

# Ozone Depolymerization of Polysaccharides in Different Materials

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*The behaviour of polysaccharides contained in different cellulosic materials is studied with respect to depolymerization by ozone in an aqueous medium. The effect of concentration in the liquid phase, temperature and time upon the depolymerization of holocellulose, bleached and unbleached pulps, microcrystalline and native celluloses is investigated. The viscosimetric degree of polymerization and the molecular weight distribution are used to monitor the process. The results show that, at low values of temperature and pH, which inhibit the production of radicals, the depolymerization rate is moderate for lignin-free materials. However, this rate and its maximum extent increase markedly with temperature. Moreover, the experiments suggest that the reactivity of ozone and the amount of radicals in the system and its physical accessibility are the key factors to explain the observed depolymerization profiles. Finally, the results for lignin-free materials are compared with those obtained with similar materials but containing residual lignin, and this study confirms that the presence of lignin in the fibre matrix increases the depolymerization of the carbohydrates.*

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*Le comportement des polysaccharides contenus dans diverses matières cellulosiques est étudié en rapport avec la dépolymérisation par l'ozone dans un médium aqueux. L'effet de la concentration en phase liquide, de la température et du temps sur la dépolymérisation de l'holocellulose, des pâtes blanchies et écruées, et des celluloses microcristallines et naturelles, fait l'objet d'un examen. Le degré viscosimétrique de polymérisation et la répartition des poids moléculaires ont été utilisés pour surveiller le processus. Les résultats indiquent qu'à faible température et bas pH, qui inhibent la production de radicaux, le taux de dépolymérisation est modéré pour les matières exemptes de lignine. Toutefois, ce taux et son étendue maximale augmentent de façon marquée à mesure que la température s'élève. De plus, les essais suggèrent que la réactivité de l'ozone et la quantité de radicaux dans le système et son accessibilité physique sont les facteurs clés qui expliquent les profils de dépolymérisation observés. Enfin, les résultats pour les matières exemptes de lignine sont comparés avec ceux obtenus avec des matières similaires mais contenant de la lignine résiduelle, et la présente étude confirme que la présence de lignine dans la fibre accroît la dépolymérisation des hydrates de carbone.*

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## INTRODUCTION

The environmental concerns in the pulp industry have forced the removal of elemental chlorine from the bleaching processes and this has enabled ozone to become an industrial reality. At present, there are about 13 commercial ozone bleaching plants throughout the USA and Scandinavia [1]. Despite this, there are still some unresolved problems in the processes of delignification and bleaching with ozone, particularly with respect to selectivity. De-

spite the large research efforts dedicated to this subject, it has not yet been possible to increase the selectivity of ozone to the same levels exhibited by chlorine and chlorine dioxide. Treatments that decrease the pulp metal contents improve the selectivity [2], but this still remains lower than desirable. A common approach to study this is to investigate independently the effect of the bleaching chemicals on carbohydrates and lignin model compounds. These are usually of monomeric type while the original polysaccharides and lignin are macromolecules thus restricting the extrapolation of the conclusions to the pulp. Some researchers made use of cotton linters [3] and  $\alpha$ -cellulose [4] to model polysaccharides and the results point to severe cellulose degradation by ozone. However, many of the published papers [5-7] concerning the effect of ozone on unbleached pulps (cellulosic materials with 2-5% of residual lignin) claim that the

degradation of polysaccharides is caused by the radicals formed as a result of the metal ions present in the pulps or of the degradation products of lignin-ozone reactions. These reported observations from lignin-free materials and from pulps containing lignin are apparently contradictory.

The main purpose of the present investigation is to clarify the role of ozone on the depolymerization of different cellulosic materials, namely lignin-free pulps. To reach this objective, distinct materials were prepared and exposed to ozone under closely controlled ozone liquid concentration and temperature. To minimize ozone self-decomposition and therefore the generation of radicals, the majority of the experiments were carried out at 4°C and a pH close to 2.5. To investigate the influence of the ozone accessibility on the depolymerization rate and on its maximum extent, materials with different degrees of crystallinity

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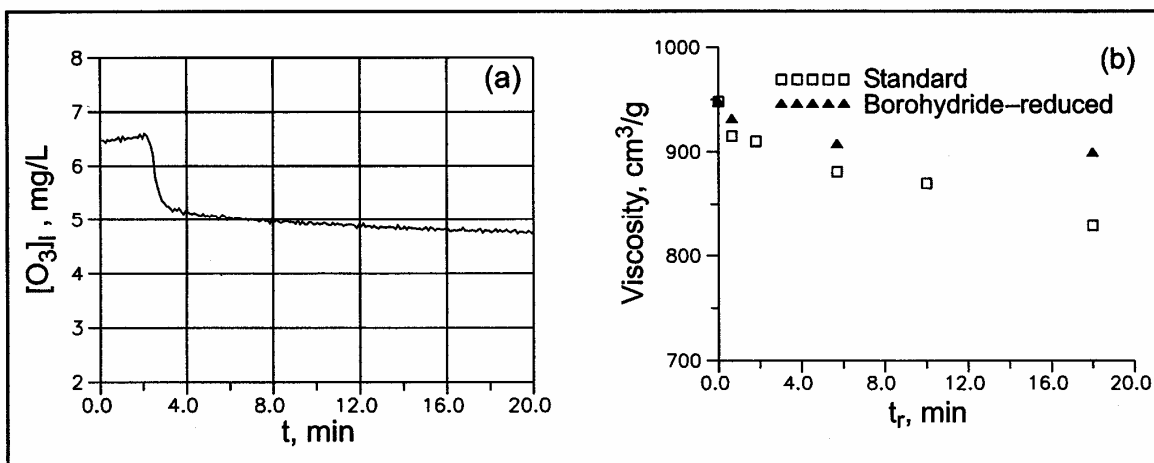


Fig. 1. Ozone profile in the liquid phase (a) and standard and borohydride-reduced pulp viscosities (b) for a set of experiments with commercial fully bleached eucalyptus pulp.

were employed. Finally, the kinetic behaviour of the depolymerization of polysaccharides in lignin-free materials was compared to that corresponding to materials containing lignin.

#### EXPERIMENTAL ARRANGEMENT

The raw materials used in this study are microcrystalline (Avicel) and native (Merck) celluloses, cotton, fully bleached eucalyptus pulp and eucalyptus holocellulose; the later was produced from an unbleached pulp, which was also used as the reference lignin-containing material. The kappa number of this pulp was 15.5 and its viscosity  $1270 \text{ cm}^3/\text{g}$ . Holocellulose was produced from the unbleached pulp by the chlorite ( $\text{pH} = 4.5$ ) method [8], with a final kappa number of 1.6 and a negligible viscosity loss.

Pine kraft pulp (kappa number = 32; viscosity  $971 \text{ cm}^3/\text{g}$ ) and the corresponding holocellulose were used in a particular case. After a pretreatment in acidic medium ( $\text{pH} \approx 2$ , 10 min, 0.25% consistency) and dewatering to 20% consistency, all samples were treated with ozone at ultra-low consistency ( $\approx 0.1\%$  solid contents) and at five different temperatures (2, 4, 23, 33 and  $43^\circ\text{C}$ ), maintaining pH just below 2.5 to inhibit ozone decomposition. The reaction experiments were carried out in a standard cylindrical glass tank ( $V = 6000 \text{ cm}^3$ ) provided with a mechanical stirrer, a gas sparger and four symmetric baffles, as follows [9]: first a volume of  $4500$  or  $5000 \text{ cm}^3$  of distilled water is saturated with ozone; then 4 or 5 g (oven dry) of solid material (pulp or other cellulosic material) is introduced into the reactor in suspension ( $500$  or  $1000 \text{ cm}^3$ ). The reactor contents at a consistency close to 0.1% were stirred at 2500 rpm. This has been shown [9] to minimize the liquid–solid mass transfer resistance. Two feeding strategies for the gas mixture were employed after saturation: in the first, the same stream of

ozone/oxygen is kept throughout the experiment; and, in the second, the gas is cut off just before the introduction of the solid material into the reactor. The ozone concentration in the gas and liquid phases is continuously measured with three electrochemical sensors and the reaction is stopped by supplying indigo to the reactor which consumes, almost immediately, all ozone in the liquid phase. The solid material was thoroughly washed with distilled water, air dried and later submitted to chemical analyses. To follow pulp depolymerization, the viscosity in copper(II) ethylenediamine (CED), before and after borohydride reduction, was determined. Moreover, the molecular weight distribution of some of these materials was determined after transformation into cellulose tricarbamate [9].

#### RESULTS AND DISCUSSION Depolymerization of Lignin-Free Materials

For lignin-free materials, consumption of ozone is low when compared to the amount available in the  $4500 \text{ cm}^3$  of water previously saturated with ozone. Figure 1 shows the profile of ozone concentration in the liquid phase for an experiment carried out at  $4^\circ\text{C}$  with a commercial eucalyptus fully bleached (DEDED) pulp. In this case, 5 g of pulp in  $1000 \text{ cm}^3$  of water was added to the reactor at  $t = 2$  min and the gas feed cut off at the same time. As a result of this dilution effect, the concentration falls very quickly from 6.6 to  $5.4 \text{ mg/L}$  and only the remaining decrease can be ascribed to consumption by the pulp. Therefore, based on such value, the following observations can be made for this fully bleached pulp:

- Ozone consumption is very low (0.07% on pulp) for a reaction time of 18 min (initial:  $[\text{O}_3]_l = 5.4 \text{ mg/L}$ ;  $t_r = 18$  min:  $[\text{O}_3]_l = 4.7 \text{ mg/L}$ );
- The reaction rate is relatively high for the first minute, decreasing markedly afterwards.

The profile of pulp viscosity can be seen in Fig. 1b. It shows that, under these reaction conditions, ozone has a moderate effect on the pulp viscosity. The corresponding profile of viscosity when determined after pulp reduction with sodium borohydride confirms a very low depolymerization rate. As expected, the values for standard viscosity, which also include the depolymerization caused by alkali-sensitive carbonyl groups introduced by ozone in the polymer [3], exhibit a slightly higher degradation rate.

The role of temperature on the depolymerization of polysaccharides can be appreciated in Fig. 2a, for the same pulp. It can be seen that carbohydrate degradation increases markedly with temperature. This behaviour can be attributed to the effect of temperature on both ozone reaction rate and radicals generation.

Figure 3 highlights the effect of the average concentration of ozone in the liquid phase at 4 and  $23^\circ\text{C}$  on the rate of degradation of polysaccharides in the same fully bleached eucalyptus pulp. The very low consumption of ozone enables all experiments, in each series, to be carried out at essentially the same liquid ozone concentration. For  $4^\circ\text{C}$  (Fig. 3a), despite an increase in the ozone concentration that is close to 5 times, the rate of degradation and its extent is only moderately enhanced. The viscosity drop increased from 7 to 16%, for a reaction time of 18 min. At  $23^\circ\text{C}$ , a similar variation in concentration resulted in a greater loss in viscosity. For the same reaction time, the viscosity drop increased from 10 to 30% (Fig. 3b).

To evaluate the influence of some physical properties of the cellulosic materials on the depolymerization by ozone, other materials were studied: commercial native and microcrystalline celluloses, cotton and holocellulose. The experiments with commercial native and microcrystalline celluloses were carried out after extraction with acetone in soxhlet during 10 h (30 cycles) to

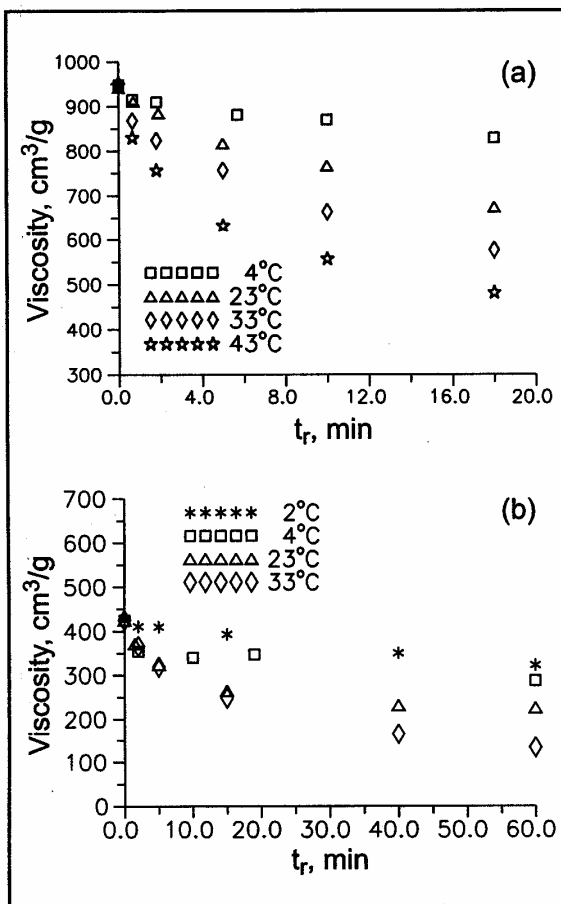


Fig. 2. Standard viscosity for a set of experiments carried out with fully bleached eucalyptus pulp (a) and native cellulose (b) at similar liquid ozone concentration ( $[O_3]_l \approx 5.0$  mg/L) and different temperatures.

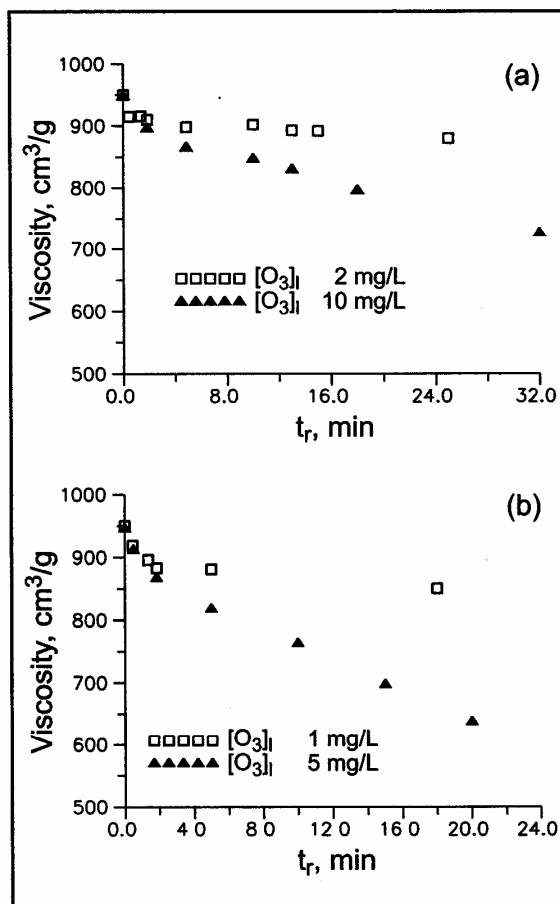


Fig. 3. Standard viscosity for experiments carried out with fully bleached eucalyptus pulp at 4°C (a) and 23°C (b) at different liquid ozone concentration.

ensure the removal of all the extractives that might react with ozone and generate radicals with a high oxidation potential [7]. The native and the microcrystalline celluloses were supplied in powder form with crystallinity indexes (C.I.) of 51 and 80%, respectively. The lower crystallinity index of native cellulose is also reflected in the specific surface area ( $5.23$  vs  $3.16$  m<sup>2</sup>/g). These materials were exposed to ozone and the effect of time for different reaction temperatures is illustrated in Fig. 2b by means of the viscosity profiles. At 2°C, it can be seen that native cellulose undergoes a very low degradation rate. In fact, for a reaction time of 60 min, pH  $\approx 2.5$  and  $[O_3]_l \approx 5.5$  mg/L, the viscosity drops from 425 to 322 cm<sup>3</sup>/g, despite the high ozone accessibility that can be inferred from its low crystallinity index and high surface area.

In order to further investigate the role of ozone upon the different cellulosic materials, the intrinsic viscosity ( $[\eta]$ ) was converted to the degree of polymerization ( $DP^{0.905} = 0.75 \times [\eta]$ ) and the scission per macromolecule [3] and the scission rate ( $\psi$ )

were estimated according to the following expressions:

$$\frac{\text{scission}}{\text{macromolecule}} = \frac{DP_0 - DP}{DP} \quad (1)$$

$$\begin{aligned} \psi &= \frac{\text{scission}}{\text{gram} \times \text{minute}} \\ &= \frac{\text{scission}}{\text{macromolecule}} \times \frac{1}{DP_0 \times 162} \\ &\quad \times 6.023 \times 10^{23} \times \frac{1}{\text{reaction time}} \end{aligned} \quad (2)$$

where  $DP_0$  and  $DP$  represent, respectively, the degree of polymerization at the beginning and at the end of a specific reaction period. Equations (1) and (2) can be used to calculate the integral scission rate (in this case,  $DP_0$  is referred to  $t_r = 0$ ) or the differential or instantaneous scission rate, in which case  $DP_0$  means  $DP$  at the previous time.

The integral scission rate for the fully bleached pulp (C.I. = 70%) and for the native cellulose (C.I. = 51%) can be observed

in Figs. 4a and b. Despite the very different physicochemical characteristics of the two materials, the profiles for the depolymerization rates are qualitatively very similar: the rate of depolymerization is time dependent and temperature shows a positive influence on the scission rate and on its extent.

Even at 2°C, native cellulose undergoes its highest scission rate in the first 2 min, decreasing thereafter to an approximately constant value (Fig. 4b). However, there is one important difference between these two materials. Native cellulose exhibits a more severe depolymerization than the fully bleached pulp as can be seen, for instance, for the run at 4°C: for a reaction time of 18 min the integral scission rate for the former is  $8.4 \times 10^{16}$  while a value of  $2.3 \times 10^{16}$  scission/(g·min) has been found for the latter. This is worth mentioning because such higher scission rate of native cellulose is not revealed by the viscosity drops. In fact, the viscosity loss for the native cellulose (C.I. = 51%) is 77 units while for the fully bleached pulp (C.I. = 70%) it is 119 units. However, the different extent of

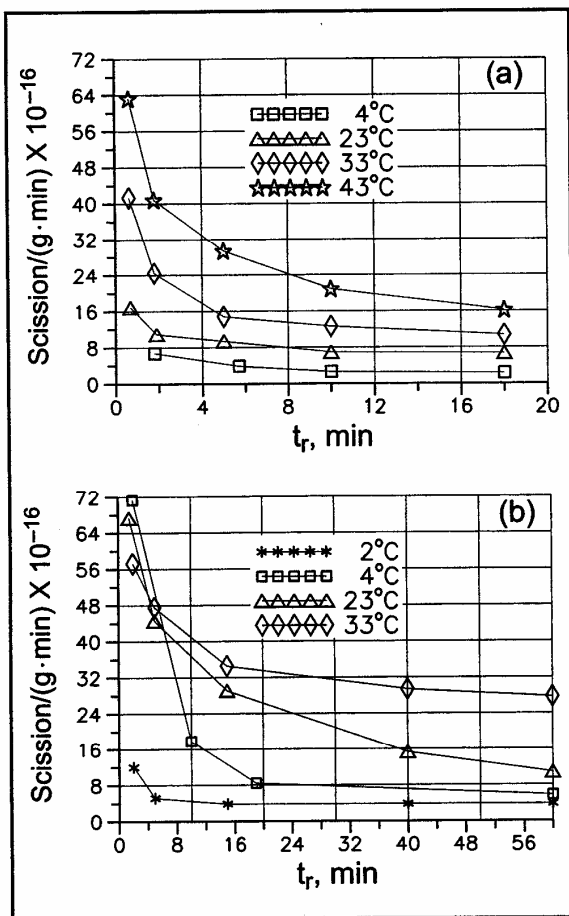


Fig. 4. Integral scission rates for the fully bleached pulp (a) and for the native cellulose (b) at different temperatures and similar liquid ozone concentration.

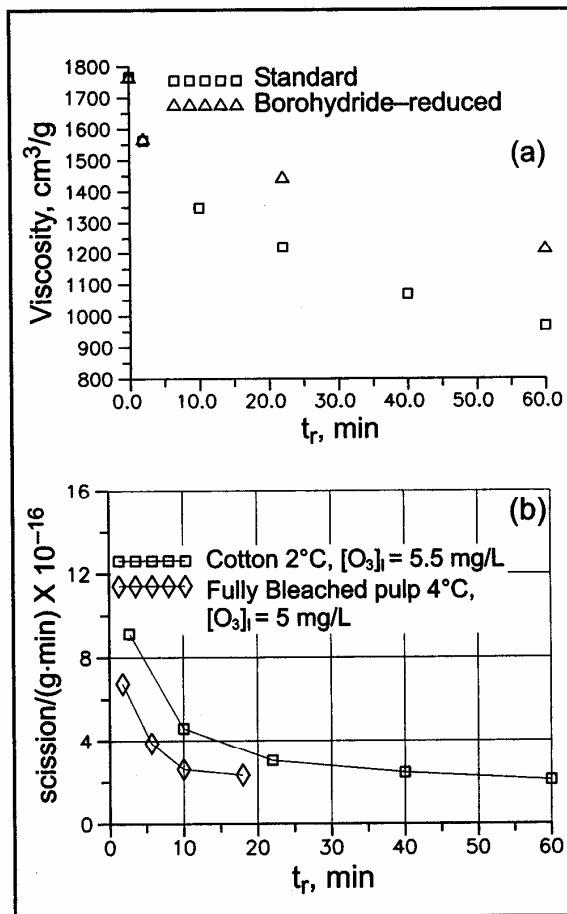


Fig. 5. Standard and borohydride-reduced viscosities (a) and integral scission rate (b) for a set of experiments carried out with cotton at 2°C.

breakage of intermonomeric linkages, measured by the scission rate, suggests that ozone accessibility (associated with the crystallinity index) might play an important role on the depolymerization rate of these materials.

When temperature increases from 2 to 4°C, the value of the integral scission rates duplicate for a reaction time of 18 min (Fig. 4b). The effect is even much higher if differential scission rate is considered. These results could only be explained by an excessively high activation energy, which suggests that the effect of temperature on the reaction rate of molecular ozone could not be the dominant factor. The enhancement of radical generation by temperature is certainly the most important reason for this behaviour.

In opposition to this, microcrystalline cellulose, which has a very high crystallinity (80%) and a very low degree of polymerization, is practically unaffected by ozone [9]. This is expected if one takes into account that the process of producing microcrystalline cellulose is based on the

extraction of the amorphous fraction by hydrolysis [10].

Cotton, with a very high initial viscosity (1767 cm<sup>3</sup>/g) and a crystallinity index of 90%, was also exposed to ozone after pre-extraction with sodium hydroxide to remove some extraneous compounds. The effect of ozone at 2°C, pH ≈ 2.5 and [O<sub>3</sub>]<sub>l</sub> ≈ 5.5 mg/L can be observed in Figs. 5a and b. Despite its higher crystallinity index (90%), when compared to the fully bleached pulp (70%), the drop in viscosity is severe. In fact, viscosity decreases from 1767 to 1348 cm<sup>3</sup>/g at 2°C, while the fully bleached pulp decreases from 948 to 870 cm<sup>3</sup>/g at 4°C, for a reaction time of 10 min. If the viscosity is converted to the number of scissions per gram and per minute, the integral scission rates at t<sub>r</sub> = 10 min are close to 4.5 × 10<sup>16</sup> and 2.6 × 10<sup>16</sup>, respectively, for cotton and fully bleached pulp (Fig. 5b). The high degradation of cotton verified in our experiments at 2°C is in very good agreement with the results reported by Godsay and Lewin [3] for experiments carried out at 25°C with cotton linters. The

results suggest that the physical properties, namely the initial degree of polymerization of the cellulose can also play a role on the depolymerization profiles.

To investigate the reaction between ozone and the polysaccharides present in an unbleached pulp, but in the absence of lignin, a lignin-free material was prepared from such a pulp by the chlorite method. A eucalyptus pulp (kappa number = 15.5) was selected because of its relatively low lignin contents and of its high viscosity (1270 cm<sup>3</sup>/g). The chlorite procedure is very selective and consequently the viscosity of the resulting material (holocellulose) remains high (1234 cm<sup>3</sup>/g), while the consumption of KMnO<sub>4</sub> leads to a kappa number of 1.6. Moreover, only one part of this consumption can be assigned to the residual lignin, according to the observations reported by Li and Gellerstedt [11] about the KMnO<sub>4</sub> consumption in the kappa number determination of hardwood pulps. Therefore, the generation of radicals as a result of the ozone-lignin reactions must be negligible. In Figs. 6a and b one can see the effect

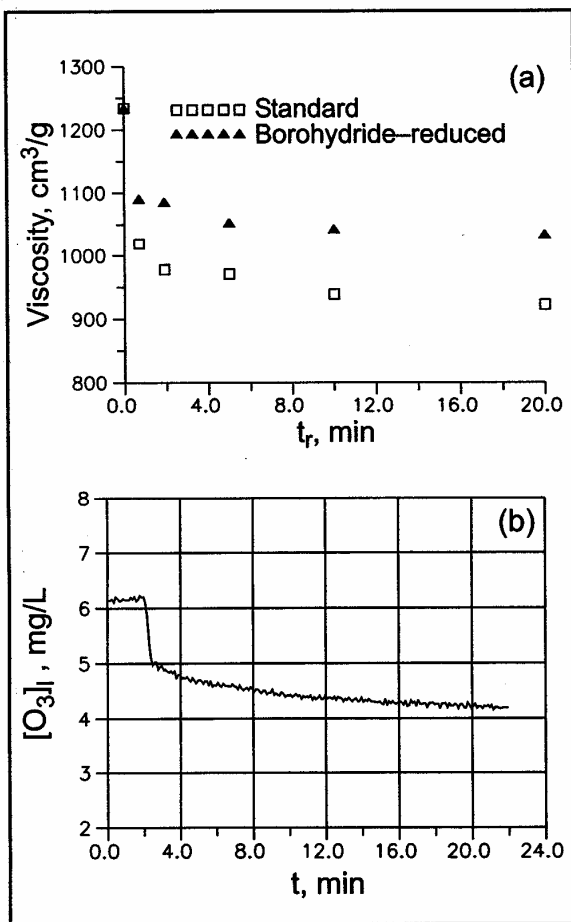


Fig. 6. Standard and borohydride-reduced pulp viscosities (a) and ozone profile in the liquid phase (b) for a set of experiments carried out at 4°C with eucalyptus holocellulose.

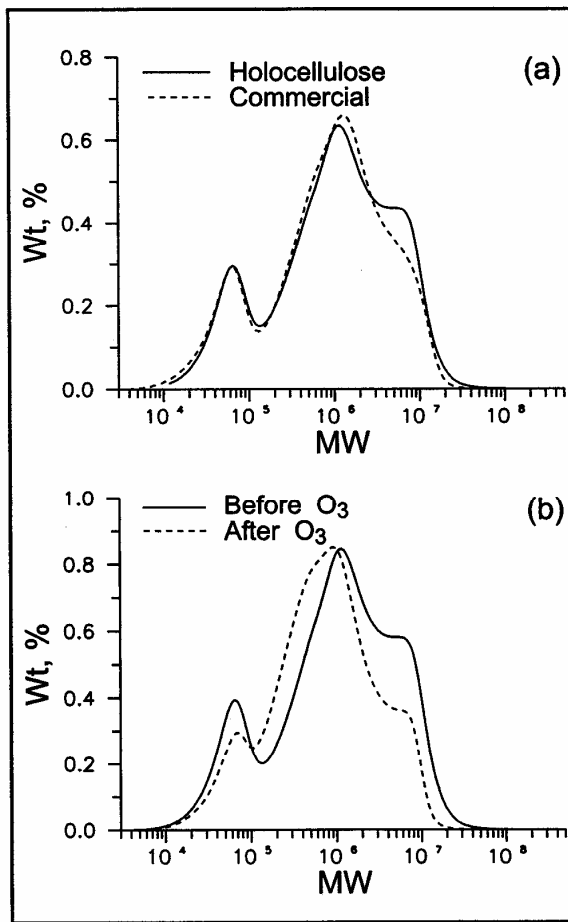


Fig. 7. Polysaccharide molecular weight distribution of a commercial eucalyptus bleached pulp and holocellulose from eucalyptus (a) and effect of ozone at 4°C on eucalyptus holocellulose (b).

of ozone on the standard and reduced viscosities of this material and the corresponding ozone concentration profile in the liquid phase. For both viscosities, there are two clear kinetic regimes for the rates of depolymerization/degradation. A very fast one, lasting for a period of time close to 2 min and a much slower thereafter. In terms of the differential scission rate (scission/(g·min)), the effect is even much more important.

A comparative analysis of Figs. 1b and 6a, respectively, for a fully bleached eucalyptus pulp (C.I. = 70%) and a holocellulose (C.I. = 67%) produced from an unbleached eucalyptus pulp reveals that the two materials exhibit different behaviours with regard to ozone. To better understand this, the molecular weight distribution (MWD) of the samples was determined by size-exclusion chromatography. Figure 7a, where the MWD of the two samples before ozone treatment are illustrated, shows that holocellulose has a larger fraction of macromolecules with high molecular

weight than the fully bleached pulp, which is also consistent with the corresponding viscosity values. According to these MWDs, one can formulate the following explanation for such distinct behaviours with respect to ozone: during the industrial bleaching process the pulp is exposed to severe reaction conditions which lead to the degradation of the larger macromolecules and to the extraction of some accessible polysaccharides. In contrast, the process of producing holocellulose is relatively mild, leaving polysaccharides with higher degrees of polymerization and good accessibility practically unaffected in the material. Thus, ozone has the ability of depolymerizing larger macromolecules, which explains why its impact on viscosity is higher in the holocellulose (Fig. 7b).

The hypothesis that the residual lignin in eucalyptus holocellulose can be responsible for the very deep initial degradation of polysaccharides must be discarded because a holocellulose produced from a pine kraft pulp in a similar way presented

lower initial and overall degradations despite its higher residual lignin content (kappa number of 3.0).

### Depolymerization of Cellulosic Materials Containing Lignin

In this section, the depolymerization of polysaccharides by ozone is discussed for an unbleached pulp (lignin-containing material) when compared to a holocellulose (corresponding lignin-free material). Figure 8a illustrates the profiles of standard viscosity for experiments carried out at 4°C and pH ≈ 2.5 with such cellulosic materials from eucalyptus pulp. Both low temperature and pH minimize the production of radicals by ozone self-decomposition. In this case, the experiments were conducted under slightly different gas flow conditions to compensate for the large differences in ozone consumption rates of the holocellulose and of the unbleached pulp. For the unbleached pulp, ozone was continuously supplied to the reactor during the experiment, while for the corresponding holocel-

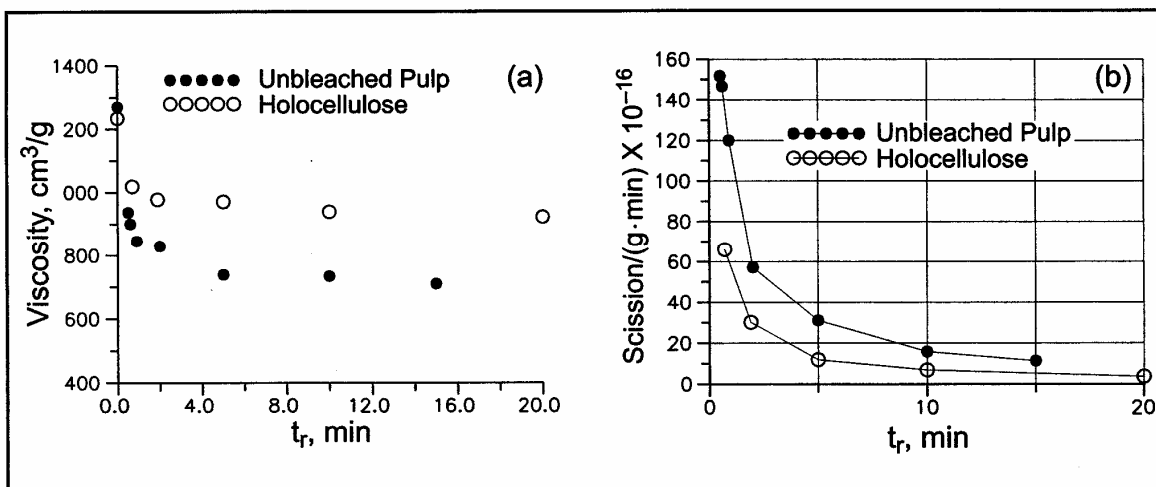


Fig. 8. Standard viscosity profiles (a), and integral scission rate (b) for unbleached pulp (kappa number = 15.5) and holocellulose eucalyptus at 4°C.

lulose the gas feed was cut off after introducing the material into the reactor. With this procedure, the time average ozone concentration in the suspension is very close for both materials (4.7 mg/L). The results demonstrate that the presence of lignin in the fibre matrix increases the polysaccharide degradation rate and its extent and the same conclusion holds for the reduced viscosity. Such differences cannot be justified by the presence of metals in the materials because both possess very low and closely similar metal contents [9]. A similar behaviour was also displayed by an unbleached pine pulp and the corresponding holocellulose [9]. The most plausible explanation for these different responses is the production of radicals with very high oxidation potentials as degradation products of the lignin-ozone reactions, as also suggested by several researchers [12,13].

## CONCLUSIONS

The effect of ozone at low temperature (2°C) and low pH on different cellulosic materials was investigated and the experiments revealed that molecular ozone depolymerizes polysaccharides at a moderate rate. Furthermore, the results suggest that ozone accessibility also plays an important role on the rate and on the extent of such degradation. The very pronounced influence of temperature upon the depolymerization is most likely due to the generation of radicals by heat effect. It was also confirmed that the lignin present in the matrix of unbleached pulp fibres enhances the depolymerization rates of the polysaccharides when compared to the behaviour of the corresponding lignin-free materials.

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KEYWORDS: POLYSACCHARIDES, DEPOLYMERIZATION, OZONE, CELLULOSE, BLEACHED PULPS, UNBLEACHED PULPS, HOLOCELLULOSE, MICROCRYSTALLINE CELLULOSE, TEMPERATURE, PH, RADICALS