

# REACTION RATES OF LIGNIN AND HEXENURONIC ACIDS WITH CHLORINE DIOXIDE, OZONE, AND SULFURIC ACID

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**Abstract.** The reaction rates of lignin and hexenuronic acids (HexA) with chlorine dioxide, ozone, and sulfuric acid were investigated. In unbleached and oxygen-delignified eucalyptus kraft pulps containing both lignin and HexA, only HexA, or only lignin reacted with chlorine dioxide, ozone, and sulfuric acid under typical bleaching conditions. The maximum reaction rates of chlorine dioxide with lignin and HexA were 57.2 and 26 mmol/kg/min, respectively, for unbleached pulp, and 26.7 and 13 mmol/kg/min, respectively, for oxygen-delignified pulp. The maximum reaction rates of ozone with lignin and HexA were 58.6 and 132 mmol/kg/min, respectively, for unbleached pulp, and 56.8 and 134 mmol/kg/min, respectively, for oxygen-delignified pulp. The maximum reaction rates of sulfuric acid with lignin, and HexA were 1.11 and 0.93 mmol/kg/min, respectively, for unbleached pulp, and 1.95 and 0.80 mmol/kg/min, respectively, for oxygen-delignified pulp. Chlorine dioxide reacts faster with HexA in the presence of the residual lignin. The kinetic results suggest that pulp treatment with ozone, when justifiable, should follow but not precede chlorine dioxide oxidation. Unbleached pulp residual lignin and HexA react twice as fast with chlorine dioxide than the lignin and HexA present in oxygen-delignified pulp, while the pulp type has no significant effect on lignin and HexA reactivity toward ozone. HexA reactions with sulfuric acid and ozone can be described by two-phase pseudo first-order reaction rates.

**Keywords:** Eucalyptus, kraft pulp, lignin, hexenuronic acids, ozone, chlorine dioxide, sulfuric acid, reaction rates.

## INTRODUCTION

Lignin was considered the principal pulp component responsible for bleaching chemical con-

sumption until the early nineties, when the importance of hexenuronic acids (HexA) was discovered. HexA are found in hardwood kraft pulps, where they can represent a significant portion of the kappa number. They are generated during kraft pulping, and the amount formed de-

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depends on the pulping process (conventional or modified), temperature, and alkali charge (Vuorinen *et al.* 1996). HexA are not removed in alkaline media (oxygen and hydrogen peroxide bleaching) but are oxidized in acidic media (chlorine dioxide and ozone bleaching), and thus consume part of the bleaching reagents applied. The HexA rate of hydrolysis is known to increase with increasing temperature and decreasing pH; but even under relatively severe conditions (1 h/110°C/pH 3.5) they are not completely removed from kraft pulp (Vuorinen *et al.* 1996; Jiang *et al.* 2000). Another undesirable aspect of HexA is that they increase the kraft pulp affinity for metals since these acids contain conjugated double bonds that are capable of chelating metals and cause pulp brightness reversion (Devenyns and Chauveheid 1997).

A hot-acid hydrolysis stage ( $A_{HT}$ ) run at pH 3.0–3.5 and 90–95°C for 120 min was proposed as an adequate treatment for removal of HexA from kraft pulps (Henricson 1997; Lachenal and Chirat 2000). However, implementation of this treatment in a mill would require a rather large investment because of the need for an acid-resistant bleaching tower and an additional pulp washer. Lower-cost alternatives to the  $A_{HT}$  stage that have been developed include hot chlorine dioxide ( $D_{HT}$ ) and hot-acid treatment followed by chlorine dioxide without intermediate washing (A/D). Both these alternatives are being used commercially, with less than ideal performance.

It is known that chlorine dioxide reacts rapidly with kraft pulp lignin, and the delignification rate is believed to depend mainly on chlorine dioxide concentration, kappa number, pH, and chloride concentration (Reeve 1996; Chandranupap and Nguyen 2000; Barroca *et al.* 2001; Tessier and Savoie 2000). Temperature, within the range used in kraft pulp bleaching, was not found to affect the chlorine dioxide delignification rate (Barroca *et al.* 2001). Chlorine dioxide *per se* does not react with HexA, but its intermediates present in the reaction medium, elemental chlorine and hypochlorous acid, do

react with these acids (Costa and Colodette 2007).

Ozone also reacts rapidly with kraft pulp lignin. The ozone delignification rate in oxygen-delignified kraft pulp was shown to depend on initial kappa number and ozone gas concentration. Initial delignification is rapid and corresponds to high ozone consumption (Chapman *et al.* 1998).

Most bleaching studies have focused on the delignification rates by following the kappa number drop. There is still a lack of knowledge of the individual reaction rates of pulp lignin and HexA with bleaching reagents commonly used. This knowledge is essential for determining the most efficient and cost-effective form of removing HexA and lignin during pulp bleaching. Therefore, the objective of this study was to determine the rates of reaction of chlorine dioxide, ozone, and sulfuric acid with both pulp lignin and HexA.

## MATERIAL AND METHODS

### Pulps

Samples of unbleached and oxygen-delignified kraft pulps were used. Both pulps were prepared from Eucalyptus spp. wood in an industrial facility equipped with an isothermal cooking (ITC) process. The unbleached and oxygen-delignified pulps were divided into three samples: the reference, containing both lignin and HexA, the “lignin-free” sample, and the “HexA-free” sample. Figure 1 presents the main procedures used to prepare these pulp samples and their principal characteristics. These three pulp types were then treated with  $ClO_2$ ,  $O_3$  and  $H_2SO_4$  in a variety of time intervals, and their total lignin and HexA contents were quantified. Brightness measurements were made on hand sheets after alkaline extraction of the treated pulps.

### Removal of pulp lignin

This process was performed with 300 g od (oven-dry) pulp samples under the following

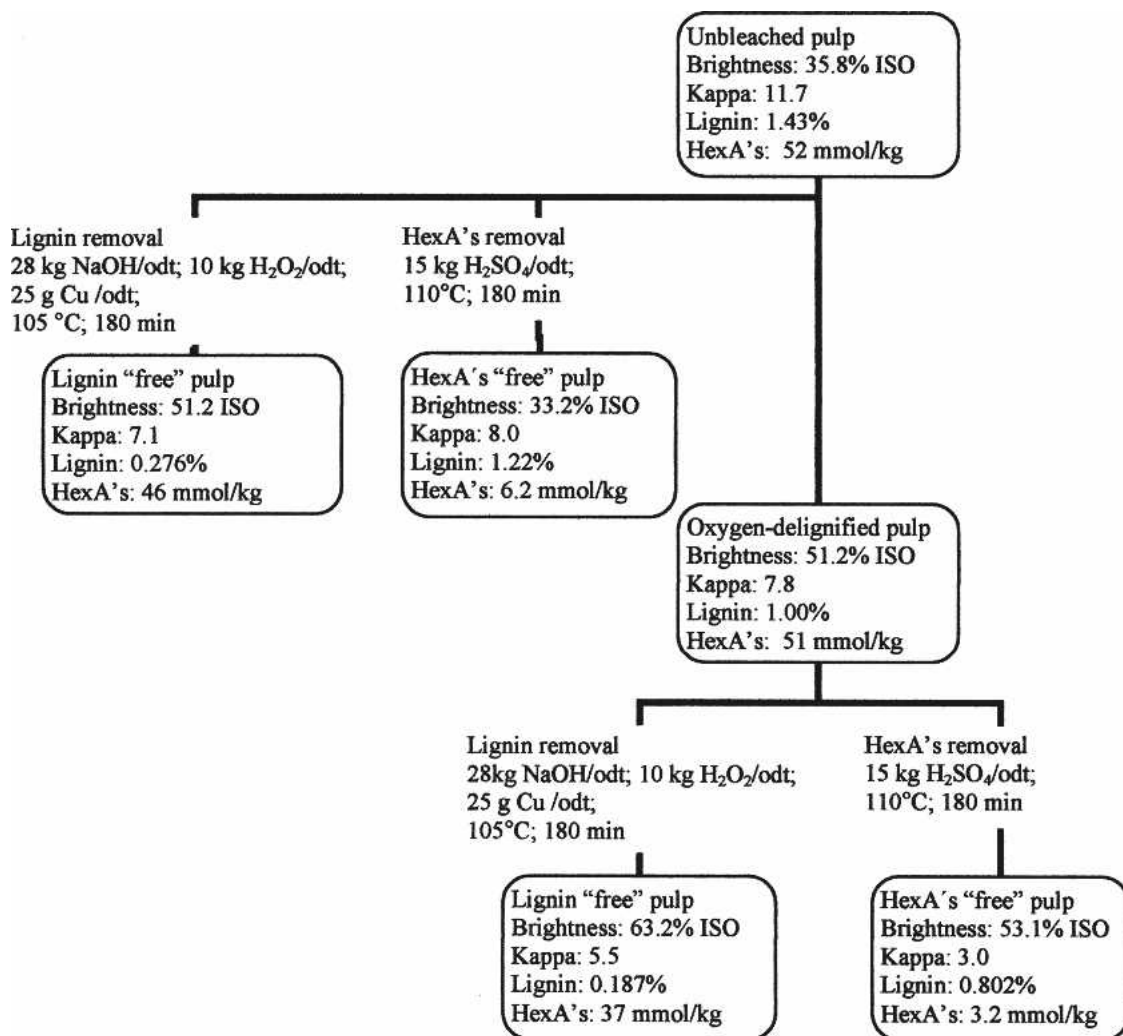


FIGURE 1. Characteristics of unbleached and oxygen-delignified reference, "lignin-free" and "HexA-free" pulps.

conditions: 10% consistency, 105°C, 180 min, 20 kg O<sub>2</sub>/t, 28 kg NaOH/t, 10 kg H<sub>2</sub>O<sub>2</sub>/t, and 25 mg/kg copper. The treatment was performed in a Mark V reactor/mixer (Quantum Technologies, Twinsburg, OH). The O<sub>2</sub>, NaOH, and H<sub>2</sub>O<sub>2</sub> charges were added after the reactor had reached the pre-established temperature, and the mixture was intermittently mixed for the reaction time. After completing the reaction, the pressure was released, residual liquor was withdrawn for analysis, and the pulp was washed with the equivalent of 11 m<sup>3</sup> distilled water per oven-dry

tonne (odt) of pulp. This treatment was repeated four times.

### Removal of pulp hexenuronic acids

This step was performed with 300 g od pulp samples under the following conditions: 10% consistency, 110°C, 180 min, and 15 kg H<sub>2</sub>SO<sub>4</sub>/t. Pulp at the desired consistency was heated to the reaction temperature, and the pre-established H<sub>2</sub>SO<sub>4</sub> charge was then added to a Mark V reactor/mixer, under constant mixing. After completing the reaction, residual liquor was withdrawn for analy-

TABLE 1. General treatment conditions.

Condition	Treatment			
	Sulfuric acid	Chlorine dioxide	Ozone	Alkaline extraction*
Consistency (%)	10	10	40	10
Time (min)	15/30/60/120/180	1/2/5/10/15/30	0.17/0.33/0.5/1/2	60
Temperature (°C)	95	60	30	70
Final pH ( $\pm 0.2$ )	3.0	3.0	3.0	11.5
NaOH (%)	—	—	—	optimized
O <sub>3</sub> (%)	—	—	0.4	—
H <sub>2</sub> SO <sub>4</sub> (%)	optimized	optimized	optimized	—
ClO <sub>2</sub> (%)	—	**KF = 0.20 and 0.30	—	—

\* Alkaline extraction performed only after the D and Z stages.

\*\* KF = kappa factor

sis and the pulp was washed with the equivalent of 11 m<sup>3</sup> distilled water per odt of pulp. This treatment was carried out with two repetitions.

**Sulfuric acid treatment (A<sub>HT</sub>).** This stage was carried out in a Mark V reactor/mixer using 300 g od pulp samples and the conditions listed in Table 1. The pulp was placed in the Mark V reactor/mixer at the desired consistency and heated to the desired temperature. The pre-established acid charge was injected under constant mixing. After the reaction time, residual liquor samples were extracted for pH analysis, and the pulp was washed with the equivalent of 11 m<sup>3</sup> distilled water per odt of pulp. This stage was repeated twice.

**Chlorine dioxide treatment (D<sub>o</sub>).** This treatment was carried out in polyethylene bags with 50 g od samples, using the conditions listed in Table 1. The bleaching liquor was added to the pulp at room temperature. The acid or alkali necessary for pH control was determined in a preliminary study. The bag was manually mixed, heated in a microwave oven to the desired temperature, and transferred to a vapor bath equipped with thermostat. After the lapsed reaction time, residual liquor was extracted from the pulp for analysis, and the pulp washed with the equivalent of 11 m<sup>3</sup> distilled water per odt of pulp. This stage was repeated twice.

**High consistency ozone treatment (Z).** Ozone treatment was performed in a rotating glass reactor, using 25 g od pulp samples and the conditions listed in Table 1. Sample pH was adjusted by adding sulfuric acid as needed with the

pulp at 6% consistency. The mixture was held at this pH for about 15 min and then dewatered in a centrifuge. Following this, the pulp was fluffed in a stainless steel laboratory fluffer and the consistency determined. The fluffed pulp sample was placed in a 3000 mL glass flask adapted to a rotary evaporator. Ozone flow of known concentration was passed through the sample and the unreacted ozone was collected in a 5% KI solution. After iodometric titration, ozone consumption was calculated. The pulp was washed with the equivalent of 11 m<sup>3</sup> distilled water per odt of pulp. This stage was repeated four times.

**Alkaline extraction (E).** After the chlorine dioxide and ozone treatments, alkaline extraction was carried out in polyethylene bags with 50 g od pulp samples using the conditions listed in Table 1. The bleaching liquor was added to the pulp at room temperature, the bag was manually kneaded and heated in a microwave oven to the desired temperature, and then transferred to a vapor bath where it was kept for the reaction time. At the end of the reaction, residual liquor samples were extracted for analysis, and the pulp was washed with the equivalent of 11 m<sup>3</sup> distilled water per odt of pulp. All extractions were repeated twice.

### Analytical procedures

Pulp hand sheet formation, kappa number, acid-insoluble lignin content, acid-soluble lignin content, viscosity, and brightness were carried out according to Tappi Standard Procedures and Useful Methods (1998). Hexenuronic acids were measured according to Vuorinen et al (1996).

### Reaction rate determination

The reaction rates for the treatments with chlorine dioxide, sulfuric acid, and ozone were calculated by determining the concentrations of lignin or HexA at given time intervals. For example, the lignin concentration of the reference oxygen-delignified pulp was 55.6 and 28.9 mmol/kg at 0 and 1 min reaction with chlorine dioxide, respectively. Hence, the rate of reaction at the 1-min time interval was equal to 26.7 mmol/kg · min [ $-(28.9-55.6\text{mmol/kg})/\text{min}$ ]. This procedure was used to calculate all other reaction rates reported. The reactant concentrations were established based on pulp mill experience. For example, the chlorine dioxide concentration was established based on a kappa factor of 0.20, which is widely used for both unbleached and oxygen-delignified pulps (Pryke and Reeve 1997). Tentatively, a higher kappa factor of 0.30 was also evaluated, but this value is excessively high for most mill applications. For example, for the reference oxygen-delignified pulp that had a kappa number of 7.8, the  $\text{ClO}_2$  concentration applied was 88 mmol  $\text{ClO}_2/\text{kg}$  pulp (kappa factor 0.20). The ozone concentration was also established based on pulp mill operation practice, and a value of 0.4% ozone based on pulp weight was applied, which is equivalent to 0.083 mmol  $\text{O}_3/\text{kg}$  pulp. In the case of sulfuric acid treatment, the acid applied was that required to drop the reaction pH medium to exactly 3.0, which was equivalent to about 0.122 mmol  $\text{H}_2\text{SO}_4/\text{kg}$  pulp. The reaction consistency was 10% for the chlorine dioxide and sulfuric acid treatments, and 40% for the ozone one. Thus, the initial concentrations of 88 mmol  $\text{ClO}_2/\text{kg}$  pulp and 0.122 mmol  $\text{H}_2\text{SO}_4/\text{kg}$  pulp were equivalent to 9.8 mmol  $\text{ClO}_2/\text{L}$  and 0.0136 mmol  $\text{H}_2\text{SO}_4/\text{L}$ , respectively. For the ozone case, the concentration of 0.083 mmol/kg was equivalent to 0.055 mmol/L.

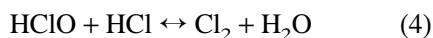
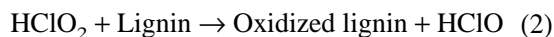
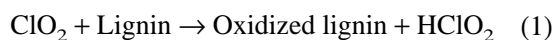
### RESULTS AND DISCUSSION

Note that the “lignin-free” and “HexA-free” pulp terminology that appears in the text hereon refers to pulps treated according to Fig 1. These pulps had greatly reduced concentrations of lig-

nin or HexA as compared with normal pulps. However, it was not possible to free these pulps completely from lignin or HexA. Therefore, the terms “lignin-free” and “HexA-free” pulps are not appropriate, and thus marked with “quotes” throughout this text. Note also that the purpose of this work was simply determining average reaction rates in time intervals, and not the reaction orders as previously reported for acid hydrolysis (Jiang et al 2006) and ozone (Tran 2006) reactions with HexA.

### Chlorine dioxide reaction rates

The rates of chlorine dioxide reactions with lignin and HexA are shown in Fig 2. Maximum reaction rates were reached within 1 min, and fell off rapidly thereafter. The lignin reaction rate was about 2-fold higher than the HexA reaction rate in both unbleached and oxygen-delignified pulps. Given that chlorine dioxide does not react directly with HexA, a greater difference in reaction rate between lignin and HexA was expected. Apparently, a significant fraction of the chlorine dioxide was converted into elemental chlorine and hypochlorous acid (Eq (4)) during the chlorine dioxide treatment, and these chemicals react indiscriminately with lignin and HexA (Costa 2001; Törngren 2002). Although several alternatives have been proposed for removing HexA, the results show that a chlorine dioxide treatment alone has great ability to remove these acids through its byproducts generated in reactions with the lignin (Eqs (1–4))



The lignin reaction rate in the unbleached pulp was twice as high as that in the oxygen-delignified pulp, while the HexA reaction rate in the unbleached pulp was about 1.5 times higher than in the oxygen-delignified pulp. Higher chlorine dioxide reaction rates with lignin were

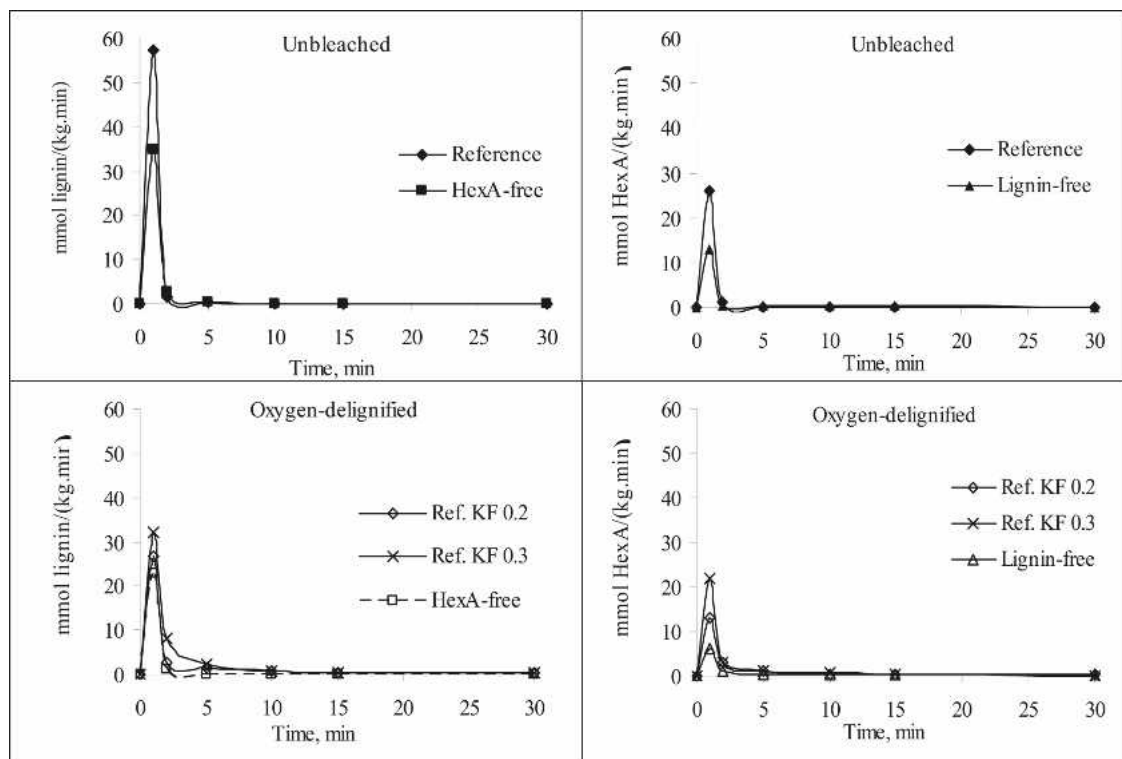


FIGURE 2. Kinetics of lignin (left column) and hexenuronic acids (right column) reactions with chlorine dioxide in reference, "lignin-free" and hexenuronic acids "free" ("HexA-free") unbleached and oxygen-delignified pulps.

found in the unbleached pulps, because of the higher concentrations of lignin and chlorine dioxide in the reaction mixture. A test was also run to compare the unbleached and oxygen-delignified pulps using equivalent chlorine dioxide doses (kg  $\text{ClO}_2$ /odt pulp) by raising the kappa factor from 0.2–0.3 for the oxygen-delignified pulp. The higher chlorine dioxide dose resulted in a 70% increase in the oxygen-delignified pulp HexA reaction rate and an 18% increase in the lignin reaction rate, illustrating the dependence of the reaction rate on the chlorine dioxide concentration.

The lignins in the unbleached and oxygen-delignified reference pulps were more reactive than in the "HexA-free" pulps. The acid treatment used to remove the HexA likely negatively affected the lignin reactivity. In fact, Tran (2006) has demonstrated that the residual lignin remaining in the pulp after HexA removal by

long acid-hydrolysis treatment is more condensed than the untreated pulp lignin. It should be noted that a lower chlorine dioxide concentration was used in this case (constant kappa factor) because the pulp had a lower kappa number after the HexA removal, and the chlorine dioxide reaction rate is known to depend on chlorine dioxide concentration (Reeve 1996). This may also explain the much lower rate of reaction of the "HexA-free" pulp toward chlorine dioxide.

The HexA in the reference pulps presented higher reactivities with chlorine dioxide than the HexA in the "lignin-free" pulps. The lignin removal treatment may have negatively affected HexA reactivity. Also, the lower kappa numbers in the "lignin-free" pulps required less chlorine dioxide (constant kappa factor), and therefore, there was a lower concentration of the chlorine dioxide hydrolysis products, elemental chlorine,

and hypochlorous acid, present to react with the HexA. Again, this may also explain the much lower rate of reaction of HexA toward chlorine dioxide in the “lignin-free” pulp.

### Sulfuric acid reaction rates

The reaction rates of sulfuric acid with lignin and HexA are presented in Fig 3. Maximum reaction rates were obtained after 15–30 min for both unbleached and oxygen-delignified pulps. It should be noted that in all cases the sulfuric acid reaction rates with lignin and HexA were quite low ( $<2$  mmol/(kg · min)).

The HexA in the reference pulps reacted more rapidly with sulfuric acid than those in the “lignin-free” pulps despite the fact that they were present in the same concentration in both pulps. This result indicates that the lignin removal process significantly decreased the reactivity of the

HexA toward sulfuric acid hydrolysis. The HexA reaction rates were higher in the unbleached pulps than in the oxygen-delignified pulps, while the lignin reaction rates were higher in the oxygen-delignified pulps than in the unbleached pulps. Somewhat surprisingly, the lignin reaction rates were higher than the HexA reactions rates with sulfuric acid in the unbleached and oxygen-delignified reference pulps. These results suggest that a significant role of the acid-hydrolysis of hardwood pulp is indeed the removal of easily accessible and highly reactive lignin fragments besides the removal of HexA.

The hot-acid hydrolysis stage ( $A_{HT}$ ) was developed to remove HexA from pulps (Vuorinen et al 1996). The results of the present study demonstrate that the rate of reaction of these acids with sulfuric acid is quite slow. Therefore, running the acid stage in the presence of chlorine

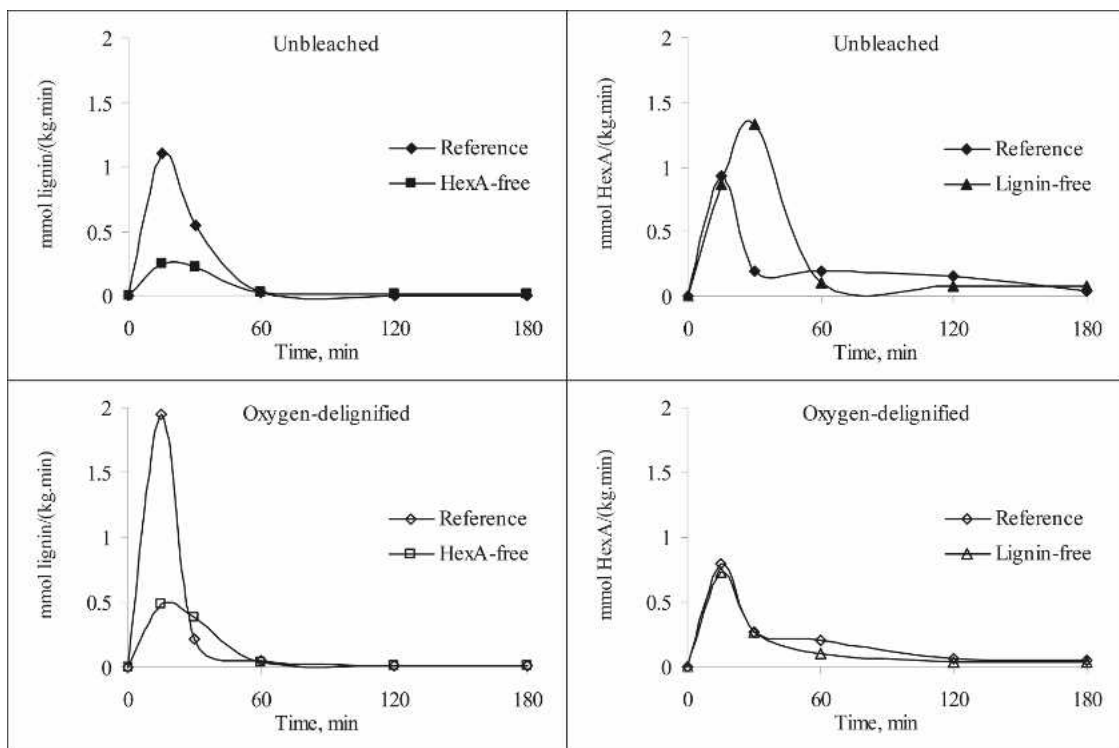


FIGURE 3. Kinetics of lignin (left column) and hexenuronic acids (right column) reactions with sulfuric acid in reference, “lignin-free” and hexenuronic acids “free” (“HexA-free”) unbleached and oxygen-delignified pulps.

dioxide ( $D_{HT}$ ) is not very effective from a kinetic standpoint since the chlorine dioxide reacts more rapidly with the HexA than the acid, decreasing the benefit of the simultaneous acid hydrolysis. The  $A_{HT}D$  technology is apparently more beneficial, given that the chlorine dioxide does not react with the HexA since these would already be hydrolyzed by the acid. However, if the  $A_{HT}D$  technology is applied without intermediate washing, as has been proposed (Henricson 1997, the so-called  $A_{HT}/D$  approach), the chlorine dioxide reacts with the organic matter dissolved during the acid hydrolysis, and bleaching results are less favorable (Eiras and Colodette 2003).

### Ozone reaction rates

The reaction rates of the ozone with lignin and HexA are presented in Fig 4. Maximum rate values were reached within the first 10 s of the

ozone treatment, and then fell sharply to low values within the first minute. The HexA reaction rates were about 2.3-fold higher than the lignin reaction rates in both unbleached and oxygen-delignified pulps. No differences were observed in lignin reaction rates between reference and “HexA-free” pulps or in HexA reaction rates between reference pulps and “lignin-free” unbleached and oxygen-delignified pulps. These results indicate that the reaction rates with ozone are independent of lignin and HexA content.

The ozone stage should be located strategically within the bleaching sequence to reduce the HexA content. Combined chlorine dioxide/ozone bleaching stages, (DZ) and (ZD), have both been used for pulp bleaching. From a kinetic standpoint, the more appropriate order is (DZ), since ozone has a much higher reaction rate than chlorine dioxide with both lignin and HexA. The combined (DZ) bleaching stage was

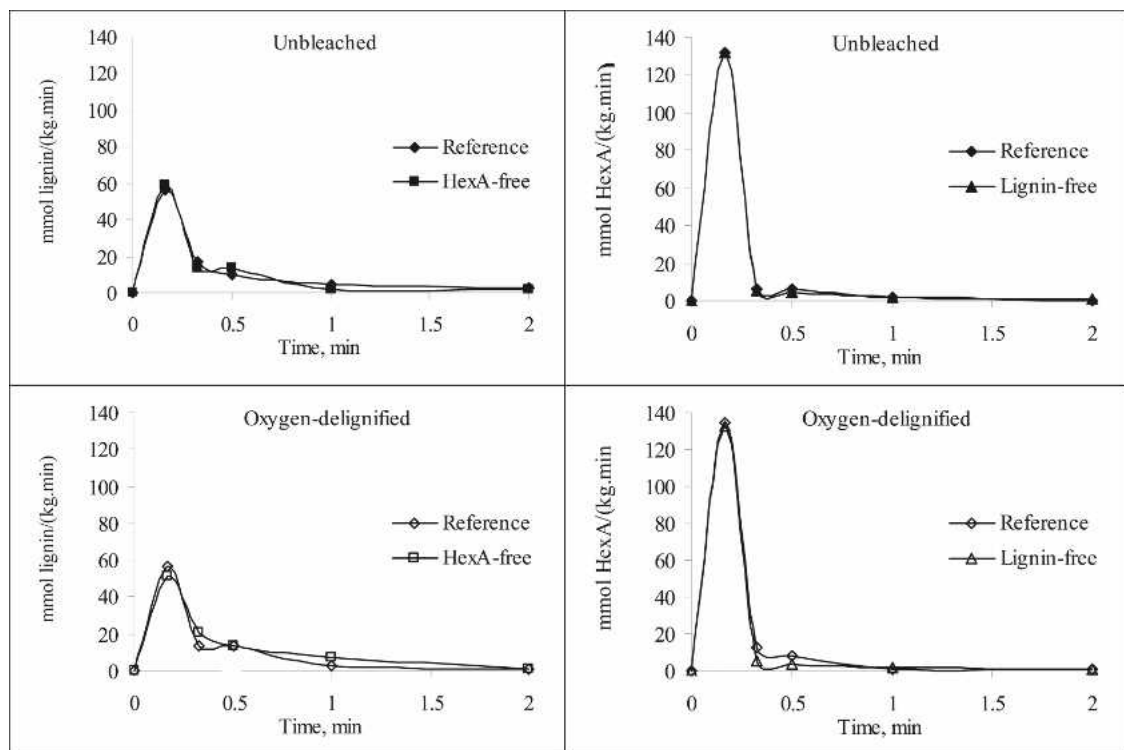


FIGURE 4. Kinetics of lignin (left column) and hexenuronic acids (right column) reactions with ozone in reference, “lignin-free” and hexenuronic acids “free” (“HexA-free”) unbleached and oxygen-delignified pulps.



TABLE 2. Maximum chlorine dioxide, sulfuric acid and ozone reaction rates with lignin and hexenuronic acids in reference, "HexA-free" and "lignin-free" unbleached and oxygen-delignified pulps.

Pulp	Reagent	Maximum reaction rate, mmol/(kg · min)			
		Unbleached pulp		Oxygen-delignified pulp	
		Lignin	HexA	Lignin	HexA
Reference	ClO <sub>2</sub>	57.2	26	26.7	13
	H <sub>2</sub> SO <sub>4</sub>	1.11	0.93	1.95	0.80
	O <sub>3</sub>	56.3	132	56.8	135
"HexA-free"	ClO <sub>2</sub>	34.7	—	22.7	—
	H <sub>2</sub> SO <sub>4</sub>	0.25	—	0.48	—
	O <sub>3</sub>	58.6	—	51.2	—
"lignin-free"	ClO <sub>2</sub>	—	13	—	6
	H <sub>2</sub> SO <sub>4</sub>	—	1.33	—	0.73
	O <sub>3</sub>	—	132	—	132

previously indicated as the preferred strategy (Toven et al 2002) based on the reactivity of residual lignin. In that study it was reported that the chlorine dioxide reacts only with free phenolic structures while ozone reacts with both free phenolic and nonphenolic moieties, and

therefore chlorine dioxide should be added to the pulp first. This may be the case for softwood pulps, but for hardwood pulps, the faster reaction rates of ozone with lignin and HexA in relation to chlorine dioxide seems to be a better rationale to explain why (DZ) outperforms the (ZD) process.

### Comparison of maximum reaction rates

Table 2 summarizes the maximum lignin and HexA reaction rates with chlorine dioxide, sulfuric acid, and ozone. In the unbleached reference pulp, chlorine dioxide, and ozone presented similar reaction rates with lignin. However, when the HexA were removed, the lignin reaction rate with chlorine dioxide was only 60% of that with ozone. In the oxygen-delignified pulp, the lignin reaction rate with ozone was over 2-fold the rate with chlorine dioxide, in both the reference and "HexA-free" pulps. The HexA re-

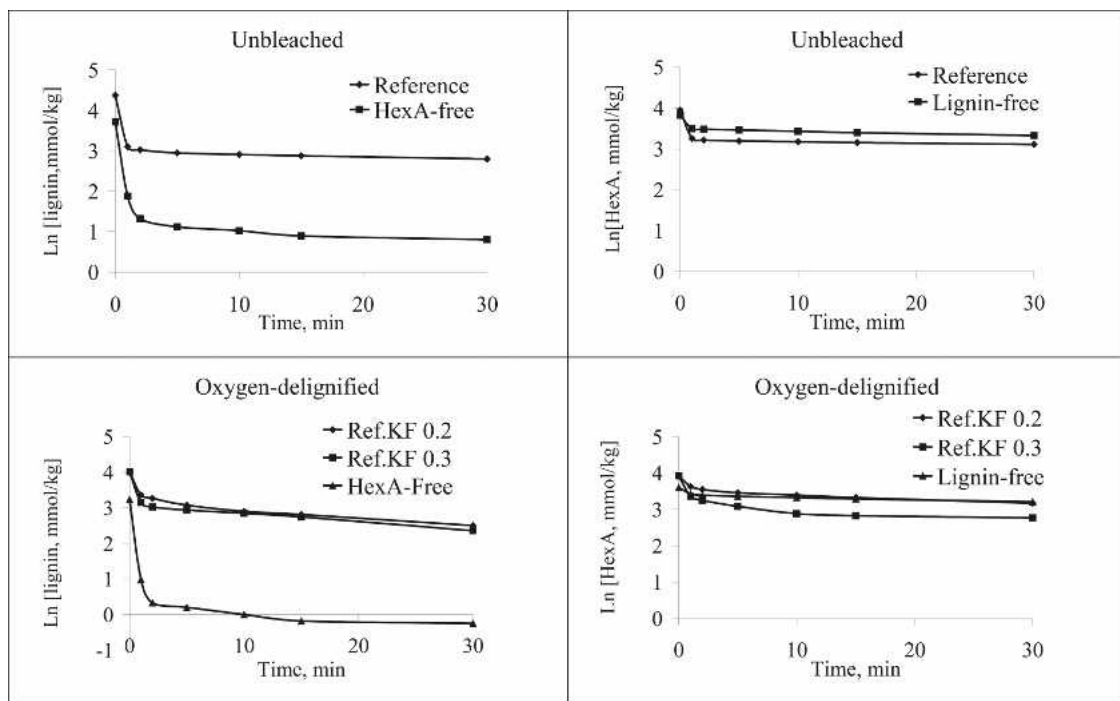


FIGURE 5. Pseudo first-order rate plots for the reaction of lignin (left column) and hexenuronic acids (right column) reactions with chlorine dioxide in reference, "lignin-free" and hexenuronic acids "free" ("HexA-free") unbleached and oxygen-delignified pulps.

action rates with ozone were 5- to 10-fold higher than with chlorine dioxide in the unbleached reference and “lignin-free” pulps, and 10- to 20-fold higher in the oxygen-delignified reference and “lignin-free” pulps. The rates of sulfuric acid reaction with lignin and HexA were only a small fraction of the rates of chlorine dioxide and ozone with these pulp constituents. Surprisingly, sulfuric acid gives higher reaction rates with lignin than HexA, in both unbleached and oxygen-delignified pulps.

### Pseudo first-order rate plots

Pseudo first-order rate plots for the reactions of chlorine dioxide with lignin and HexA tend to indicate a two-phase reaction process, a very fast initial phase within the first minute and a sluggish second phase afterward (Fig 5). This is explained by the rapid consumption of the chlorine dioxide by lignin and HexA in the first phase, leaving basically no oxidant left to react with the

pulp components in the second phase. These two very distinct phases would likely not have been seen if chlorine dioxide were added in excess, which is not a usual practice in the industry. However, for the sulfuric acid reaction with lignin and HexA, two distinct reaction phases are observed in the pseudo first-order plots (Fig 6). Since sulfuric acid was present throughout the entire reaction time at constant pH (3.0), it can be assumed that there are easy and difficult to remove HexA and lignin fractions in the pulps. In the case of lignin, the first phase, lasting about 30 min, likely removed the so-called acid-soluble lignin commonly present in hardwood kraft pulps. After 30-min reaction, hardly any lignin was removed since the operational conditions (pH 3.0, 95°C) were not sufficiently strong to hydrolyze the acid-insoluble lignin fraction. A different behavior was observed in the pseudo first-order plot for HexA reaction with sulfuric acid. A fast first-phase reaction occurred for the first 15–20 min, and a distinctly slower second-

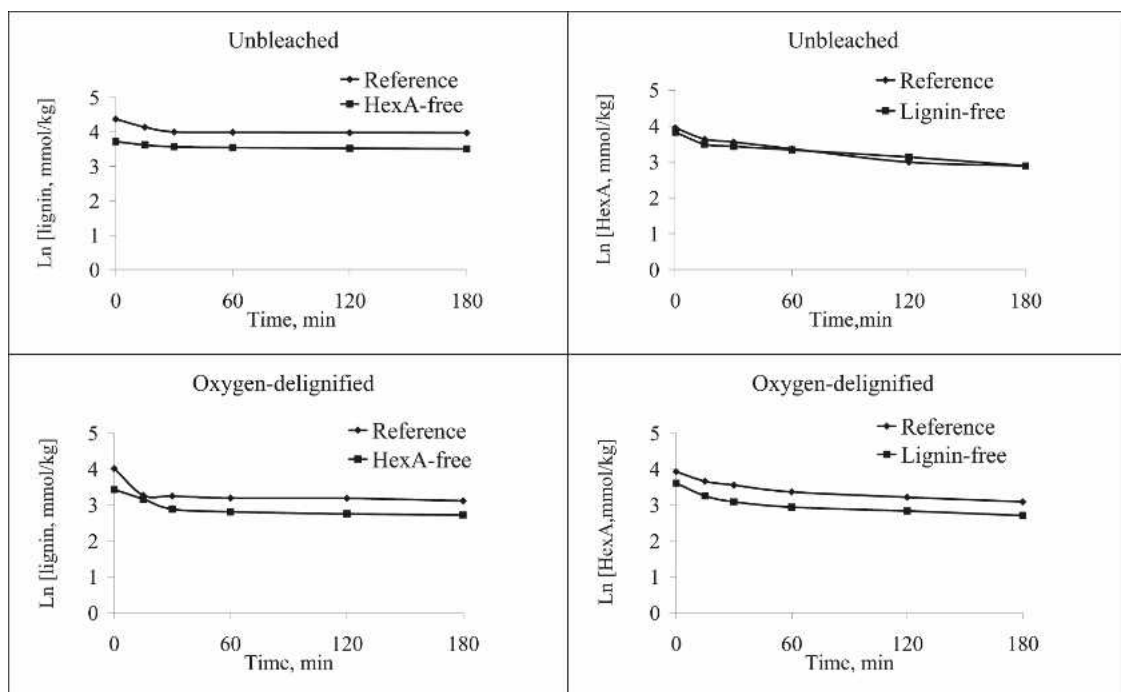


FIGURE 6. Pseudo first-order rate plots for the reaction of lignin (left column) and hexenuronic acids (right column) reactions with sulfuric acid in reference, “lignin-free” and hexenuronic acids “free” (“HexA-free”) unbleached and oxygen-delignified pulps.

phase reaction occurred during the remaining time. Likely, the easy-to-remove HexA fraction was hydrolyzed in the first phase whereas the more acid-resistant fraction was removed in the second phase. This same trend was found in a recent study by Jiang et al (2006) for different pulp furnishes.

Ozone is known to react readily both with lignin and HexA. The pseudo first-order plots shown in Fig 7 indicate a very distinct two-phase reaction of ozone with HexA. Similar results have been reported by Tran (2006). The first-phase reaction with HexA is completed within 0.2 min and then becomes negligible. Likely, a fraction of the HexA present in the pulp is resistant to ozone and only the easy-to-remove HexA fraction responds to ozone treatment. In the case of lignin, the two distinct phases were not found, suggesting that pseudo first-order rate mechanisms are not applicable because the lignin reaction with ozone is mass-transfer limited. High shear mixing was provided during the entire reaction time

(2 min) without ozone depletion. Likely, reaction of ozone with lignin involves multiple slowly-decreasing rates of reaction that depend upon ozone diffusion within the pulp fiber wall.

## CONCLUSIONS

Although chlorine dioxide reacts about twice as fast with lignin as with HexA in unbleached and oxygen-delignified pulps, the rate of reaction with HexA is still significant. The reaction of chlorine dioxide with HexA is higher in the presence of lignin. HexA react significantly faster with chlorine dioxide than with pure sulfuric acid. Pulp hydrolysis with sulfuric acid removes lignin at a faster rate than it removes HexA. Oxygen delignification reduces the reactivity of pulp HexA with sulfuric acid. Ozone reacts 2.4 times faster with HexA than with lignin, both in unbleached and oxygen-delignified pulps. Among the three reagents investigated, ozone presented the highest rates of reaction with

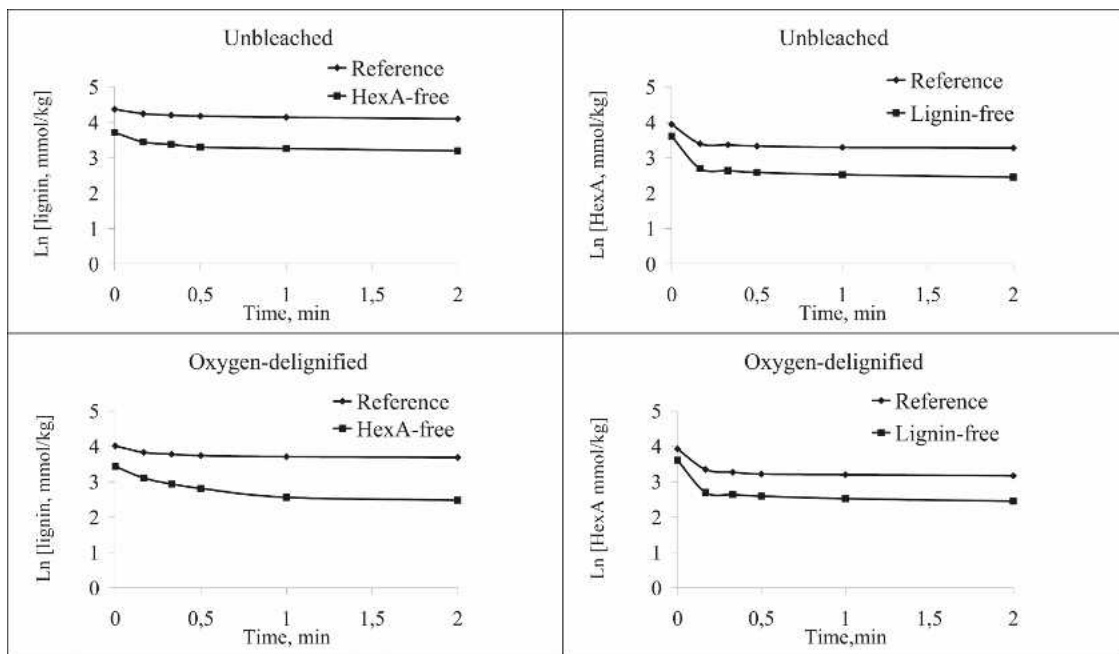


FIGURE 7. Pseudo first-order rate plots for the reaction of lignin (left column) and hexenuronic acids (right column) reactions with ozone in reference, "lignin-free" and hexenuronic acids "free" ("HexA-free") unbleached and oxygen-delignified pulps.

HexA and lignin. HexA reactions with sulfuric acid and ozone can be described by two-phase pseudo first-order reaction rates.

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#### REFERENCES

- BARROCA MJM, SIMÕES RMS, CASTRO JA (2001) Kinetics of chlorine dioxide delignification of a hardwood kraft pulp. *Appita J* 54(2):190–195.
- CHANDRANUPAP P, NGUYEN KL (2000) Effect of pH on kinetics and bleaching efficiency of chlorine dioxide delignification. *Appita J* 53(2):108–110.
- CHAPMAN AA, NGUYEN KL, COOK RA (1998) Instantaneous effectiveness of ozone bleaching at high consistency. *Appita J* 51(1):57–61.
- COSTA MM (2001) The effect of hexenuronic acids on eucalyptus kraft pulp bleachability. PhD Thesis. Federal University of Viçosa. 182 pp.
- , COLODETTE JL (2007) The impact of kappa number composition on eucalyptus kraft pulp bleachability. *Braz J Chem Eng* 24(1):61–71.
- DEVENYNS J, CHAUVEHEID E (1997) Uronic acid and metals control. International Symposium On Wood And Pulping Chemistry, Montreal, Canada. V1: M5-1–M5-4.
- EIRAS KM, COLODETTE JL (2003) Eucalyptus kraft pulp bleaching with chlorine dioxide at high temperature. *J Pulp Pap Sci* 29(2):64–69.
- HENRICSON K (1997) AHL-Stage—A new bleaching stage for kappa reduction and metal profile control. International Emerging Technologies Conference and Exhibition, Orlando, FL.
- JIANG ZH, BOUCHARD J, BERRY R (2006) Evidence for the formation of lignin-hexenuronic acid-xylan complexes during modified kraft pulping processes. *Holzforschung* 60:137–142.
- , LIEROP BV, BERRY R (2000) Hexenuronic acid groups in pulping and bleaching chemistry. *Tappi J* 83(1):167–175.
- LACHENAL D, CHIRAT C (2000) High temperature ClO<sub>2</sub> bleaching of hardwood kraft pulp. *Tappi J* 83(8):96.
- REEVE DW (1996) Chlorine dioxide in delignification. Pages 261–286 in C. W. Dence and D. W. Reeve, eds. *Pulp bleaching—principles and practice*. Tappi Press, Atlanta, GA.
- PRYKE D, REEVE DW (1997) A survey of ClO<sub>2</sub> delignification practices in Canada. *Tappi J* 80(5):153–161.
- TAPPI STANDARD PROCEDURES AND USEFUL METHODS (1998) Tappi Press. Atlanta, GA.
- TESSIER P, SAVOIE M (2000) Chlorine dioxide bleaching kinetics of hardwood kraft pulp. *Tappi J* 83(6):50–55.
- TÖRNGREN A (2002) Hexenuronic acid reactions in chlorine dioxide bleaching—aspects on *in situ* formation of molecular chlorine. *Nord Pulp Pap Res* 17(2):179–182.
- TOVEN K, GELLERSTEDT G, KLEPPE P, MOE S (2002) Use of chlorine dioxide and ozone in combination in prebleaching. *J Pulp Pap Sci* 28(9):305–310.
- TRAN AV (2006) High-consistency ozonation of hardwood kraft pulp. *Holzforschung* 60(6):685–690.
- VUORINEN T, BURCHERT J, TELEMAN A, TENKANEN M, FAGERSTROM P (1996) Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. International Pulp Bleaching Conference, Washington, DC.