

Further Understanding on the Cause of Cellulose Degradation during Ozone Bleaching

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ABSTRACT

Kraft pulps, both fully bleached and unbleached were subjected to ozone bleaching in the presence of various solvents. The objective was to evaluate the contribution of the ozone direct attack and secondary radical attack to the cellulose degradation during the course of ozone bleaching. During ozonation of the fully bleached pulp, the viscosity loss at the same ozone charge is largest for the 90% acetic acid, followed by water, then 70% tert-butanol and finally 70% methanol. These results cannot be explained by the radical theory and we concluded that the ozone direct attack is mainly responsible for the cellulose degradation in such a system. For the unbleached pulp, it was found that the presence of organic solvent significantly decreases the viscosity loss during ozone bleaching. This is due to the radical scavenging effect of the solvents. Therefore, we concluded that in an unbleached pulp system the cellulose degradation is mainly due to the attack of radical species, particularly hydroxyl radicals, which are generated from the ozone-lignin reactions.

INTRODUCTION

Cellulose degradation during ozone bleaching can be influenced by the amount and structure of the residual lignin of the pulp entering the ozone stage. The effect of lignin on cellulose degradation during ozone bleaching is complicated. Both a protective and a promotive effect have been proposed in literature [1,2]. We found earlier that more carbohydrate degradation occurs when a carbohydrate model compound (methyl- β -D-glucoside) is treated with ozone in the presence of a lignin model compound than without the lignin model compound [3]. This was explained by the hypothesis that hydroxyl radicals are formed from ozone-lignin reactions and these hydroxyl radicals are mainly responsible for the degradation of the carbohydrate model compound studied. This conclusion was supported by the work of a Japanese research group [4], however, it may not be directly applied to the ozonation of pulp. During ozone bleaching of pulp, since it is a heterogeneous reaction, the radicals produced from lignin-ozone reactions may not live long enough to travel to the cellulose region of the pulp fibers, and they can be consumed by lignin, thereby preventing the carbohydrates from being attacked. The objective of this study is to determine the effect of both ozone direct attack and secondary radicals attack on cellulose degradation during ozone bleaching of pulp. Our approaches are (i) to compare the ozonation of fully bleached pulp with the ozonation

of unbleached pulp and (ii) to perform the ozonation in the presence and absence of radical scavengers. The addition of various organic solvents, such as acetic acid, methanol, ethanol and tert-butyl alcohol, is known to have a significant protective effect on the selectivity of ozone bleaching [5,6,7]. Two different mechanisms have been suggested to explain the positive effect of these organic solvents on the lignin-cellulose selectivity. The first is that the solvents function as scavengers of hydroxyl radicals which are considered to be responsible for the cellulose degradation [5]. The other is that the solvents deswell the cellulose and swell the lignin fractions of pulp. As a result the cellulose and lignin portions of the pulp are respectively less and more accessible to ozone, thus explaining the improved selectivity [4,8]. In this paper these two mechanisms are further examined and evidence for the prevalence of the first will be given.

EXPERIMENTAL

Pulp Preparation Technique

A calculated amount of an organic solvent was added to never dried pulp of a consistency of about 30% to obtain the desired concentration of the organic solvent in the aqueous phase. The pulp was well mixed with the solution by kneading in a polyethylene bag. The pH of the liquid phase was adjusted to around 2 with the addition of 4N H_2SO_4 . The pulp was pressed

to about 40% consistency and very well fluffed at room temperature.

Ozonation Technique

Ozone bleaching was performed in a standard rotovap equipment modified with a fritted glass dispersion tube inserted in the rotating round bottom flask where the fluffed pulp was placed. The rotating flask was immersed in a glycol bath for temperature control. Ozone (in air) was introduced through the gas dispersion tube into the flask and the unreacted ozone leaving the flask was captured in a gas washing bottle filled with a KI solution. Immediately after the completion of ozonation the flask was purged with N₂ to quickly remove the unreacted O₃. The purging is particularly important when ozonating fully bleached pulp. The ozone consumption by the pulp was determined by following the iodometric titration. The followings are the general reaction conditions: temperature 25°C, consistency 40%, pH adjusted to 2, flow rate 1 lt/min, O₃ concentration in the gas phase~ 48 mg/lt.

former. This difference is relatively small compared to the total viscosity loss of 7.6 mPa.s from 23.2 to 15.6 mPa.s for H₂O impregnated, fully bleached pulp at an ozone charge of 3%. A conclusion which can be drawn from these results is that the protective effect of 70% MeOH (and 70% t-BuOH) on the cellulose degradation is small for fully bleached pulp, while impregnation with 90% HAc leads to increased cellulose degradation compared to that of H₂O impregnated pulp.

It has been shown from previous studies [9,10] that the formation of hydroxyl radical occurs through three pathways: ozone decomposition catalyzed by transition metal ions, the ozone-lignin reactions and the ozone self-decomposition. Since, the lignin and transition metal contents of fully bleached pulp are known to be very low [2], the formation of hydroxyl radicals from the first two pathways can be neglected. Also, ozone self decompositions at a pH 2 is of minor importance as has been demonstrated by Pan [11] and by our own results of the ozonation of methyl β -D-glucopyranoside (M β G) [9]. Methanol, t-butyl alcohol and acetic acid are well known scavengers of hydroxyl

Table 1. Ozonation of Fully Bleached Hemlock Kraft Pulp

H ₂ O			70% MeOH			70% t-Butanol			90% HAc		
O ₃ chge. (%)	O ₃ conc. (%)	Visc. (mPa.s)	O ₃ chge. (%)	O ₃ conc. (%)	Visc. (mPa.s)	O ₃ chge. (%)	O ₃ conc. (%)	Visc. (mPa.s)	O ₃ chge. (%)	O ₃ conc. (%)	Visc. (mPa.s)
0	--	23.2	0	---	23.2	0	---	23.2	0	---	23.2
1.0	0.06	19.1	1.0	0.078	20.7	1.0	0.087	20.5	---	---	---
2.0	0.104	17.4	2.0	0.168	18.8	2.0	0.151	18.3	2.0	0.116	14.8
3.0	0.129	15.6	3.0	0.269	17.0	3.0	0.259	15.8	---	---	---

Conditions : 25°C, 40% consistency, pH 2 (except for 90% HAc), gas flow rate 1 lt/min, O₃ gas concentration 48 mg/lt, 4 g o.d. pulp, Bleaching sequence to produce the fully bleached pulp: DEDED

RESULTS AND DISCUSSION

Fully Bleached Pulp

The results obtained with fully bleached pulp are summarized in Table-1. The results show that the viscosity loss at the same ozone charge is largest for the 90% acetic acid (HAc) system, followed by H₂O, then 70% t-BuOH and finally 70% methanol (MeOH). However, when the viscosities of the H₂O impregnated pulp are compared with those of the 70% MeOH impregnated pulp, at the same ozone charge, it is seen in Table 1 that in all cases the viscosities of the latter pulps are only 1.4-1.6 mPa.s higher than that of the

radicals [12]. Therefore, the cellulose degradation during ozonation of fully bleached pulp impregnated with high concentrations of these radical scavengers will be mostly, if not solely, due to direct attack of ozone. However, it is difficult to draw any conclusion regarding the relative importance of hydroxyl radical attack and direct ozone attack in the case of fully bleached pulp impregnated with acidified water based on a comparison with the cellulose degradation of the pulps impregnated with 70% MeOH, 70% t-BuOH or 90% HAc. The reason for this is that the ozone concentration in these solvent systems is different from that of the acidified water system so that the degree of direct ozone attack changes. In other words, the reduction (or elimination) of cellulose radical attack in

these solvent systems is accompanied by a change in the amount of direct ozone attack on cellulose. For example, the viscosity drop of 8.4 mPa.s (from 23.2 to 14.8 mPa.s) for fully bleached pulp impregnated with 90% HAc at 2% ozone charge is significantly larger than that of the pulp impregnated with water 5.8 mPa.s (from 23.2 to 17.4 mPa.s). It is also known [9] that the saturated O_3 concentration in 90% HAc is about four times higher than that in an acidified water. Therefore, the increased cellulose degradation for fully bleached pulp impregnated with 90% HAc must be due to an increased rate of direct attack of ozone as a result of the higher ozone concentration in 90% HAc, despite the suppression of cellulose degradation by the radical scavenging effect of acetic acid.

It was verified that the acid hydrolysis of cellulose by acetic acid itself was not responsible for the increased viscosity loss in the 90% HAc, fully bleached pulp system. This was shown by repeating exactly the ozonation procedure with the fully bleached

are generated? As we have pointed out earlier, ozone self-decomposition is not significant under the present conditions. In our experiments, the pulp was acidified to pH 2 by H_2SO_4 at 3% consistency and then pressed to 40% consistency. A majority of manganese and copper plus a significant amount of iron would be removed from the pulp by this process. Our earlier results [13] and other [14] also show that the addition of manganese does not lead to extra viscosity loss during ozonation of unbleached pulp. Addition of iron or copper at 50 ppm level can only cause minor viscosity loss, for example 1-2 mPa.s. Therefore, the majority of radicals responsible for the heavy viscosity loss for unbleached pulp must be formed from the lignin-ozone reactions.

The results in Table 2 can be explained by the hypothesis that hydroxyl radicals generated by the fast reactions between lignin and ozone are mainly responsible for the cellulose degradation. When the unbleached pulp is impregnated with high

Table 2. Ozonation of Unbleached Hemlock Kraft Pulp

H ₂ O				70% MeOH			70% t-Butanol		
O_3 chge. (%)	O_3 conc. (%)	Kappa No.	Visc. (mPa.s)	O_3 chge. (%)	O_3 conc. (%)	Visc. (mPa.s)	O_3 conc. (%)	Kappa No.	Visc. (mPa.s)
0	--	27.7	30.3	0	---	30.3	---	27.7	30.3
1.0	0.82	16.7	18.3	1.0	0.85	24.9	0.84	14.7	22.2
2.0	1.39	9.9	13.2	2.0	1.39	21.7	1.39	7.3	16.6
3.0	1.69	6.1	11.2	3.0	1.77	19.7	1.79	4.2	14.0

Conditions : 25°C, 40% consistency, pH 2, gas flow rate 1 l/min, O_3 gas concentration 48 mg/l,

pulp impregnated with 90% HAc except that now no ozone was added. Duplicate experiments showed a loss in the pulp viscosity of 0.0 and 0.1 mPa.s as a result of this treatment.

Unbleached Pulp

The ozonation results with unbleached Hemlock kraft pulp are summarized in Table 2. Because most of the O_3 supplied to the unbleached pulp is consumed by lignin [11], one would expect a reduced direct attack of ozone on cellulose. However, results in Table 2 and Figure 1 show that in the absence of organic solvent, the viscosity loss for unbleached pulp is much greater than that of fully bleached pulp at the same ozone charge. Obviously the excess viscosity drop of the unbleached pulp is the result of radical attack on cellulose. Now the question arises as to how radicals

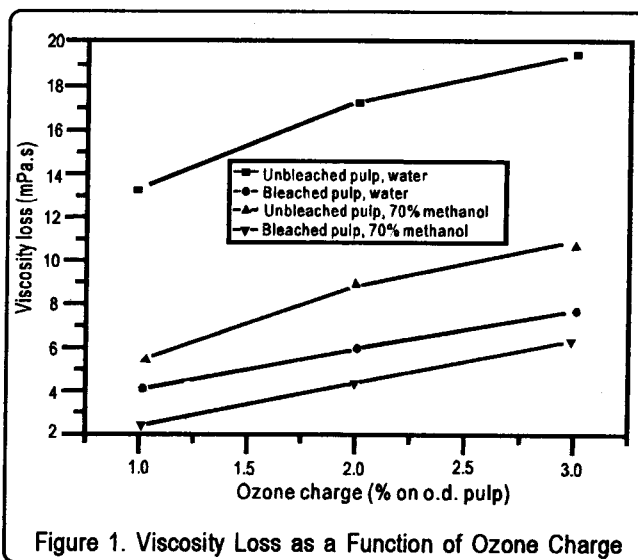
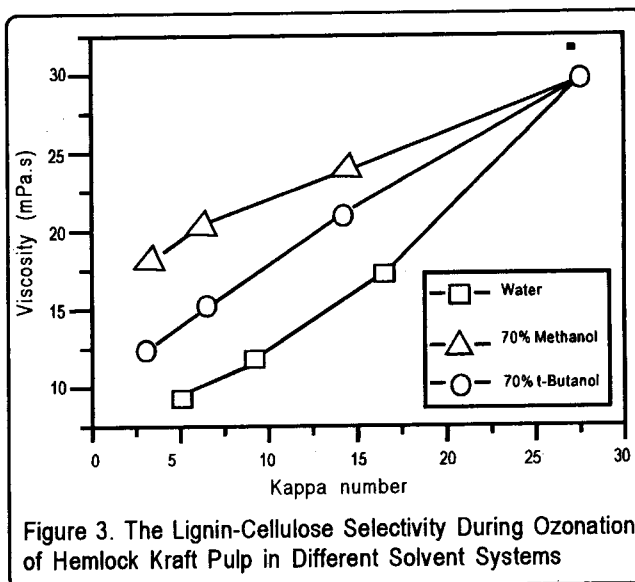
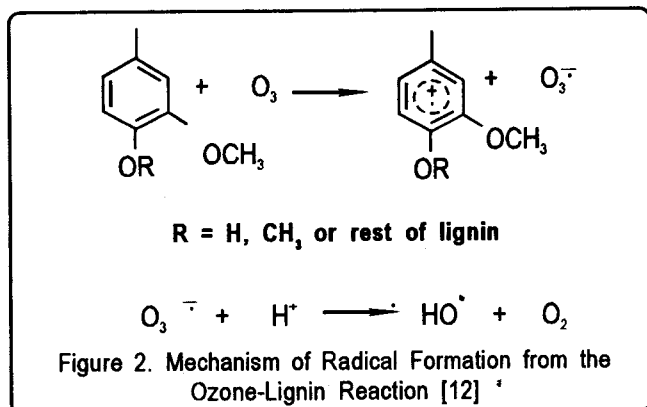


Figure 1. Viscosity Loss as a Function of Ozone Charge

concentration of methanol or tert-butanol, the bleaching selectivity increases dramatically. When water is used as the impregnation liquor, cellulose is mainly degraded by hydroxyl radicals. The improvement in selectivity by either methanol or t-butanol must be related to radical scavenging capability of the solvent. Figure 1 also shows that the viscosity loss of unbleached pulp impregnated with 70% methanol is markedly smaller than that of the water impregnated pulp, but still larger than that of fully bleached pulp.

This suggests that even 70% methanol is not capable of scavenging all the radicals generated by the lignin-ozone reactions. This is consistent with our earlier study [3] of the ozonation of methyl- β -D-glucoside (M β G) in 70% methanol, which showed that M β G is still slightly degraded in 70% methanol when a lignin model, creosol, is present, while M β G is totally protected in 1% methanol in the absence of lignin model compound. The formation of hydroxyl radicals by the fast reactions between ozone and lignin probably occurs through an electron transfer mechanism which can proceed at acidic conditions as shown in Figure-2.

Figure 3 shows the lignin-cellulose selectivity curves for the ozonation of the unbleached pulp in different solvent systems. It can be seen that the ozone selectivity for pulp impregnated with 70% t-butanol is in between that of 70% MeOH and H₂O. The explanation for this behaviour is that radicals are not as well scavenged by 70% t-butanol as by 70% methanol. According to Hoigne and Bader [15], the rate constant of the t-butanol-hydroxyl radical reaction is $0.47 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ while that of the reaction between methanol and a hydroxyl radical is $0.85 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Also the molar concentration of 70% methanol is 2.3 times higher than that of 70% t-butanol, so that the hydroxyl radical scavenging rate of 70% t-butanol is 4.2 times smaller than that of 70% methanol.



Finally, our results do not support the swelling theory. If deswelling is a major factor, the fully bleached pulp impregnated in high concentration of methanol should show much higher viscosity than the pulp impregnated with water. On the other hand, the reality is that the viscosity loss of the fully bleached pulp impregnated with 70% methanol is only 1.4 units higher than the pulp impregnated with H₂O at 3% ozone charge. This difference is not significant compared to 8.5 units shown by the unbleached pulp.

CONCLUSIONS

For the fully bleached pulp impregnated with an acidified aqueous solution of a solvent radical scavenger the cellulose degradation is mostly caused by direct ozone attack. When impregnated with different solvents, the pulp has different viscosity losses during ozonation and it can be explained by the difference in ozone solubility in these solvent systems. For the unbleached pulp, the cellulose degradation during ozone bleaching is mainly caused by hydroxyl radicals generated from the O₃-lignin reactions and the large improvement in lignin-carbohydrate selectivity in the presence of high concentration of alcohols is due to the radical scavenging effect of these solvents.

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