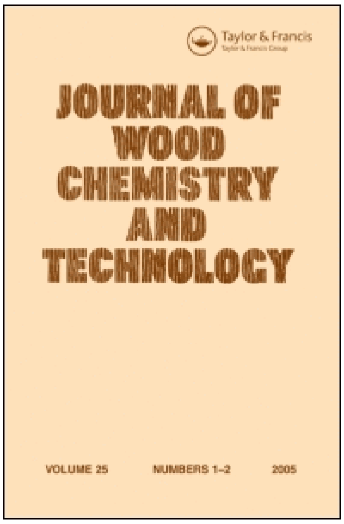


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Initial Delignification and Cellulose Degradation of Conventional and Ethanol-Assisted Ozonation

X. Z. Zhang[a]; G. J. Kang[a]; Y. Ni[a]; A. R. P. van Heiningen[a]; A. Mislankar[b]; A. Darabie[b]; D. Reeve[b]
[a] Dr. Jack McKenzie Limerick Pulp and Paper Centre University of New Brunswick, Fredericton, New Brunswick, Canada [b] Pulp and Paper Centre, University of Toronto, Toronto, Ontario

To cite this Article Zhang, X. Z. , Kang, G. J. , Ni, Y. , van Heiningen, A. R. P. , Mislankar, A. , Darabie, A. and Reeve, D.(1998) 'Initial Delignification and Cellulose Degradation of Conventional and Ethanol-Assisted Ozonation', Journal of Wood Chemistry and Technology, 18: 2, 129 — 157

To link to this Article: DOI: 10.1080/02773819809349573

URL: http://dx.doi.org/10.1080/02773819809349573

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 18(2), 129–157 (1998)

INITIAL DELIGNIFICATION AND CELLULOSE DEGRADATION OF CONVENTIONAL AND ETHANOL-ASSISTED OZONATION

X.Z. Zhang, G.J. Kang, Y. Ni and A. R. P. van Heiningen
Dr. Jack McKenzie Limerick Pulp and Paper Centre
University of New Brunswick, Fredericton, New Brunswick, Canada

A. Mislankar, A Darabie and D. Reeve
Pulp and Paper Centre, University of Toronto
Toronto, Ontario, M5S 1A4

ABSTRACT

It has been proposed that the initial regime of pulp ozonation is a diffusion controlled process, due to the low solubility of ozone and its very fast reaction with lignin. However, whether the process is governed by diffusion on a fibre wall scale (macro diffusion control), on a (micro)fibril scale (micro diffusion control), or by reaction with lignin located on the fibre surface followed by diffusion control is an open question. In order to address this, a 31 kappa Hemlock kraft pulp impregnated with acidified (pH = 2.0) water or acidified (pH = 2.0) ethanol-water (70% w/w) was ozonated at high consistency in a differentially operated packed bed reactor. The cellulose degradation and pulp delignification rates were determined from the change in pulp viscosity and kappa number with ozonation time.

Transmission electron microscopy (TEM) was used to visualize the lignin distribution of $KMnO_4$ stained fibre walls. The TEM pictures clearly show reacted lighter regions at exposed fibre surfaces, which are sharply separated from unreacted darker areas inside the fibre wall. Therefore, these pictures support the macro diffusion theory. The macro diffusion theory was used to describe the progress of delignification and cellulose degradation as a sharp reaction front moving through the fibre wall from the external fibre surface towards the lumen. In agreement with this so called diffusion controlled shrinking core model, the present experimental results show that the delignification and cellulose degradation increase proportionally with the square root of the ozonation time. The effects of ozone partial pressure and ethanol-water impregnation on the delignification and cellulose degradation rates are also described.

INTRODUCTION

It is generally accepted that ozone has a relatively low lignin-carbohydrate selectivity, which limits its charge to less than 1% for practical bleaching of chemical pulp.[1] In recent years intensive research efforts have been directed towards improvement of the selectivity of ozone bleaching. Among others, this has led to the establishment of the optimum operating conditions,[2] the identification of the effect of bleaching sequences,[3,4] a review of additives for viscosity preservation[2] and to the development of solvent assisted ozonation processes.[5,6] Recent studies on the mechanism of oxidation of lignin and cellulose model compounds by ozone have confirmed that the poor selectivity of ozone is caused by the formation of radicals from the ozone-lignin reactions.[7,8,9,10] These radicals attack lignin and cellulose at a comparable rate.[7] Therefore it is likely that the kinetics of cellulose degradation are related to that of delignification during ozone bleaching of chemical pulp.

Because of the high reactivity of ozone towards lignin, mass transfer resistances must be considered when attempting to describe the ozonation kinetics. In high consistency ozone bleaching three rate limiting steps have been identified[11,12,13] as: 1) transfer of ozone from the bulk gas phase to the surface of the fibre wall, 2) dissolution of ozone in the liquid phase at the surface of the fibre wall, followed by diffusional transport of ozone through the fibre wall to the lignin reaction sites, and 3) chemical reaction with lignin. It has been argued that diffusion of ozone through the liquid-filled pores inside the fibre wall is the rate controlling step for delignification.[12,13,14,15] However, this description needs further refinement as to whether the diffusion of ozone is limited on a scale of (macro) pores which span the entire fibre wall, or by (micro) pores on the size level of (micro) fibrils. Furthermore, it has recently been proposed[16] that the lignin-rich fibre surface[17,18,19] might consume a significant amount of ozone before the diffusion resistance inside the fibre wall becomes important. The amount of surface lignin was estimated to be about 10% of all lignin,[19] and covers about 23% - 30% of the surface of pine kraft fibres.[17,18]

If diffusion of ozone at the (micro) fibril scale is rate limiting, it follows that the ozone concentration in the macro pores is uniform throughout the entire fibre wall, and only decreases to zero inside the (micro)fibrils according to kinetics governed by diffusion. In other words, under this so called micro diffusion control a uniform delignification is obtained on a scale of the fibre wall, while non uniform delignification occurs at the (micro)fibril level.

When diffusion through the liquid filled (macro) pores limits the ozone consumption rate during pulp bleaching, the delignification kinetics are governed by the rate of movement of a relatively sharp ozone-lignin reaction front through the fibre wall.[12] This so called macro pore diffusion controlled behaviour is schematically represented in FIGURE 1. Also shown in FIGURE 1 is a sharp cellulose degradation front, resulting from attack by radicals generated by ozone-lignin reactions in the reaction front.

In order to distinguish between the three different mechanisms, i.e. micro diffusion, macro diffusion and surface reaction controlled behaviour, the lignin distribution in the transverse direction through the fibre wall was determined in the present study using TEM-EDXA pictures of manganese stained ozonated fibres. Furthermore, the prevailing mechanism was also tested by comparison of experimental pulp ozonation kinetics of delignification and cellulose degradation with that of the corresponding theoretical rate expressions.

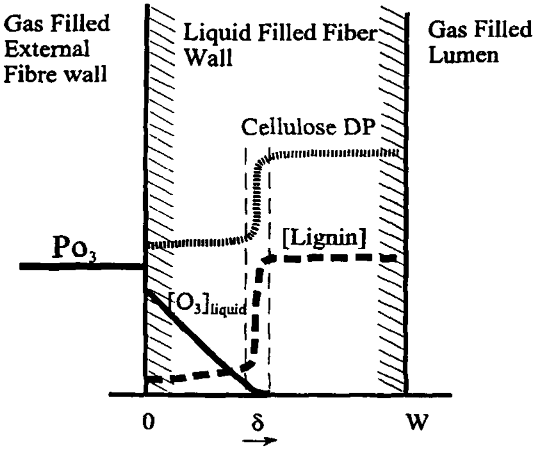


FIGURE 1. Schematic view of macro-diffusion controlled mechanism of ozone bleaching of pulp

EXPERIMENTAL

Due to the high reactivity of ozone with lignin, the ozone delignification kinetics are difficult to determine with commonly used set-ups, such as a rotating flask,[5,12,20] a packed bed,[2,14,21] or a stirred batch reactor.[22] However, if the ozone supply rate is kept at such a high level that the ozone concentration remains constant around individual fibres, then the intrinsic kinetics of ozone bleaching can be determined by measuring the changes in the lignin content and pulp viscosity as a function of ozonation time. An experimental set-up, which satisfies these requirements is a so-called differential reactor consisting of a thin packed bed of well fluffed pulp fibres.

Differential Reactor and Experimental Set-up

A schematic flow diagram of the experimental system is given in FIGURE 2. The differential reactor is a 6 cm (i.d.), 350 ml glass wash bottle,

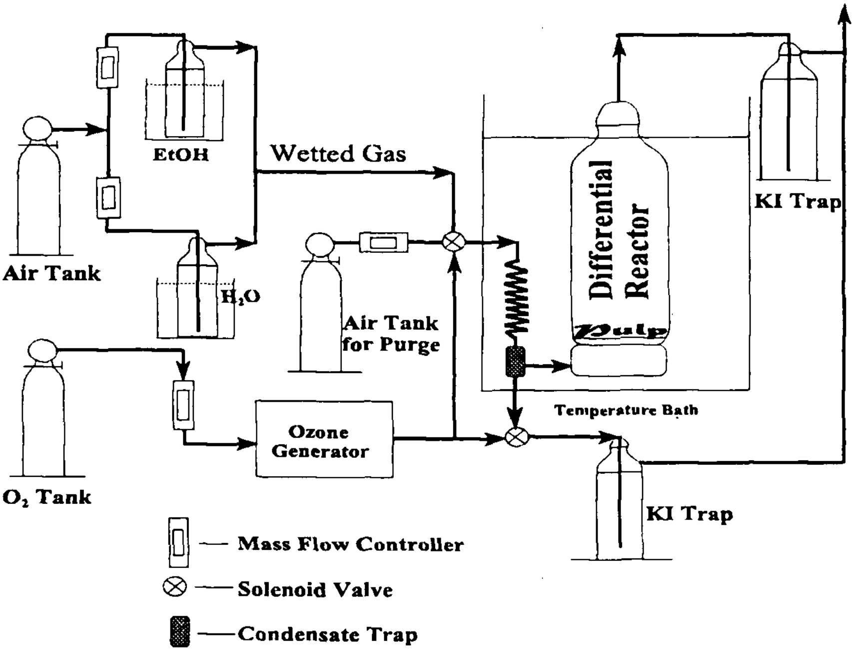


FIGURE 2. Schematic flow diagram of the experimental set-up

with a thin layer of well-fluffed pulp fibres deposited on its course porous glass distributor. Unless otherwise specified, 0.3 g o.d. pulp fibres were carefully distributed in an even bed height of about 7 mm. The open structure and the small amount of pulp, combined with a relatively high gas flow rate of 4 L/min, assured that all the fibres were exposed to approximately the same inlet ozone gas concentration.

Since the pulp consistency and composition of the liquid phase affect the ozone bleaching process,[1,5,23] a significant change in these variables due to evaporation during an experiment must be avoided. This was done by pre-moisturizing the dilution air stream. The vapour concentration was controlled by the temperature and the flow rate of the air contacting water and/or ethanol in their respective wash bottles. A condensation trap was installed just before the differential reactor inside the temperature bath to remove any droplets which may be formed upon cooling the ozone containing gas feed stream.

Ozone was generated from oxygen by a PCI model GL-1 ozone unit and diluted with the conditioned air stream. The flow rates were controlled by mass flow controllers. The ozonation time was accurately set with an electronic timer which activated the two solenoid valves. The temperature in the thermostated pulp bed was verified occasionally with a thermocouple.

Experimental Procedures

A Hemlock kraft pulp with a kappa number of 31 and viscosity of 35 mPa.s was used. To minimize any effect of transition metal ions on ozonation, the pulp was pre-treated with a H_2SO_4 solution of pH = 2 at 20°C for 30 minutes, followed by a DTPA treatment at pH = 5 and 20°C for 30 minutes. The pulp was then well washed with distilled water. About 10 grams of oven-dried pulp was impregnated for about five minutes by kneading with about 750 mL of either water or a 70% (w/w) ethanol solution, both at pH = 2, respectively for conventional and ethanol-assisted ozonation. The pulp slurry was then brought to the desired consistency by pressing and centrifugation. Subsequently, the pulp was treated in a fluffer contactor operating at 3450 rpm for 10 seconds. The well-fluffed pulp was then transferred into a closed plastic bag for moisture equilibration. After equilibration a pulp sample was taken for consistency and occasionally for ethanol concentration determination (by GC with dioxane as internal standard). Unless otherwise indicated, the ozonation was performed at 10°C and a total gas flow rate of 4 L/min. The consistencies during conventionally and ethanol-assisted ozonation were 38 and 34% respectively. After ozonation the pulp was diluted to a consistency of about 1% with a 70% (w/w) ethanol solution. The slurry was immediately neutralized to a pH of 6.5 ~

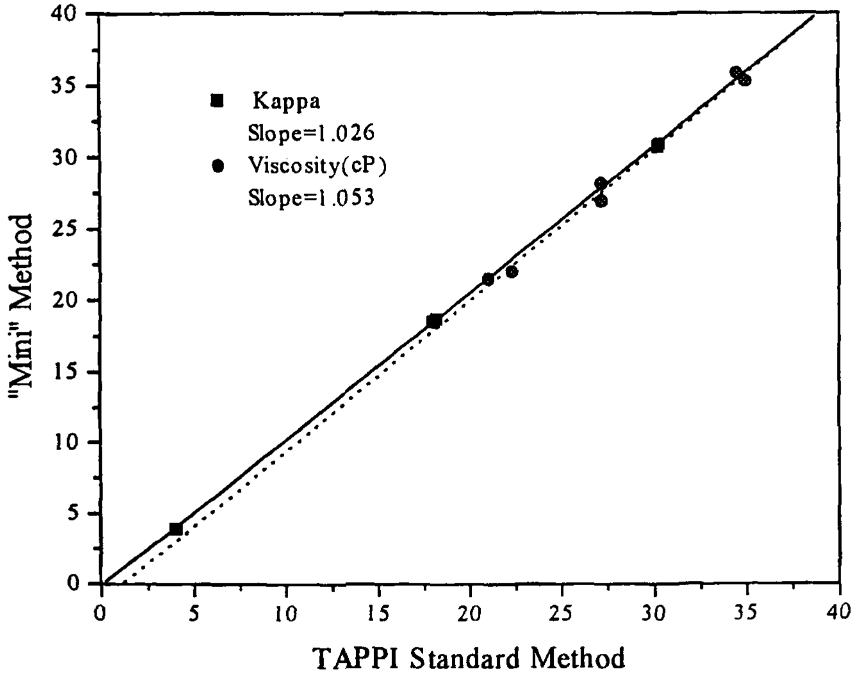


FIGURE 3. Comparison of the "Mini" Methods with the TAPPI Standard Methods of kappa number and viscosity determination

8.5 with 1N NaOH to avoid acid hydrolysis of cellulose. Then the lignin was extracted with this solution at 80°C for 1.5 hours. After extraction, the pulp was well washed with deionized water, air dried overnight and stored for kappa number and viscosity determination, and TEM-EDXA analysis.

Modified Kappa Number and Viscosity Tests

Because of the small amount of pulp available, the TAPPI Standard Methods[24] for the kappa number (T236 cm-85) and viscosity (T230 om-89) were scaled down to so called "Mini" Methods. The chemical dosages and the amount

TABLE 1.
Conditions for Kappa Number and Viscosity Tests

	Chemical Dosages and Amount of Pulp	TAPPI Standard Method	"Mini" Method
Kappa Number	Oven-dried Pulp (g) (kappa range from 31 to 2)	1 - 35	0.01 - 0.35
	Volume of 0.1 N $KMnO_4$ (mL)	100	1
	Volume of 4N H_2SO_4 (mL)	100	1
	Total Volume (mL)	1000	10
Viscosity	Oven-dried Pulp (g)	0.25	0.05
	Volume of CED (mL)	25	5
	Volume of H_2O (mL)	25	5

of pulp used for the Standard and "Mini" Methods are listed in TABLE 1. The results obtained with the Standard Methods and the "Mini" Methods are compared in FIGURE 3. The differences between the two methods are less than 6% for both the kappa and viscosity tests, which is within experimental error.

TEM-EDXA Sample Preparation

The ozonated and ethanol extracted pulps were further treated with 2% NaOH (on pulp) at 10% consistency and 80°C for 1.5 hours, and then well washed with distilled water before potassium permanganate staining.[25,26] This method consisted of immersing approximately 20 mg of the NaOH extracted pulp in a 2.5% (w/w) aqueous solution of potassium permanganate. The pulp slurry was kept under nitrogen to avoid oxidation and stirred at room temperature for 30 minutes. The pulp was then filtered and washed with deionized water to remove excess permanganate. Subsequently, the pulp was suspended in water, and fibres were randomly selected under a microscope using a fine forceps and placed on an Agar bed. This was required for alignment of the fibres before being embedded in Spurr resin (supplied by Marivac Limited). The fibres in the Agar bed were dehydrated by sequential exposure to the following liquids, 50%, 70%, and 100% ethanol followed by 75% and 100% propylene oxide, each for 30 minutes. The fibre wall and lumen were then gradually infiltrated with 100% Spurr resin and placed under vacuum overnight. Subsequently the samples were embedded in the same Spurr resin except that the accelerator was now increased by 50% compared to the original resin in order to accelerate the curing process at 60°C for 15 hours.[27]

The resin blocks were trimmed under a dissecting microscope and sectioned on an ultra microtome using glass knives. Thin sections of 90-100 nm were obtained using a diamond knife. The presence of Mn in the fibre samples was determined with a transmission electron microscope (HITACHI H-600 AB TEM) coupled with an energy dispersive X-ray analyser (EDXA LINK AN10/85) at 75 kV with an illuminating current of 0.5×10^{-9} amperes. The X-ray intensity of the manganese was measured over 500 seconds (0.4 μm spot size).

RESULTS AND DISCUSSION

Preliminary Experiments

First it was investigated whether the pulp consistency and the ethanol concentration remained constant during the ozonation experiments. The results obtained at a gas flow rate of 4 L/min are shown in FIGURE 4. It can be seen that there is no significant change in consistency. Also, the ethanol concentration increases only slightly from about 60 to about 70% (w/w); a change which has a small impact on the ozonation behaviour.[23]

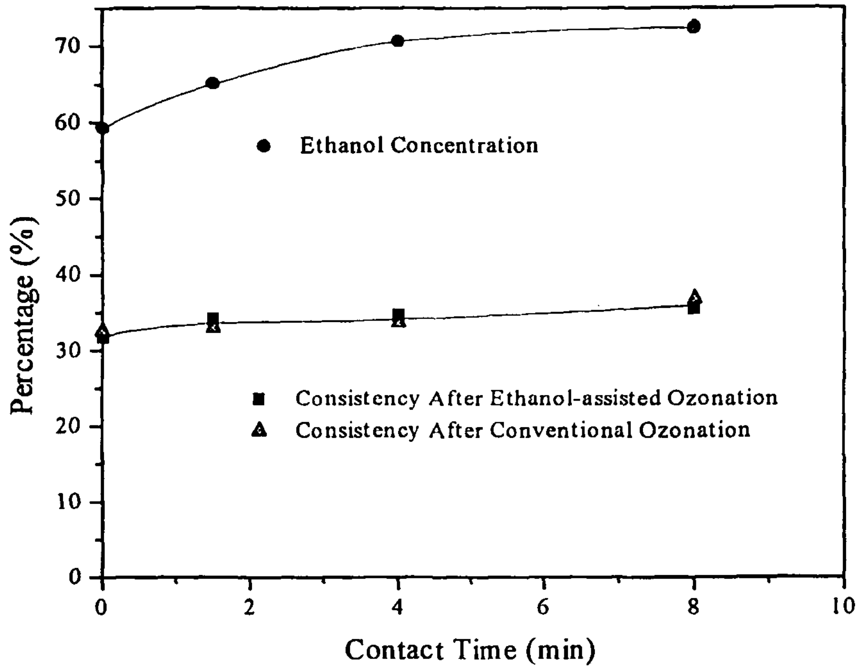


FIGURE 4. Change in ethanol concentration and pulp consistency (10°C and gas flow rate of 4 L/min) during ozonation

The effect of gas flow rate on the delignification kinetics was also studied. It is shown in FIGURE 5 that the delignification is not significantly affected by the gas flow rate at an ozone partial pressure, P_{O_3} of 0.5 kPa for both ethanol-assisted and conventional ozonation. Hence, it can be concluded that the kinetics obtained in the present system are not limited by ozone supply and external mass transfer limitations.

A further series of experiments were conducted to study the influence of bed height and pulp mass at otherwise identical conditions. The bed height was adjusted by careful compaction of the 0.3 g o.d. pulp with a glass rod. The

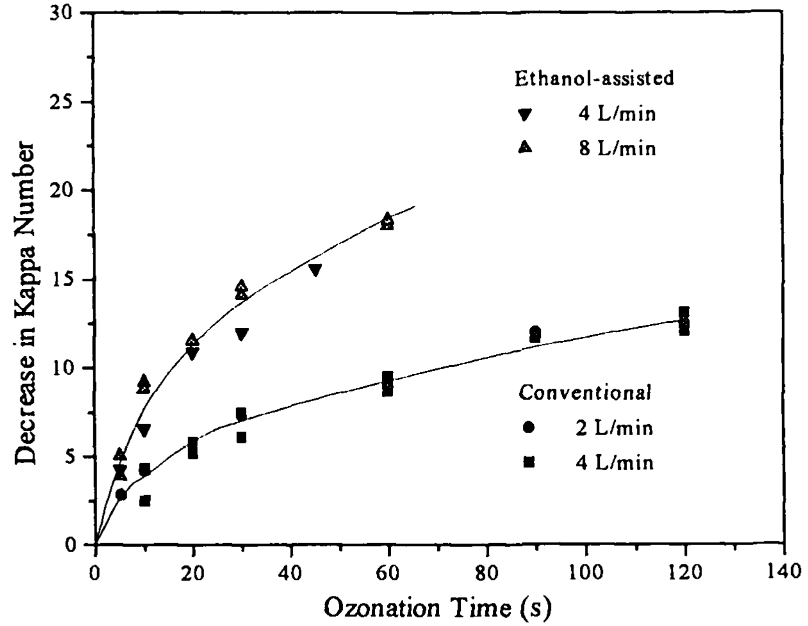


FIGURE 5. Effect of gas flow rate on ozone delignification (10°C and P_{O_3} of 0.5 kPa)

results in FIGURE 6 show that both the bed height and an increase in pulp mass to 0.5 g o.d. do not significantly affect the final kappa number after 20 seconds of ozonation. This further supports that intrinsic kinetic data are obtained with the present set-up, and that the delignification is uniform throughout the fibre bed.

Mechanism of Ozonation

The development of delignification and cellulose degradation during ozone bleaching at an ozone partial pressure of 0.5 kPa is shown in FIGURES 7 and 8 respectively. Based on the decrease in kappa (FIGURE 7) and the fractional increase in the number of glycosidic bond cleavages in cellulose (Δ(1/DP), see

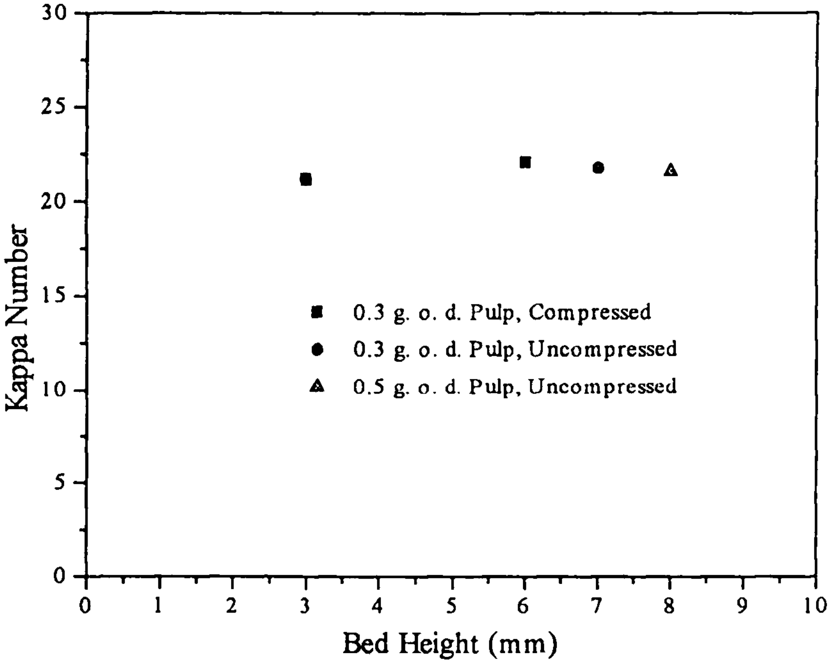


FIGURE 6. Effect of bed height and pulp mass on final kappa number (20 seconds, P_{O_3} :0.5 kPa)

FIGURE 8) one can identify three different regimes: the initial regime (IR), the transition regime (TR) and the final regime (FR).

In the initial regime the rates of both delignification and cellulose degradation are very high. In the final regime the increase in delignification becomes minimal, while the cellulose degradation increases approximately linear with ozonation time. The transition regime forms the connection between the initial and final regimes. Since the majority of delignification and cellulose degradation takes place in the initial regime, the present paper focuses on the delignification and cellulose degradation during the initial regime of ozone bleaching.

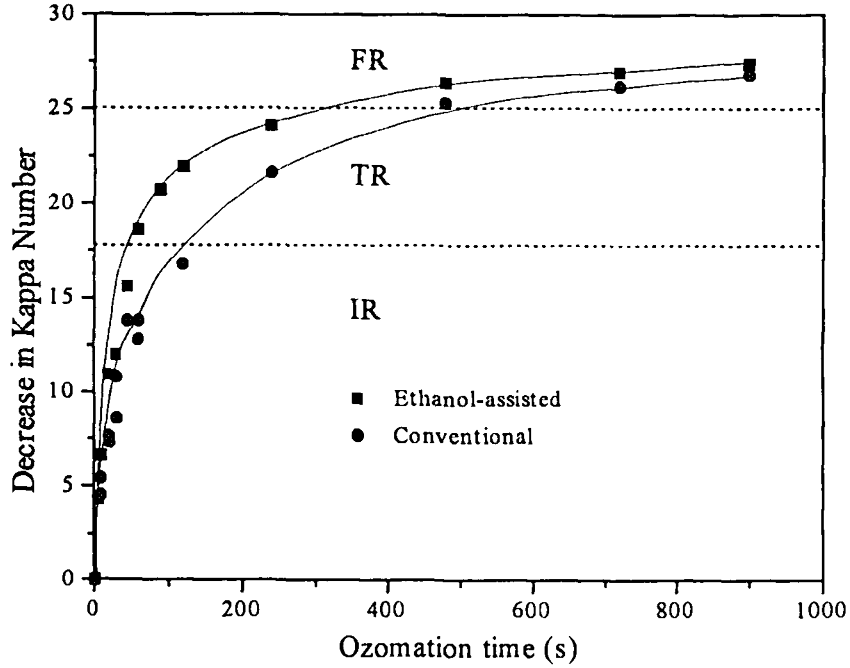


FIGURE 7. Development of delignification during ozone bleaching (P_{O_3} of 0.5 kPa, 10°C and pH of 2)

Since Transmission Electron Microscopy with Energy Dispersive X-ray Analysis (TEM-EDXA) measures concentrations of heavier elements on a microscope scale, it can be used to characterize the lignin distribution across a fibre wall when the lignin is labelled by an element which is (almost) not present in the pulp. For example, after chlorination this technique has been successfully applied to determine the distribution of chlorolignin in the fibre wall of Spruce kraft pulp.[28] In the present study the distribution of lignin in the fibre wall was obtained by TEM-EDXA after labelling the lignin with manganese using a staining technique with aqueous $KMnO_4$.[25,26] It is believed that manganese

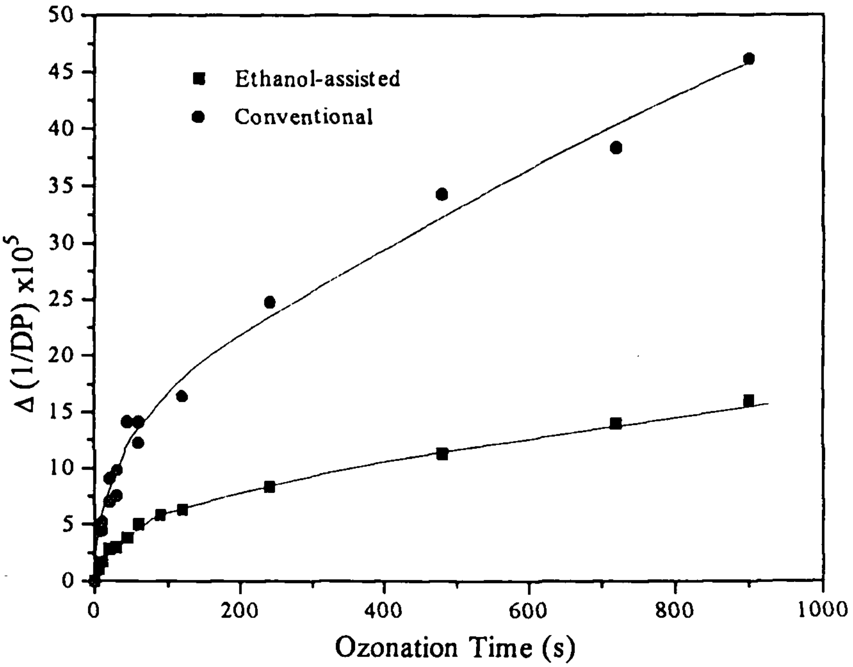
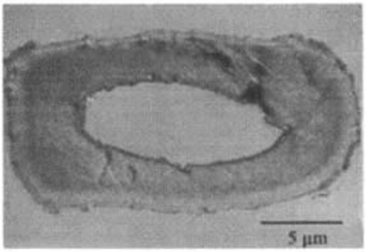


FIGURE 8. Development of cellulose degradation during ozonation (P_{O_3} of 0.5 kPa, 10°C and pH of 2)

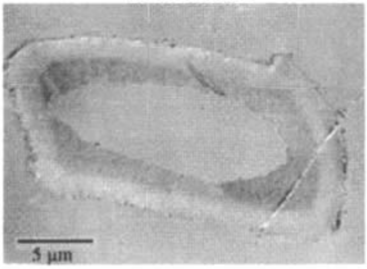
selectively binds to the lignin structure through inorganic ester type linkages.[29,30] Therefore, when determining the relative distribution of Mn in the fibre wall by TEM-EDXA, one indirectly obtains a picture of the lignin distribution.

TEM micrographs of permanganate stained Hemlock kraft pulps ozonated for 20, 30 and 120 seconds are displayed in FIGURE 9. The lignin-rich and lignin-deficient regions are visible as the darker and lighter zones respectively as was verified by TEM-EDXA analysis of the same pictures for manganese. The sharp separation between the darker and lighter zones represents a sudden change in the lignin content of the fibre wall. Therefore, these demarcation lines can be

1. 20 seconds



2. 30 seconds



3. 120 seconds

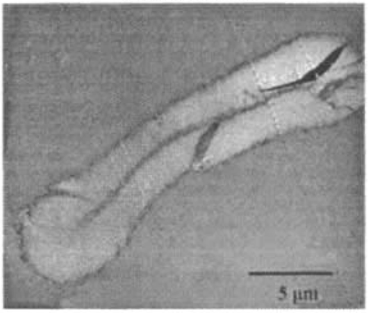


FIGURE 9. TEM Micrographs of transverse sections of $KMnO_4$ stained Hemlock kraft pulp ozonated at 10°C, pH of 2 for different lengths of time and extracted with 2% NaOH for 1.5 hours at 80°C

interpreted as the location of the ozone-lignin reaction front at that particular time, and thus supports the macro diffusion controlled mechanism rather than the micro diffusion controlled mechanism. A similar lignin distribution has been observed by Kojima et al.[31] in UV micrographs of ozonated Spruce CTMP fibres. Since CTMP pulp has a much higher lignin content than the present kraft pulp, these results suggest that the rate determining step of ozonation in the initial regime is the same for high or low lignin content pulp. Another important observation from FIGURE 9 is that the location of the lignin front in micrograph 2 is located further into the fibre wall towards the lumen than that in micrograph 1. This behaviour provides further support for the validity of the macro diffusion controlled mechanism of pulp ozonation. Based on micrograph 3 in FIGURE 9, it appears that after 120 seconds the ozonation reaction front has reached the lumen.

The behaviour seen in FIGURE 9 was generally observed for most of the 10 fibres which were analyzed at each of the three ozonation conditions. The single fibres displayed in FIGURE 9 were selected because they all had about the same fibre wall thickness. In some of the other fibres corresponding to the conditions of micrograph 1 and 2, the penetration depth of the reaction front was non-uniform or there was no penetration at all along a limited part of the circumference of the fibre. The likely explanation for this behaviour is that fibres were touching each other at these locations or that the fibre floc density was particularly high at this position, so that ozone did not reach or was depleted in this region respectively.

Since surface lignin is directly accessible for ozonation, the rate of attack of this lignin would be limited by mass transfer of ozone from the bulk gas phase. Accordingly, if the surface lignin plays an important role in the overall reaction kinetics, one would expect that the initial delignification rate would depend on the ozone supply rate. However, FIGURE 5 shows that the delignification rate is unaffected by the gas flow rate. Therefore, it can be concluded that the presence of surface lignin has a negligible influence on the overall reaction kinetics of ozone bleaching.

Rates of Delignification and Cellulose Degradation in the Initial Regime

With the confirmation that the initial stage of pulp ozonation is governed by diffusion of ozone in the liquid-filled (macro) pores of the fibre wall, the initial regime can now be interpreted as the period whereby for all the fibres the lignin reaction front is still located somewhere inside the fibre wall. On the other hand, the final regime represents the situation whereby for most of the fibres the reaction front has reached the lumen surface. The transition regime may be interpreted as being caused by the presence of residual lignin which has a relatively low reactivity towards ozone, and/or by the natural distribution of the fibre width of pulp.

It has been shown by Griffin et al.[12] that during the initial regime the movement of the lignin reaction front is proportional to the square root of the product of the ozonation time and the ozone partial pressure in the bulk of the gas phase. Assuming that the same amount of lignin is degraded at the lignin front irrespective of its location, and that significant delignification during this regime only occurs inside the reaction front, it follows that:

$$\Delta(K) = k_{lf}(P_{O_3} \times t)^{1/2} = k'_{lf}t^{1/2} \qquad (1)$$

where $\Delta(K)$ is the decrease in kappa number during ozonation time t, P_{O_3} is the ozone partial pressure in the bulk of the gas phase, and k_{lf} and k_{lf}' are rate constants for delignification. Similarly, if it is now assumed that a fixed fraction of the ozone which reacts with lignin in the reaction front leads to radicals,[9,10] and that a fixed small fraction of these radicals leads to cellulose chain scission, it can be derived[32] that:

$$\Delta\left[\frac{1}{DP}\right] = k_{cf}(P_{O_3} \times t)^{1/2} = k'_{cf}t^{1/2} \qquad (2)$$

where $\Delta(1/DP)$ is the fractional increase in the number of glycosidic bond cleavages in cellulose during ozonation time t, DP is the average degree of polymerization of the cellulose chains, and k_{cf} and k_{cf}' are rate constants of cellulose degradation. $\Delta(K)$ is calculated as $K_0 - K_t$, where K_0 is the kappa number of 29.2 measured after extraction of the unbleached pulp by a 70% (w/w) ethanol solution, and K_t is the ethanol extracted kappa number at ozonation time, t. $\Delta(1/DP)$ is calculated as $1/DP_t - 1/DP_0$, with DP_0 and DP_t being the average degree of polymerization of cellulose before ozonation and after ozonation time, t, respectively. The DP was calculated from the viscosity data using the empirical equation:[33]

$$DP = [0.75\log(954 \text{ viscosity (cP)} - 325)]^{1.105} \qquad (3)$$

The experimental results of ozone delignification and cellulose degradation obtained at $P_{O_3} = 0.5$ kPa to 2.9 kPa are presented in FIGURES 10 and 11 respectively. They show that $\Delta(K)$ and $\Delta(1/DP)$ change linearly with the square root of ozonation time, $t^{1/2}$ during the initial regime. However, when the delignification increases beyond $\Delta K \approx 18$, the straight line relationship in FIGURE 10 no longer holds. Therefore, we propose that at $\Delta(K)$ of about 18 the reaction front has reached the lumen in a significant number of fibres. In other words, the macro diffusion controlled kinetics of the initial regime described by equations (1) and (2) are only valid up to a delignification of about 18 kappa number for this particular pulp. The reaction kinetics of both delignification and cellulose degradation of the transitional and final regimes are respectively only partly or not at all governed by macro diffusion, and will be discussed in future publications.

The rate constants, k_{lf}' and k_{cf}', of both conventional and ethanol-assisted ozonation during the initial regime are listed in TABLE 2. They are obtained from the slopes of the straight lines in FIGURE 10 and 11 respectively. It can be seen that the delignification rate during ethanol-assisted ozonation is

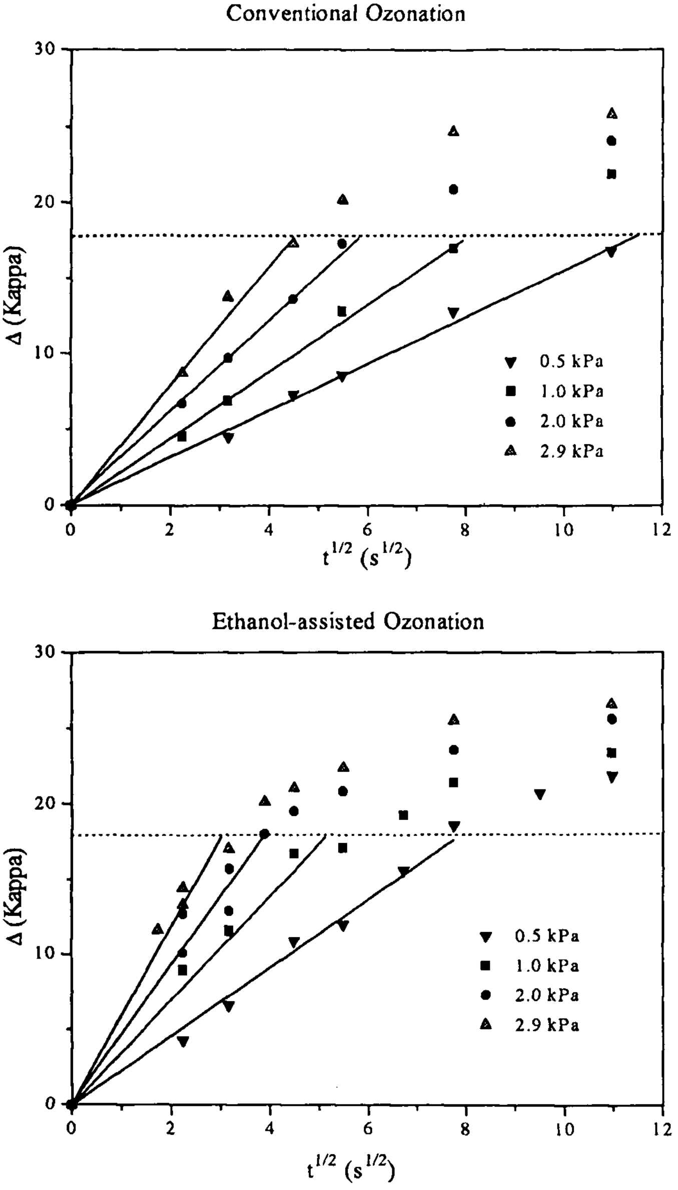
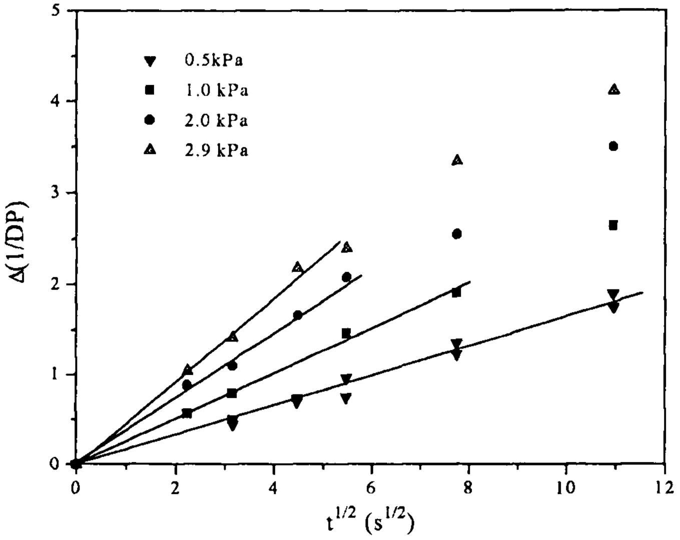


FIGURE 10. Kinetics of delignification during conventional and ethanol-assisted ozone bleaching (P_{O_3} of 0.5 kPa, 10°C and pH of 2)

Conventional Ozonation



Ethanol-assisted Ozonation

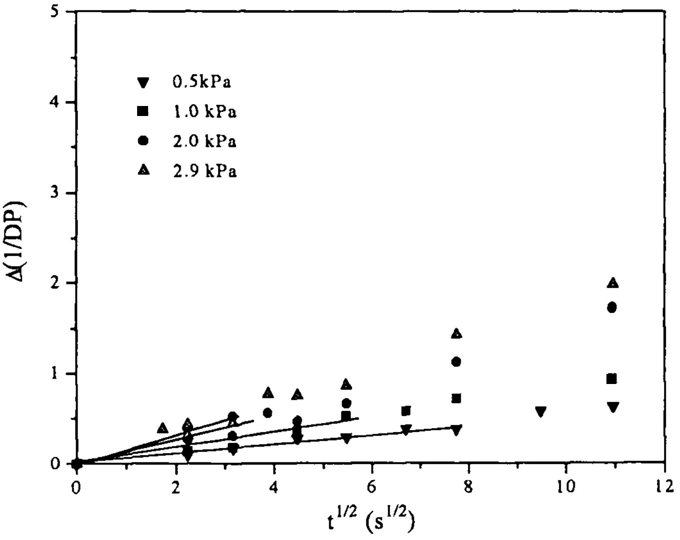


FIGURE 11. Kinetics of cellulose degradation during conventional and ethanol-assisted ozone bleaching (P_{O_3} of 0.5 kPa, 10°C and pH of 2)

TABLE 2.
Rate Constants of Delignification (k_{lf}') and Cellulose Degradation (k_{cf}')

Ozone Partial Pressure (kPa)	Conventional Ozonation		Ethanol-assisted Ozonation	
	Delignification $k_{lf}' \pm$ SD* ($\text{kappa} \times s^{-0.5}$)	Cellulose Degradation $k_{cf}' \pm$SD ($DP^{-1} \times s^{-0.5}) \times 10^5$	Delignification $k_{lf}' \pm$ SD ($\text{kappa} \times s^{-0.5}$)	Cellulose Degradation $k_{cf}' \pm$ SD ($DP^{-1} \times s^{-0.5}) \times 10^5$
0.5	1.57 ± 0.03	1.64 ± 0.04	2.32 ± 0.05	0.535 ± 0.02
1	2.13± 0.10	2.53 ± 0.04	3.46 ± 0.16	0.824 ± 0.08
2	3.10 ± 0.03	3.73 ± 0.06	4.69 ± 0.21	1.40 ± 0.12
2.9	4.00 ± 0.12	4.56 ± 0.11	5.90 ± 0.25	1.80 ± 0.13

* SD = Standard Deviation

consistently higher than that of conventional ozonation. As explanation it is proposed that the rate of ozone diffusion inside the fibre wall is higher in ethanol-assisted ozonation than that in conventional ozonation because the ozone solubility is higher in an ethanol solution than that in water.[34] The impregnation solution has the opposite effect on the rate of cellulose degradation, with now a much lower rate constant for pulp impregnated with ethanol-water than that with acidified water. The explanation for this effect is that ethanol acts as a radical scavenger and thus has a protective effect on the cellulose degradation.

Effect of Ozone Partial Pressure on Delignification and Cellulose Degradation

A ln-ln plot of the rate constants of delignification (k_{lf}') versus P_{O_3} for both conventional and ethanol-assisted ozonation is shown in FIGURE 12. The slopes of the fitted straight lines are found to be 0.528 ± 0.032 and 0.516 ± 0.024 for conventional and ethanol-assisted ozonation respectively. Since these values are within experimental error equal to 0.5, it shows that delignification is

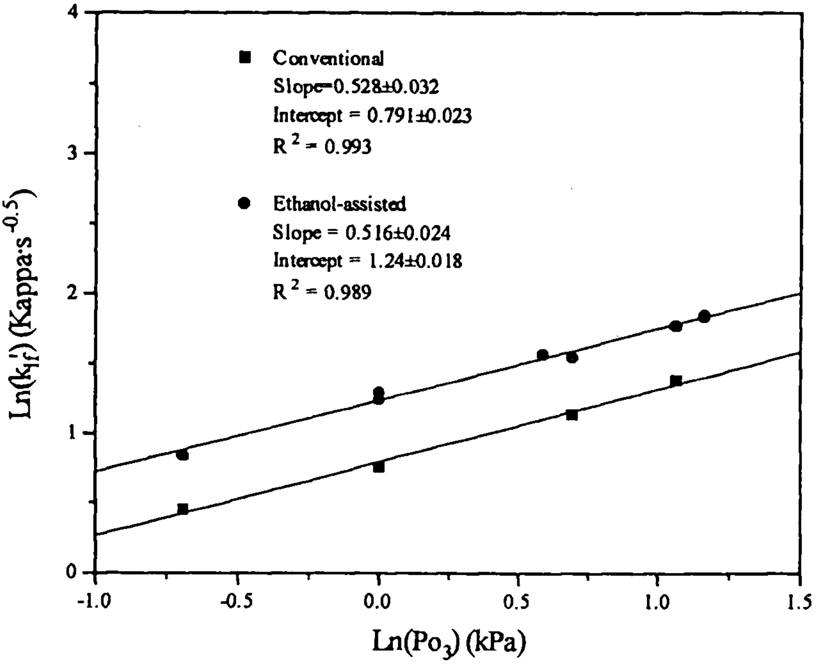


FIGURE 12. Effect of ozone partial pressure on delignification (10°C and pH of 2)

well described by equation (1), and provides further confirmation that the diffusion of ozone towards the lignin reaction front governs the rate of delignification.

The P_{O_3} independent rate constant of delignification, k_{lf}, can be calculated from the straight line correlations in FIGURE 12 as 2.21 ± 0.05 kappa·(kPa·s)$^{-0.5}$ and 3.46 ± 0.06 kappa·(kPa·s)$^{-0.5}$ for conventional and ethanol-assisted ozonation respectively. The significance of these numbers is that they allow prediction of the optimum ozonation time which occurs when the initial period is completed (for the present pulp when Δ(K) is equal to about 18). It should be noted that k_{lf}

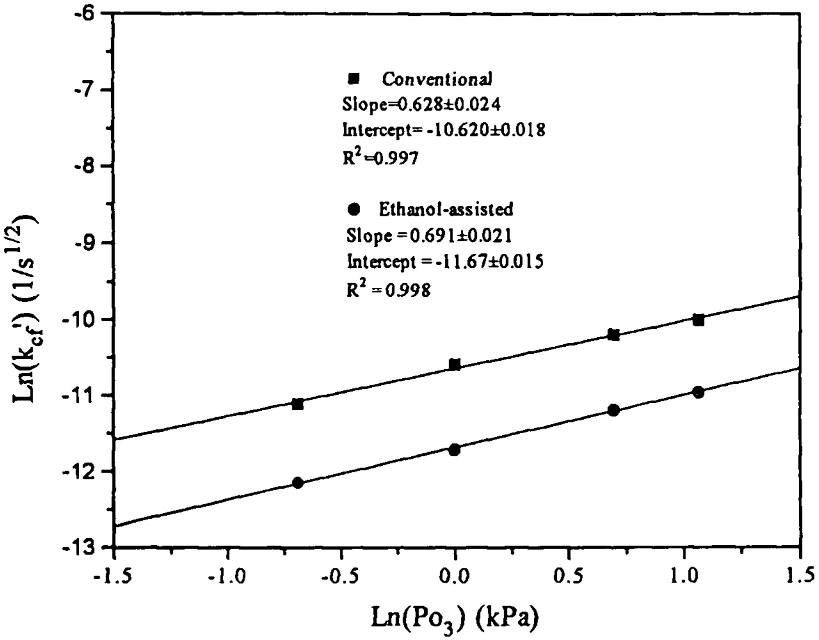


FIGURE 13. Effect of ozone partial pressure on cellulose degradation (10°C and pH of 2)

depends on pulp consistency, temperature, and the kappa number of the unbleached pulp.

The effect of ozone partial pressure on cellulose degradation is also determined by plotting k_{cf}' versus P_{O_3} on a ln-ln scale in FIGURE 13. For cellulose degradation of conventional and ethanol-assisted ozonation the P_{O_3} exponents are found to be 0.628 ± 0.024 and 0.691 ± 0.021 respectively. The significant difference with the theoretical value of 0.5 of the exponent in equation (2) indicates that a more comprehensive analysis is needed to describe the radical formation in the ozone-lignin reaction front, a subject which we will address in a following paper.[32]

The P_{O_3} independent rate constant, k_{cf}, for cellulose degradation during conventional and ethanol-assisted is calculated from FIGURE 13 as 2.4 ± 0.04 × 10^{-5} ($kPa^{0.628} \cdot s^{-0.5}$) and 0.86 ± 0.01 × 10^{-5} ($kPa^{0.691} \cdot s^{-0.5}$) respectively. Accordingly, equation (2) should be rewritten as:

$$\left[\frac{1}{DT_t}\right] - \left[\frac{1}{DP_o}\right] = k_{cf}(P_{O_3})^x \times t^{1/2} \qquad (4)$$

where k_{cf} is the P_{O_3} independent rate constant of ozone degradation of cellulose in the initial regime, and x is the exponent given above. Since the value of x is larger than 0.5, the lignin-cellulose selectivity will deteriorate slightly as the ozone partial pressure increases.

Effect of Ozone Partial Pressure on the Lignin-Cellulose Selectivity

The lignin-cellulose selectivity can be expressed by equation (5) as:

$$\text{Selectivity} = \frac{\Delta(K)}{\left[\frac{1}{DT_t} - \frac{1}{DP_o}\right]} = \frac{\frac{\Delta(K)}{t^{0.5}}}{\frac{\left[\frac{1}{DP_t} - \frac{1}{DP_o}\right]}{t^{0.5}}} = \frac{k_l \times (P_{O_3})^{0.5}}{k_{cf} \times (P_{O_3})^x} \qquad (5)$$

For conventional ozonation this becomes:

$$\text{Selectivity} = \frac{2.21 \times (P_{O_3})^{0.5}}{2.4 \times 10^{-5} \times (P_{O_3})^{0.628}} = 9.21 \times 10^4 \times (P_{O_3})^{-0.128} \qquad (6)$$

while for ethanol-assisted ozonation the selectivity is described by:

$$\text{Selectivity} = \frac{3.46 \times (P_{O_3})^{0.5}}{0.86 \times 10^{-5} \times (P_{O_3})^{0.691}} = 40.2 \times 10^4 \times (P_{O_3})^{-0.191} \qquad (7)$$

The above equations show that at a given ozone partial pressure a higher

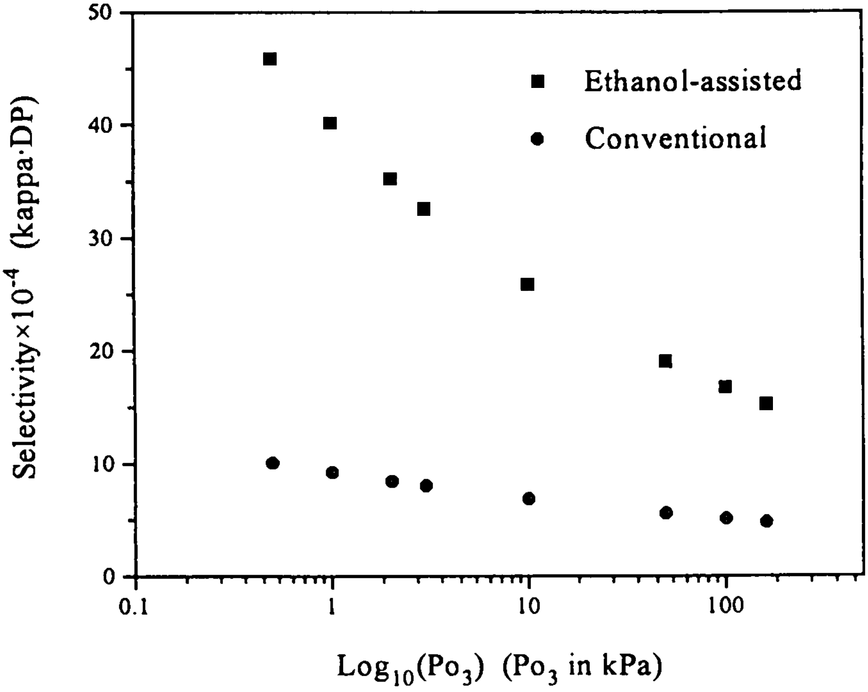


FIGURE 14. Prediction of the effect of P_{O_3} on ozone-lignin selectivity (10°C and pH of 2)

selectivity is obtained for ethanol-assisted ozonation than that for conventional ozonation. This is due to the combined effect of the higher solubility of ozone and the radical scavenging effect of ethanol in a 70% (w/w) ethanol solution. Comparison of the ozone pressure exponents in equations (6) and (7) shows a larger negative value for the ethanol-assisted ozonation. This implies that the selectivity of the ethanol-assisted ozonation is more sensitive to P_{O_3} than that of conventional ozonation. Consequently, ethanol-assisted ozonation should preferably be operated at lower ozone partial pressures. By plotting the selectivity against P_{O_3} on a logarithm scale in FIGURE 14, it can be seen that for conventional ozonation the selectivity decreases with increasing ozone partial pressure.

The results in FIGURE 14 may be used to compare high and medium consistency ozonation, whereby for medium consistency the ozone partial pressure at the exhaust of the medium consistency mixer must be used (assume perfect mixing in the MC mixer), and the logarithmic mean partial ozone pressure between the inlet and outlet of the (plug flow) reactor for high consistency ozonation. For example, with the partial pressure of ozone at the outlet of a MC mixer estimated at about 13.8 kPa (assuming 85% consumption of 12% (w/w) ozone in oxygen at a total pressure of 11.5 atmosphere)[37], and using the logarithmic mean ozone partial pressure of the Union Camp high consistency system[35] of about 1.2 kPa, one obtains a selectivity for the high consistency system which is 37% higher than that of the medium consistency system. It has been noted[36] that the literature on selectivity differences between medium and high consistency systems is contradictory. However, as pointed out[36] this may be an effect of the pulp-ozone mixing apparatus used at the different consistencies rather than being a direct consequence of pulp consistency.

CONCLUSIONS

A differential reactor system has been used to study the kinetics of pulp ozonation. The results were shown to be independent of gas flow rate, degree of pulp packing, and pulp bed height. Small scale test methods for kappa number and viscosity were developed. The values obtained by these test methods are in good agreement with the TAPPI Standard Methods.

The experimental data show that pulp ozonation is characterized by three regimes: a diffusion controlled regime, followed by a transition regime and a final regime. By the TEM-EDXA technique, it is proven that the delignification kinetics in the initial regime are governed by diffusion of ozone through liquid-filled (macro) pores in the fibre wall towards a lignin reaction front which moves from the external surface of the fibre wall towards the lumen.

The validity of this so-called diffusion controlled shrinking core behaviour of ozone delignification in the initial regime is confirmed by the experimental finding that the rate of ozone delignification is proportional to $(P_{O_3} \times t)^{1/2}$. The rate of cellulose degradation, however, does not fully agree with this simple theoretical expression based on the shrinking core model since it is found that the cellulose degradation rate is proportional to $P_{O_3}^{x} \times t^{1/2}$, with x being slightly larger than 0.5. As a result, the selectivity of ozonation in the initial regime decreases slightly with increasing ozone partial pressure. The results also show that a higher selectivity is obtained for ethanol-assisted ozonation than that for conventional ozonation. This difference is thought to be due to the combined effect of the higher solubility of ozone in aqueous ethanol and the radical scavenging effect of ethanol in the 70% (w/w) ethanol solution used in the present investigation.

REFERENCES

1. N. Liebergott, B. van Lierop, and A. Skothos, TAPPI J. 75, 145 (1992)

2. N. Liebergott, B. van Lierop, and A. Skothos, TAPPI J. 75, 117 (1992)

3. N. Liebergott, B. van Lierop, B.C. Garner, and G.J. Kubes, TAPPI J. 67, 76 (1984)

4. C. Chirat, R. Angelier, M. Viardin, and D. Lachenal, 1996 International Pulp bleaching Conference, 197, (1996)

5. G.J. Kang, Y. Ni, A.R.P. van Heiningen, 82nd CPPA Annual Meeting, B303 (1996).

6. M. Solinas and T. Murphy, Pulp and Paper, 70, 133 (1996).

7. M. Ek, J. Gierer, K. Jansbo, and T. Reitberger, Holzforschung, 43, 391 (1989)

8. T. Eriksson, and T. Reitberger, Proceedings of the 8th ISWPC, Helsinki, Vol.2, 349 (1995).

9. G.J. Kang, Y. Zhang, Y. Ni, and A.R.P. van Heiningen, J. Wood Chem. and Tech., 15, 413 (1995).

10. K. Magara, T. Ikeda, Y. Tomimura, and S. Hosoya, 1996 International Pulp Bleaching Conference, Washington D.C., 553 (1996).

11. D.E. White, T. Gandek, M.A. Pikulin, and W.H. Friend, Pulp and Paper Canada, 94, T242 (1993).

12. R. Griffin, Y. Ni, and A.R.P. van Heiningen, CPPA 81st Annual Meeting, A117 (1995).

13. T. Gandek, 1995 AIChE Symposium Series No 311, 92, 50 (1996).

14. Z. Osawa, and C. Schuerch, Tappi, 46, 79 (1963).

15. A.A. Katai and C. Schuerch, J. Polymer Sci., Part A-1, 4, 2683 (1966).

16. L.A. Carlsmith, O. Luthi, J. Bouchard, 1996 International Pulp Bleaching Conference, 183 (1996).

17. A. Suurnäkki, A. Heijnesson, J. Buchert, U. Westermark, and L. Viikari, Proceedings of the 8th ISWPC, Helsinki, 1, 237 (1995).

18. J. Laine, and P. Stenius, Proceedings of the 8th ISWPC, 1, 589 (1995).

19. J.R. Wood, and D.A.I. Goring, P & P Mag. Can., 74, T309 (1973).

20. A. Kassebi, J.S. Gratzl, C-L. Chen, 1982 TAPPI Pulping Conference, 327 (1982).

21. R.P. Singh, Tappi, 65, 45 (1982).

22. L.A. Carlsmith, O. Luthi, H. Barclay, CPPA 82nd Annual Meeting, 67 (1996).

23. X.Z. Zhang, Y. Ni, and A.R.P. van Heiningen, 1996 International Pulp Bleaching Conference, Washington, 601 (1996).

24. TAPPI Test Methods 1994-1995, TAPPI Press, Atlanta, Georgia, 1994.

25. A.J. Kerr, and D.A.I. Goring, Cellulose Chem. Techn., 9, 563 (1975).

26. K. Ruel, F. Barnoud, A. Goring, Wood Sci. & Techn., 12, 799 (1956).

27. R. Spurr, J. of Ultrastructure Research, 26, 31 (1969).

28. S.J. Kuang, S. Saka, and D.A.I. Goring, J. of Wood Chem. Tech., 4, 163 (1984).

29. D. Hopwood, J. of Histochemistry and Cytochemistry, 1, 323 (1969).

30. J. Luft, Journal of Biophysical and Biochemical Cytology, 2, 799 (1956).

31. Y. Kojima, S. Yoon, T. Kayama, Mokuzai Gakkaishi, 34, 697 (1988).

32. X.Z. Zhang, Y. Ni, and A.R.P. van Heiningen, Paper to be published.

33. H. Sihtola, B. Kryklund, L. Laamanen, and L. Palenius, Paperi Ja Puu, 45, 225 (1963).

34. X.Z. Zhang, J.H. Li, Y. Ni, and A.R.P. van Heiningen, paper to be published.

35. P.M. Gottlieb, W.E. Wells, S. Riddick Miller and T.S. Tadas, TAPPI J., 77, 117 (1994)

36. B. van Lierop, A. Skothos and N. Liebergott, Pulp Bleaching: Principles and Practice, C.W. Dence and D.W. Reeve, Editors, Tappi Press, p. 327 (1996)

37. G. Homer, Canadian Liquid Air, Vancouver, Private Communication (1998)