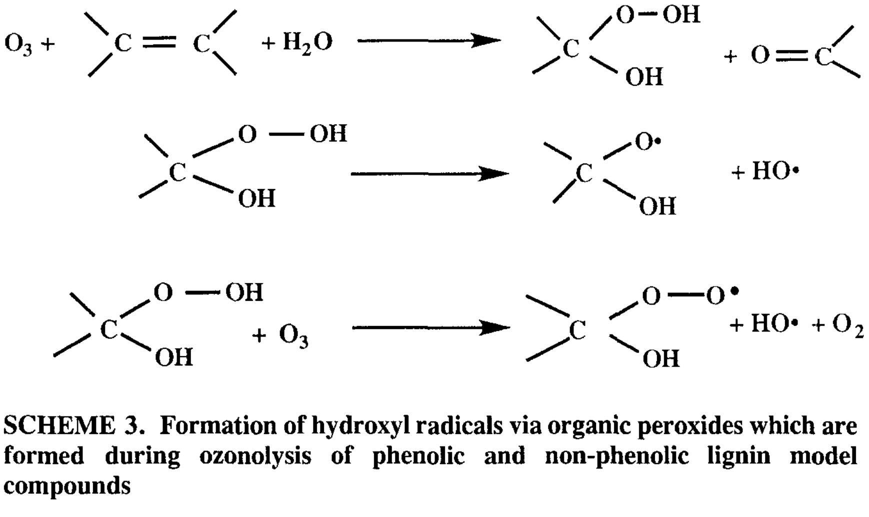
important in this particular case [3]. When a lignin model compound is added to this system at the same concentration as the carbohydrate, the ozone will be mostly consumed by the lignin model compound due to its much higher reactivity towards ozone [4]. As a result, the ozone concentration in solution will be reduced so that the contribution of the direct attack on MßG will become even smaller since the direct attack on the MßG is first order in ozone concentration [5]. An enhanced carbohydrate reaction was, however, observed when creosol was added (see Fig. 1). This suggests that the increased reaction is caused by additional hydroxyl radicals formed from the ozone-lignin reaction. Several possible mechanisms for this radical formation may be suggested [6,7]:

A. Formation of hydroxyl radicals via hydrogen abstraction from a phenolic compound (Scheme 1); B. Formation of hydroxyl radicals via phenolate formation and a one-electron transfer (Scheme 2); C. Formation of hydroxyl radicals via organic peroxides which are formed during ozonolysis of phenolic and non-phenolic lignin model compounds (Scheme 3). All these reaction routes lead to formation of hydroxyl radicals which explains the increased reaction of MßG observed in Fig. 1.

Mechanism B (Scheme 2) requires that the phenolic group be dissociated to form a phenolate anion, which is pH dependent. In order to find out if the promoting effect of creosol is still present at acidic conditions as in conventional



SCHEME 2. Formation of hydroxyl radicals via phenolate formation and a one-electron transfer



SCHEME 3. Formation of hydroxyl radicals via organic peroxides which are formed during ozonolysis of phenolic and non-phenolic lignin model compounds

ozone pulp bleaching, a new series of experiments was performed at an initial pH of 2 (adjusted with sulphuric acid). A separate experiment confirmed that the MßG degradation due to acid hydrolysis did not occur under the present condition because of the low temperature (25°C). The results in Fig. 3 show that the presence of creosol at pH 2 still enhances the MßG reactions. Similar to Fig. 2, the data in Fig. 3 is replotted as $\ln[\text{MßG}]_t/[\text{MßG}]_0$ versus ozone charge (Fig. 4). By extrapolating line b to zero ozone charge, an extrapolated value of

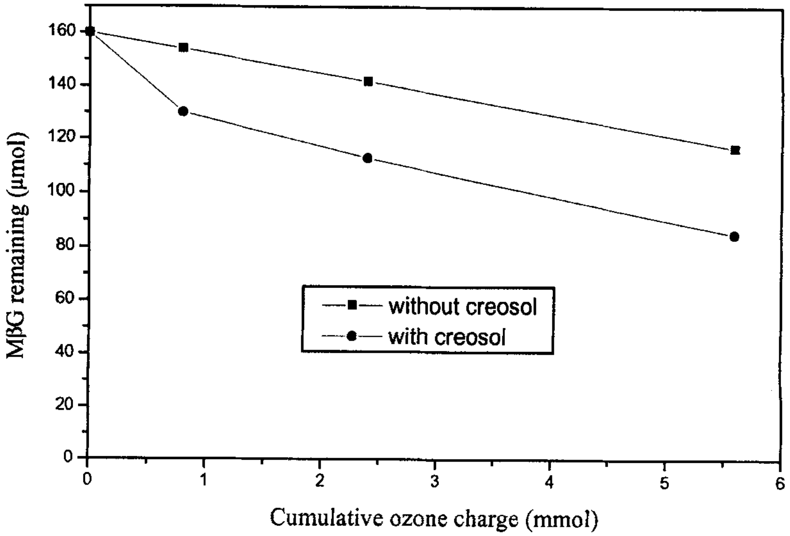


FIGURE 3. Effect of the creosol addition on the degradation of MßG during ozone treatment in water at pH 2.

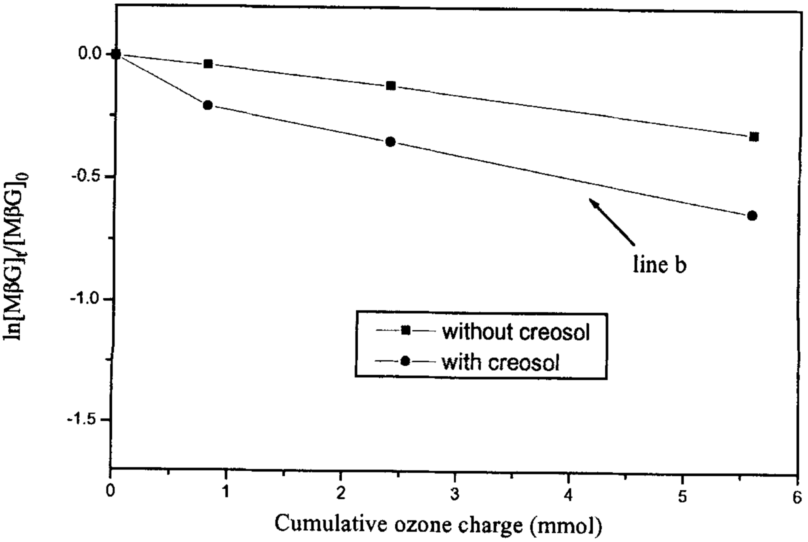


FIGURE 4. Quantitative determination of the MßG degradation due to the creosol addition during ozone treatment in water at pH 2.

TABLE 1
Ozonation of MßG in the Presence of Lignin Model Compounds

Lignin model	O_3 consumed (mmol)	Lignin reacted (mmol)	MßG reacted (mmol)	MßG reacted (%) (on starting MßG)
---	0.89	---	0.24	12.0
creosol	4.35	2.00	0.59	29.5
vanillin	4.19	1.78	0.75	37.5
catechol	3.85	1.94	0.58	29.0
veratrole	3.64	1.58	0.44	22.0
3,4-dimethyl benzyl alcohol	3.00	1.47	0.43	21.5

Conditions: MßG: 2 m mol, lignin model compounds: 2 m mol, 200 mL water, O_3 charge: 6 m mol

$\ln[MßG]_t/[MßG]_0 = -0.14$ is obtained. This corresponds to a reaction of MßG by 13% due to the presence of creosol when the initial pH is adjusted to 2. Therefore, the promoting effect of creosol on the reaction of MßG becomes smaller in acidic solutions. This suggests that the formation of hydroxyl radicals becomes less when mechanism B is suppressed. However, the formation of hydroxyl radicals, presumably from the ozone-creosol reaction is not eliminated.

Effect of other lignin monomers

The effect of other lignin model compounds than creosol on the reaction of MßG was also investigated (Table 1). It can be seen that both phenolic and non-phenolic lignin models show a promoting effect on the degradation of carbohydrate but the effect of the former appears to be stronger.

Radical formation via mechanisms A (Scheme 1) and B (Scheme 2) applies only to free phenolic compounds. Moreover, it is known that ozonolysis of phenolic lignin models is faster than that of non-phenolic lignin models [4], thus leading to a faster formation of organic peroxides, which in turn might lead to a more extensive formation of radical species. The stronger promoting effect of free phenolic lignin models can thus be explained. It is worthwhile to notice that, among the lignin model compounds studied, vanillin exhibits the strongest effect. The carbonyl function in vanillin weakens the O-H bond of the phenolic hydroxyl group by conjugation with aromatic ring [8] and thus greatly facilitates the radical formation via mechanism A (Scheme 1). For similar reason, the pKa value of vanillin is lower than that of creosol and thus radical formation via mechanism B is also favoured. These arguments might explain that the strongest promoting effect is obtained with vanillin.

It is known that ozone can introduce free hydroxyl groups into aromatic rings by electrophilic substitution [9]. Therefore, free phenolic structures can be formed during the reaction between ozone and non-phenolic lignin models. The hydroxyl radical formation via mechanisms A and B can therefore be valid also for non-phenolic lignin structures. It is also possible that radicals can be formed directly via mechanism C without involvement of free phenolic hydroxyl groups.

In comparison of the effect of veratrole and that of 3,4-dimethoxyl benzyl alcohol, it is observed that these two models basically show the same effect, indicating that alcoholic groups in the side-chain do not significantly influence the radical formation from the ozone-lignin reaction.

Effect of addition of radical scavenger

In order to scavenge the hydroxyl radicals which are produced from self-decomposition of ozone and from the ozone-lignin reaction, methanol is added during ozone treatment of MßG in the presence of creosol, and the results are presented in Fig. 5. For comparison, the reaction of MßG in 1.0% MeOH is also included in the same figure. In all three cases creosol is completely consumed at an ozone charge of 0.8 m mol. As can be seen in the figure, the addition of 3.0% MeOH(0.93 M) reduces the reaction of MßG drastically. Increasing the methanol concentration to 70% (19 M) further reduces the degradation. However, the degradation is still larger than that in 1.0% MeOH without the presence of creosol. These results demonstrate that the carbohydrate reaction

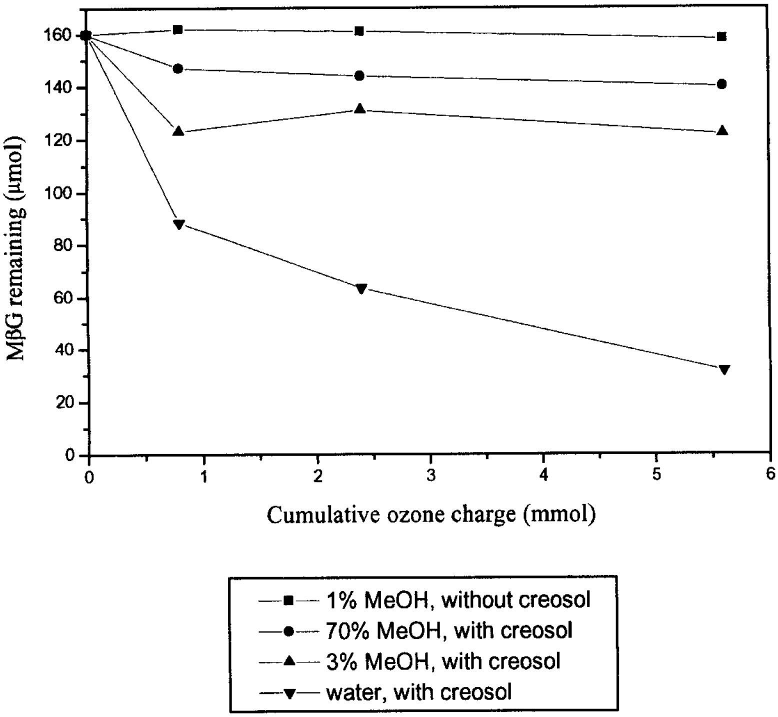


FIGURE 5. Effect of the presence of methanol on the degradation of MßG due to the creosol addition during ozone treatment.

cannot be completely eliminated when lignin is present even at a methanol concentration of 70%.

The initiation reaction for the self-decomposition of ozone in aqueous alkaline media to produce radical species has a rate constant between 40 - 70 M^{-1}s^{-1} [10,6]. In acidic aqueous media, the rate constant for the initiation reaction of ozone decomposition is significantly lower [11]. The direct ionic reaction between ozone and MßG should also proceed at a slow rate [12,5], which means that eventual radical formation from ozone-carbohydrate reaction can be expected to be slow. On the other hand, ozone reacts with phenolic compounds at a much higher rate. For example, a rate constant of 3.0 x 10^4 M^{-1}s^{-1} is obtained for undissociated pcresol. For dissociated *p*-cresol, a rate constant higher than 1.4 x 10^9 M^{-1} s^{-1} has been estimated [13]. In the case of creosol, it is therefore reasonable to assume that the rate constant lies in a range of 10^4-10^9 M^{-1} s^{-1} which is much higher than the rate constant of ozone self-decomposition or ozone-carbohydrate reaction. This means that the radical formation via mechanism A and/or B proceeds at a much higher rate than that via ozone self-decomposition or ozone-carbohydrate reaction. Therefore, a much larger concentration of radical scavenger is needed in order to eliminate the effect of radical formation from the ozone-creosol reaction than that from ozone self-decomposition or ozone-carbohydrate reaction. This may explain the observation that there is a more extensive reaction of MßG with creosol present even in 70% methanol as compared to that in 1.0% methanol without the addition of creosol.

Ozonation of Dextran in the Presence of Lignin Model Compounds

In order to obtain information regarding the effect of lignin on the chain cleavage of polymeric carbohydrate compounds, a carbohydrate polymer, dextran, was subjected to ozone treatments in aqueous solution containing 2.2% tert-butanol in the presence of creosol or veratrole. Fig. 6 shows the relative changes in molecular weight of dextran versus ozone charge, and Fig. 7 shows the amount of lignin model compound remaining during the same ozonation. As is illustrated in Fig. 6, the presence of 2.6 mmol creosol in the 20 g/L dextran solution promotes the degradation of dextran until creosol is practically consumed (see Fig. 7). Subsequently, the degradation of dextran proceeds approximately at the same rate as that without the presence of a lignin model compound. On the other hand, addition of the same amount of veratrole showed a protective effect. When veratrole is almost consumed after 6.40 m mol ozone charge (see Fig. 7), the degradation proceeds again at about the same rate as that without the addition of lignin model.

It has been shown that the depolymerization of dextran in 2.2% aqueous tert-butyl alcohol is due to the direct ionic attack by ozone [3]. When lignin model

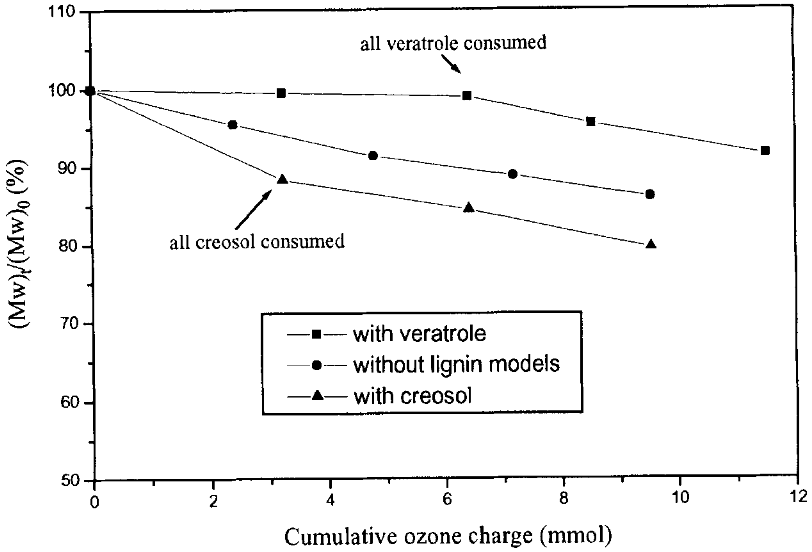


FIGURE 6. Effect of the presence of creosol or veratrole on the degradation of dextran during ozone treatment in 2.2% tert-butanol.

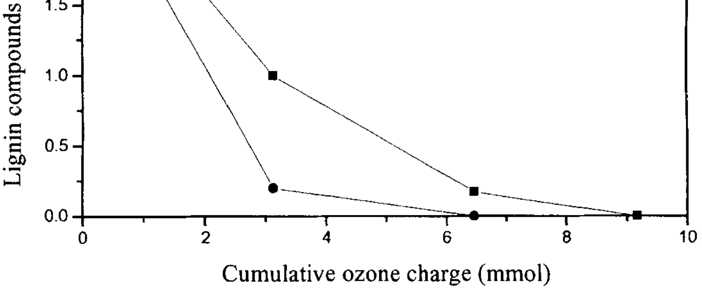


FIGURE 7. The amount of creosol or veratrole remaining during ozone treatment of dextran in 2.2% tert-butanol.

compounds are added, less ozone will be available for direct attack of dextran because ozone is consumed by lignin in a parallel reaction (competition mechanism). On the other hand, the addition of lignin model compounds results in the formation of hydroxyl radicals which will promote the dextran degradation if the concentration of the radical scavenger (tert-butyl alcohol) is insufficient for their elimination. In the case of creosol, the latter effect is dominating, so that the addition of creosol leads to increased degradation of dextran. In the case of veratrole, the competition mechanism is dominating, so that an overall protective effect is observed. The small reduction in the molecular weight of dextran when veratrole is still present suggests that the concentration of 2.2% tert-butyl alcohol is sufficient to scavenge the additional radicals generated by the ozonation of veratrole. This is also consistent with the less rapid consumption of the lignin model and presumably slower formation of hydroxyl radicals for non-phenolic lignin compounds as compared to that of phenolic lignin compounds.

Ozonation of Fully Bleached Kraft Pulps in the Presence of Lignin Model Compounds

Ozone treatments of fully bleached pulps were performed at pH 2 and in the presence of creosol and veratrole. The results are summarised in Table 2. For ozonation in 3.0% MeOH without any addition of lignin models (Exp. No. 1), the pulp viscosity drops from 23.2 mPa·s to 18.9 mPa·s after ozonation. Since the rate of self-decomposition of ozone in this system is relatively small, the presence of 3.0% MeOH without any lignin model is sufficient for effective capture of hydroxyl radicals. Therefore the observed reduction in the pulp viscosity from 23.2 to 18.9 mPa·s in Exp. No. 1 must be mostly due to the direct attack of ozone on cellulose. When 0.25% creosol is added to the fully bleached pulp, the pulp viscosity drops from 23.2 mPa·s to 17.7 mPa·s (Exp. No.2), i.e. an extra viscosity loss of 1.2 mPa·s compared to that without any creosol. An even higher viscosity drop is observed with addition of 0.5% creosol (Exp. No.3). Additions of 0.25 % and 0.5% veratrole also lead to an extra

TABLE 2
Ozonation of Fully Bleached Pulp (Viscosity = 23.2 mPa·s) in the Presence of Lignin Model Compounds

Exp. No.	Lignin added (% on o.d. pulp)	Lignin remaining (% on o.d. pulp)	O_3 charge (% on o.d. pulp)	O_3 consumed (% on o.d. pulp)	Viscosity (mPa·s)	Δ viscosity (mPa·s)
1	Blank[a]	---	2.0	0.10	18.9	---
2	Creosol[a] (0.25)	0	2.0	0.28	17.7	-1.2
3	Creosol[a] (0.5)	0	2.0	0.43	17.4	-1.5
4	Creosol[a] (1.0)	0	2.0	0.92	19.0	+0.1
5	Veratrole[a] (0.25)	0	2.0	0.28	17.9	-1.0
6	Veratrole[a] (0.5)	0	2.0	0.40	18.3	-0.6
7	Blank[b]	---	2.0	0.11	20.3	---
8	Creosol[b] (1.5)	0	2.0	1.25	21.0	+0.7
9	Veratrole[b] (1.0)	0	2.0	0.95	21.3	+1.0

[a]: 3.0% MeOH as impregnating solvent

[b]: 10% MeOH as impregnating solvent, Δ viscosity = (viscosity of the pulp ozonated in the presence of the lignin - viscosity of the pulp ozonated in the absence of the lignin)

viscosity loss, although to a lesser extent than that at the same addition of creosol (Exp. No.5 and 6). However, at higher loadings of creosol or veratrole (Exp. No.4, 8, 9), the viscosity drop becomes less than that of experiment No. 1, so that a protective effect of the lignin models is obtained.

These results can also be interpreted in terms of the competition and radical mechanisms used to explain the dextran degradation results in the previous section of this paper. At the lower charge of lignin , the radical mechanism dominates, whereas at the higher additions of lignin the competition mechanism is prevalent, leading respectively to a degrading and protective effect. These results are also consistent with the findings of Jacobson et al. [1] and Chirat et al. [2] that the lignin in low-kappa and high-kappa number pulps leads respectively to enhanced and reduced cellulose degradation during pulp bleaching compared to that of fully bleached pulp.

The larger promoting effect observed with creosol than with veratrole at the low charge levels and, the smaller protective effect observed with creosol than with veratrole at the high charge levels (compare Exp. No 8 and 9) again confirm the easier formation of radical species when phenolic lignin structures are involved.

Comparison of the results from fully bleached pulp with those from the carbohydrate model compound studies, representing a heterogeneous reaction system and a homogeneous reaction system respectively, reveals that the effect of radical species on the carbohydrate degradation is much less in the former case. This is probably due to the fact that the radical species generated from the ozone-lignin reactions are so reactive that they are consumed rapidly by the immediate surroundings (next to the lignin gels) and likely will not diffuse further into the carbohydrate-rich regions (cellulose gels). However, in a homogeneous system, the carbohydrate model compounds are immediately available to the in-situ generated radical species, resulting in more extensive reactions.

CONCLUSIONS

The present study shows that the presence of lignin model compounds can both suppress and promote the carbohydrate degradation during ozone bleaching. The protective effect of the lignin presence is due to the fact that it competes with carbohydrates for the ozone available in the system. On the other hand, the ozone-lignin reaction gives rise to formation of hydroxyl radicals which promotes the carbohydrate degradation.

The results suggest that much more hydroxyl radicals are formed via ozone-lignin reactions than via ozone self-decomposition or ozone-carbohydrate reaction. Compared to non-phenolic lignin structures, phenolic lignin structures give rise to a more rapid formation of hydroxyl radicals, thus resulting in a more pronounced effect on carbohydrate degradation. Therefore in order to reduce the severe cellulose degradation during ozone pulp bleaching, it appears necessary to trap as many of the radicals arising from the ozone-lignin reaction as possible and to reduce the rate of reaction of the direct attack of ozone on cellulose.

EXPERIMENTS

Creosol, veratrole, methyl-ß-D-glucopyranoside (MßG) and dextran with a weight averaged molecular weight of 74,800 were purchased from Aldrich. the molecular weight standards, pullulan, were purchased from SHOWA DENKO K.K. Japan. Chemicals and solvents were A.C.S. reagent grades. The water used was first distilled and then deionized. The fully bleached pulp used in this study was produced from hemlock kraft pulp by a DEDED bleaching sequence. Its viscosity is 23.2 mPa.s and its brightness 89% ISO.

Ozonation of MßG

An aqueous solution of the appropriate solvent (200 mL) containing 160 μmol (unless otherwise specified) with or without the addition of a lignin model compound of 160 μmol (unless otherwise specified) was ozonated at 25°C in a gas washing bottle by bubbling ozone/air gas (10.6 mg O_3/L air) into the solution at a flow rate of 0.2 L/minute. Ozone was generated from dry air (dew point -60°C) by a PCI model-1 ozone generator. The duration of ozonation was calculated from the ozone charge required and the ozone production rate. When the desired ozone charge was reached the ozone supply was stopped and the reaction system was immediately purged with air to remove any residual ozone remaining in the solution. Lignin model compounds and MßB were analyzed by Gas Chromatography (GC) [3].

Ozonation of Dextran

Dextran (4 g) with averaged molecular weight of 74,800 was dissolved in an aqueous solution of tert-butyl alcohol (2.2%) (200 mL) with or without the addition of either 2.6 m mol of creosol or 2.6 m mol of veratrole. The solution was placed in a gas-washing bottle and ozonated at 25° C in the same fashion as for MßG. Creosol and veratrole were analyzed by GC. The molecular weight of dextran was determined by Gel Permeation Chromatography (GPC) [3], which was calibrated by Pullulan standards.

Ozonation of Fully Bleached Pulps

4.27 g of air-dried fully bleached pulp (corresponding to 4.0 g o.d. pulp) prepared from a DEDED bleaching sequence was soaked in 150 mL 3.0% or 10% methanol solution in which a certain amount of creosol or veratrole had been dissolved. The pH of this solution was adjusted to pH 2 by 2 M sulphuric acid before it was added to the pulp. After the pulp was kneaded for 10 minutes in a plastic bag, it was pressed to 40% consistency and then fluffed. Ozone treatments were performed at 25 °C in a rotating spherical glass reactor. The O_3/air gas flow was 1.0 L/min and the O_3 concentration in the gas phase was 48 mg/L. After the desired ozone charge was reached, the glass reactor was immediately purged with air from a separate gas line for 4 min and then the pulp was taken out of the reactor. The pulp after ozonation was mixed with 50 mL water and kneaded for 10 minutes in a plastic bag. Finally some liquid was squeezed out and used for analysis of the remaining amount of creosol or veratrole by GC. The ozonated pulp was finally thoroughly washed again with water prior to the viscosity determination.

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