Comparison of Oxalate Formation in Peroxide Bleaching of Softwood and Hardwood Mechanical Pulps

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Abstract

Four mechanical pulps, namely, Spruce TMP, Aspen CTMP, Maple CTMP and Eucalyptus CTMP, were subjected to alkaline peroxide bleaching at various conditions, and their oxalate formation were compared in terms of bleaching conditions, pulp brightness, brightness gain and peroxide consumption. Results show that under similar bleaching conditions, the softwood TMP always produced less oxalate than the three hardwood CTMP pulps. However, the oxalate formation at a given brightness gain depends on the unbleached pulp brightness, and pulps with higher original brightness produced less oxalate for a given brightness target. The difference in the amount of oxalate formed per unit of brightness gain was small between the spruce TMP, maple CTMP and eucalyptus CTMP. For the same pulp the $Mg(OH)_2$-based peroxide process produced similar or slightly more oxalate than the NaOH-based process for a given brightness target. Kinetic models were also developed to compare the oxalate formation process and the brightening process.

Introduction

Scaling problems such as equipment fouling and plugging can cause expensive downtime of a production line. As pulp and paper mills are using less fresh water, scaling problems become more frequent due to build-up of organic and inorganic materials in the process water. Calcium oxalate, calcium carbonate and barium sulfate are the three major substances that cause scaling problems. These compounds have low solubility in water and tend to deposit on washer wires, shower nozzles, filtrate tanks, pumps and pipe lines, where a shear force, temperature or pH shock exists [1,2]. Calcium oxalate, in particular, can form porcelain-like hard scale on equipment surfaces which is extremely difficult to remove [3,4].

Bleached chemi-thermal mechanical pulp (BCTMP) or high yield pulp (HYP) is a major commercial product in the pulp and paper industry. Oxalate-related scaling problems in the production of BCTMP/HYP have recently been studied [4-9]. It was shown that in the production of BCTMP oxalate is mainly produced from the alkaline peroxide bleaching process although wood raw materials themselves can contain various amounts of oxalate [5,6]. During peroxide bleaching of mechanical pulps lignin chromophores such as quinones react with peroxide to form muconic acid structures that are colorless to give a brightening effect. The muconic acid structures may be further oxidized by peroxide to yield oxalate and other degraded lignin products [10]. Therefore, the oxalate formation depends on the availability of lignin chromophores. New chromophores such as quinones can also be generated by alkaline darkening reactions during alkaline peroxide bleaching of mechanical pulps [11-13]. These newly generated chromophores can react with peroxide and contribute further to the oxalate formation [5]. It has been observed that under similar bleaching conditions, a maple CTMP had more oxalate formation than a spruce TMP [6], which was explained by the difference in lignin structures between softwood and hardwood. Hardwood lignin has 30-50% guaiacyl type and 50-70% syringyl type units, while the guaiacyl type units in softwood lignin accounts for 90-95%. Results on lignin model compounds (vanillin, creosol, syringaldehyde, and 2,6-dimethoxyphenol) have shown that much more oxalate is formed from the syringyl lignin compounds than from the guaiacyl structures under the same reaction conditions [6]. Also the kinetic of oxalate formation has a rapid initial phase, followed by a much slower phase [5,6], but no kinetic model has been reported for oxalate formation during peroxide bleaching of mechanical pulps.

The main objective of this study is to compare the oxalate formation systematically between the hardwood and softwood mechanical pulps in alkaline peroxide bleaching in order to obtain better understanding on the process parameters affecting the oxalate formation. Variables included wood species, pulp types, unbleached pulp brightness, peroxide charge and alkalinity, brightness levels of bleached pulp, reaction temperature and time. Softwood and hardwood mechanical pulps were compared in terms of oxalate formation based on the bleaching conditions, brightness targets, brightness gain, peroxide consumption and reaction kinetics. Kinetic models for the oxalate formation reaction as well as for the brightening reaction were developed to gain better understanding of the underlying mechanism of the oxalate formation in peroxide bleaching of mechanical pulps.

Experimental

Materials

Three unbleached mechanical pulp samples, Softwood TMP (61.9% ISO, mainly spruce), Aspen CTMP (74.5% ISO) and Maple CTMP (45.8% ISO) were obtained from three different Canadian pulp mills, and one eucalyptus CTMP (36.5% ISO) pulp sample was from a Brazilian mill. Chemicals were reagent grades purchased from Scientific Fisher except sodium silicate (40%, National Silicate), magnesium hydroxide (61% slurry, Martin Marietta Magnesia Specialties).

Methods

The Aspen CTMP was a mill-chelated sample so it was used for bleaching as received without further chelation treatment in the lab. Chelation of the other three pulps was performed at 3% pulp consistency, pH 6.0 and 70°C for 30 minutes with 0.4% DTPA (as 40% solution). Then the pulp suspension was thickened to about 25% consistency in a Büchner funnel with a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines. The chelated pulp was then used for peroxide bleaching.

The peroxide bleaching experiments were conducted in plastic bags using the following conditions: 16% pulp consistency, 1.0-6.2% H_2O_2, 0.13% Epsom salt (for the NaOH-based process), 2.6% silicate (40 Bé), 0.6-5.0% NaOH or 0.7-2.5% $Mg(OH)_2$, at 60-80°C for 5-180 minutes. All the required chemicals for bleaching were first added into a beaker to prepare bleach liquor by the following order: water, sodium hydroxide or magnesium hydroxide, silicate, magnesium sulfate, and hydrogen peroxide. The bleach liquor was then added to pulp that was pre-heated to the reaction temperature, and mixing was provided with kneading for one minute in a plastic bag. At the completion of the bleaching time, the pulp slurry was cooled down immediately with cold running water. Part of the pulp slurry was used for oxalate analysis based on a procedure detailed before [5], and the rest was then filtered in a Büchner funnel with a 200-mesh Teflon screen to about 25% pulp consistency. The obtained filtrate was used for the measurement of end pH and residual peroxide according to the PAPTAC standard methods (J.16P). The pulp cake was then dispersed into a 1% pulp suspension with deionized water, and its pH adjusted to 5.0 with sulfurous acid, and then handsheets were prepared and measured for optical properties according to the TAPPI standard methods (T205 sp-95 and T220 sp-96).

Results and Discussion

Effect of Alkali Charges

Previous results have shown that caustic soda and peroxide charges are key factors affecting oxalate formation in the NaOH-based peroxide bleaching of mechanical pulps [6]. Here we compared the amount of oxalate formed from peroxide bleaching between the softwood and hardwood mechanical pulps, at various caustic soda charges with a fixed peroxide dosage.

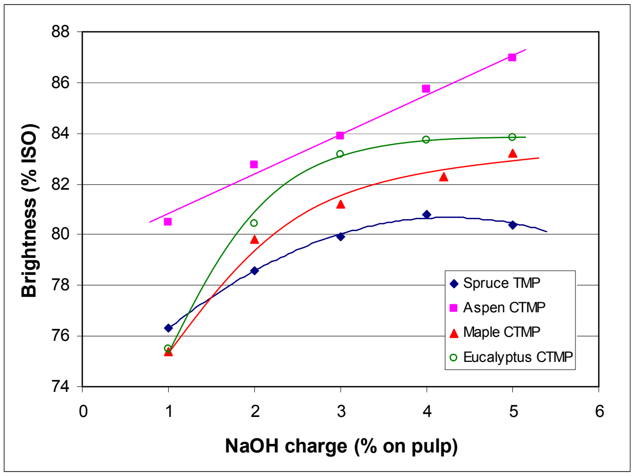


Figure 1. Effect of caustic charge on pulp brightness during peroxide bleaching of different mechanical pulps. (6.2% H_2O_2, 0.13% Epsom salt, 2.6% silicate (40 Bé), 0.6-5.0% NaOH, 16% pulp consistency, 80°C and 180 minutes).

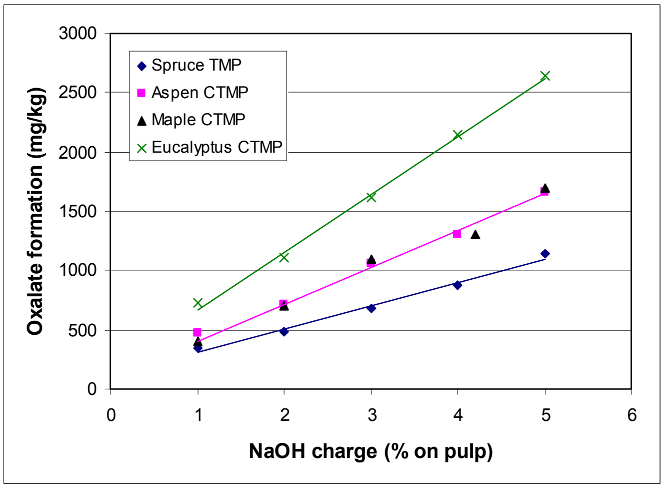


Figure 2. Effect of caustic charge on oxalate formation in alkaline peroxide bleaching of four mechanical pulps. (Other bleaching conditions were the same as in Figure 1).

Figure 1 shows the brightness of four mechanical pulps after peroxide bleaching at various caustic charges with peroxide dosage fixed at 6.2%. Pulp brightness increased with the alkali charge but leveled off at about 3-4% NaOH. An exception was the aspen CTMP pulp that had a much higher initial brightness (74.5% ISO). Its brightness increased linearly with the caustic charges in the whole range investigated. Figure 2 shows the amount of oxalate formed during peroxide bleaching under the same conditions. For all the four pulps (Spruce TMP, Aspen CTMP, Maple CTMP and Eucalyptus CTMP), the oxalate formation increased linearly with the caustic charge, which is in good agreement with the early results [6]. However, the softwood TMP produced the least amount of oxalate, while the eucalyptus CTMP produced the most. The amount of oxalate from the maple CTMP and aspen CTMP was similar although their unbleached pulp brightness was very different. It is noted that the difference in oxalate formation between the softwood and hardwood mechanical pulps became larger and larger as the caustic soda charge increased.

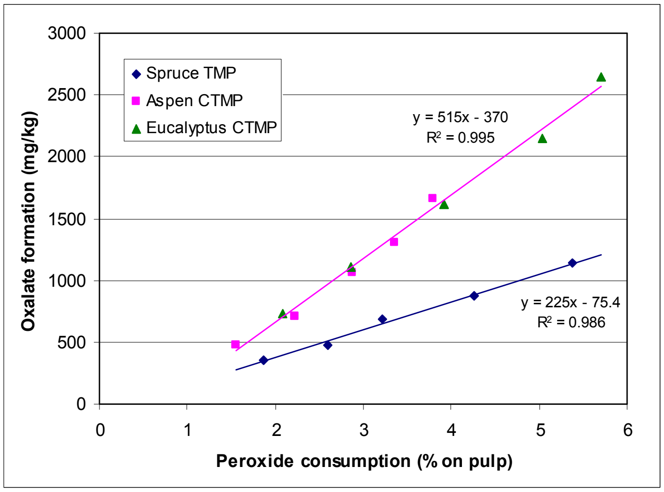


Figure 3. Oxalate formation versus peroxide consumption in alkaline peroxide bleaching with various caustic charges. (Other bleaching conditions were the same as in Figure 1).

Figure 3 shows that the oxalate formation is correlated well to peroxide consumption at various caustic soda charges. Oxalate is formed from the reactions of lignin with peroxide. Chromophores such as quinones are attacked by hydroperoxyl anion and converted to muconic acids, which can further be oxidized by peroxide to yield oxalic acids [10]. Figure 3 also shows that the oxalate formation curve for the softwood TMP has a smaller slope than that for the hardwood CTMP pulps, due to the fact the syringyl lignin structures lead to more oxalate formation than the guaiacyl lignin structures [6].

Table I. Comparison of oxalate formation between different mechanical pulps in peroxide bleaching under the optimized alkali to peroxide ratio

H_2O_2 dosage (%)	NaOH charge (%)	End pH	H_2O_2 consumed (%)	Brightness (% ISO)	Oxalate formation (mg/kg)	Oxalate/ H_2O_2 consumption	Oxalate/ Brightness gain
Spruce TMP							
1.0	0.6	7.45	0.6	69.16	135	225	18.6
2.0	1.2	7.81	1.19	73.11	296	249	26.4
4.0	2.6	8.56	2.39	77.23	539	226	35.2
6.2	4.2	8.86	4.26	80.68	873	205	46.5
Maple CTMP							
1.0	0.6	6.92	0.62	66.53	330	532	15.9
2.0	1.2	7.03	1.2	73.8	520	433	18.6
4.0	2.6	7.82	2.64	79.91	940	356	27.6
6.2	4.2	8.52	3.57	81.46	1330	373	37.3
Eucalyptus CTMP							
1.0	0.6	8.43	0.64	60.59	445	695	18.5
2.0	1.2	8.68	1.29	70.27	730	566	21.6
4.0	2.6	9.10	2.8	80.35	1380	493	31.5
6.2	4.0	9.56	5.03	83.73	2150	427	45.5

We also compared the oxalate formation between hardwood and softwood mechanical pulps under the optimal alkali to peroxide ratio with respect to the brightness gain. Results in Table I shows that the softwood TMP produced significantly less oxalate than the hardwood CTMP pulps under the same bleaching conditions. Among the two hardwood mechanical pulps, the eucalyptus CTMP consistently had the higher oxalate formation than the maple CTMP. This is also true if the comparison is based on the ratio of oxalate formation to peroxide consumption. However, when the comparison is made on the ratio of oxalate formation to brightness gain, the difference between the three pulps is small (last column of Table I).

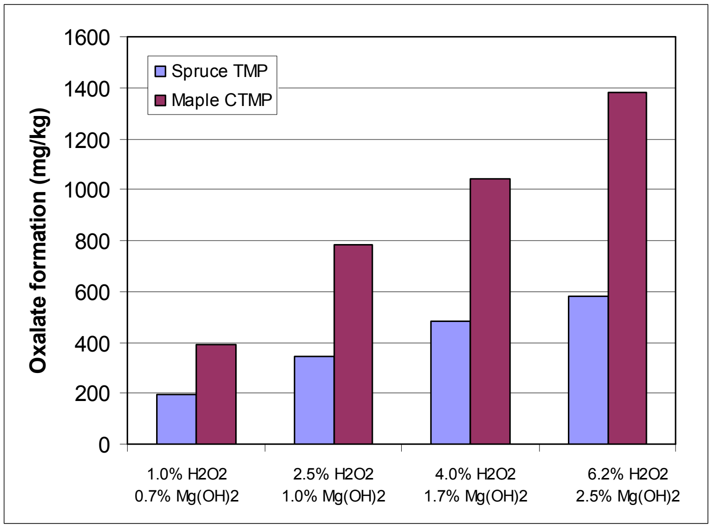


Figure 4. Oxalate formation in the $Mg(OH)_2$-based peroxide bleaching process. (Other bleaching conditions: 2.6% silicate (40 Bé), 16% pulp consistency, 80°C and 180 minutes).

Oxalate Formation in the $Mg(OH)_2$-based Peroxide Bleaching Process

Figure 4 compares the amount of oxalate formed from the spruce TMP and maple CTMP in the $Mg(OH)_2$-based peroxide bleaching at four levels of chemical charges to achieve different brightness targets. The maple CTMP pulp produced about twice of the amount of oxalate from the spruce TMP. The oxalate formation versus the brightness of bleached pulp was plotted in Figure 5. In the brightness range of about 70 to 80 % ISO, the spruce TMP produced significantly less oxalate than the hardwood CTMP for a given brightness target. However, the difference became much smaller between the two pulps if the comparison is based on the ratio of oxalate formation to brightness gain (Figure 6 vs. Figure 4).

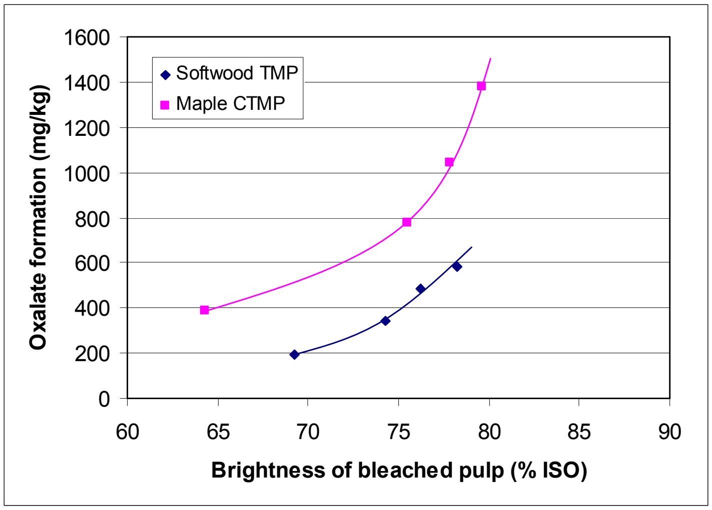


Figure 5. Oxalate formation and pulp brightness in $Mg(OH)_2$-based peroxide bleaching. (Bleaching conditions were the same as in Figure 4).

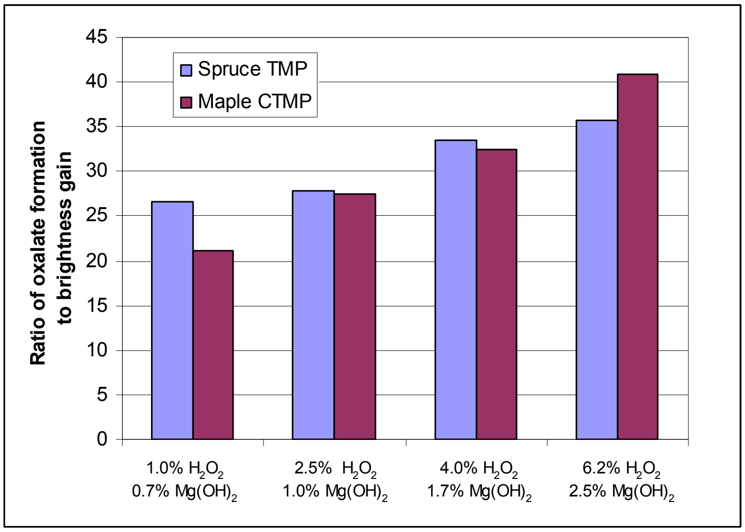


Figure 6. The ratio of oxalate formation to brightness gain in $Mg(OH)_2$-based peroxide bleaching. (Bleaching conditions were the same as in Figure 4).

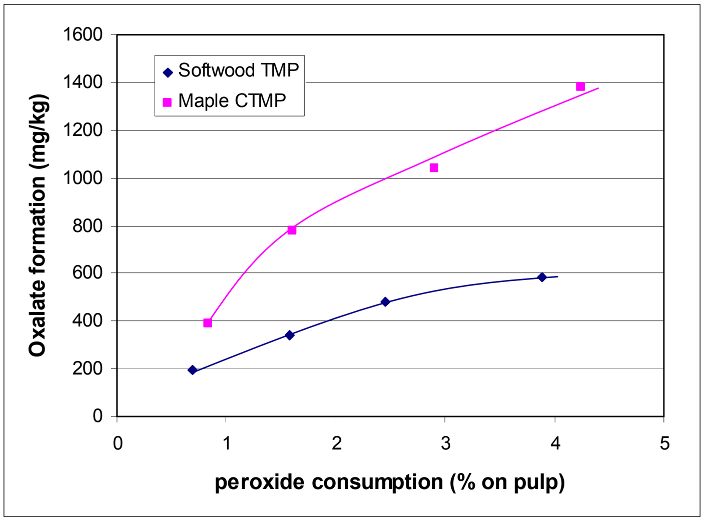


Figure 7. Oxalate formation and peroxide consumption in the $Mg(OH)_2$-based peroxide bleaching. (Bleaching conditions were the same as in Figure 5).

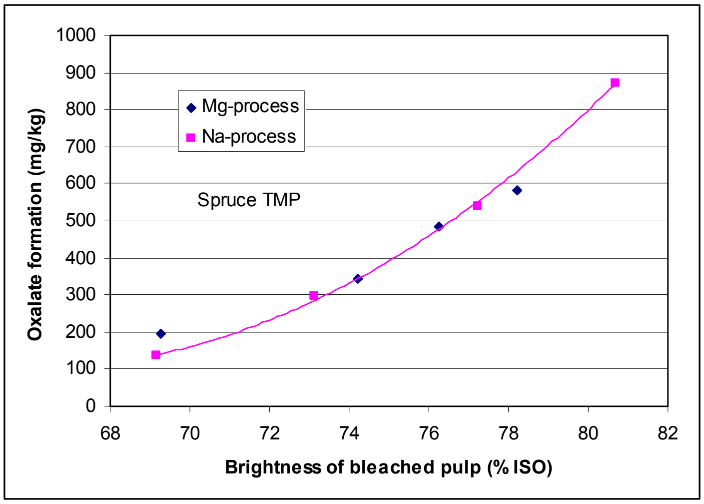


Figure 8. Comparison of oxalate formation in the $Mg(OH)_2$-based and NaOH-based peroxide bleaching of the spruce TMP. (16% pulp consistency, 1.0-6.2% H_2O_2, 0.13% Epsom salt (for the NaOH-based process), 2.6% silicate (40 Bé), 0.6-5.0% NaOH or 0.7-2.5% $Mg(OH)_2$, 60-80°C and 180 minutes).

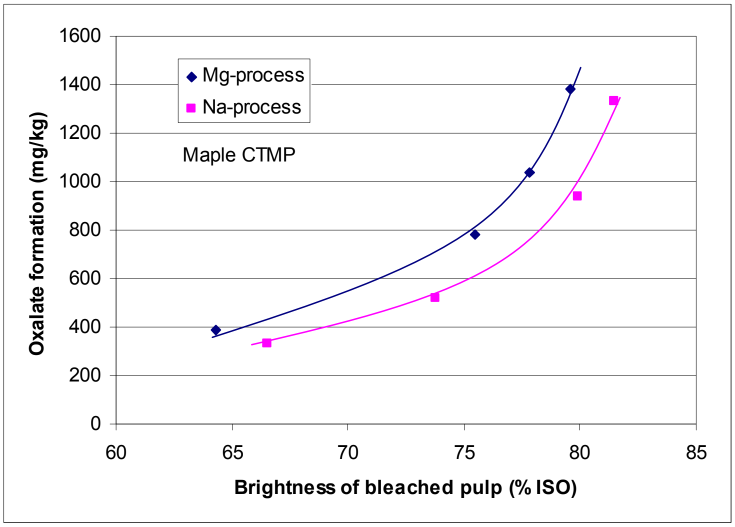


Figure 9. Comparison of oxalate formation in the $Mg(OH)_2$-based and NaOH-based peroxide bleaching of the maple CTMP. (The bleaching conditions were the same as in Figure 8).

Figure 7 compares the oxalate formation based on the peroxide consumption. More oxalate was formed from the hardwood CTMP than from the softwood TMP at the same peroxide consumption, which is in agreement with the results obtained using the NaOH-based bleaching process (Figure 3 and Table I). However, in the $Mg(OH)_2$-based process the oxalate formation did not increase linearly with peroxide consumption as it did in the NaOH-based process. Instead, the increase leveled off quickly. This is probably due to the peroxide decomposition caused by the transition metal ions such as iron and manganese contained as impurities in the industrial grade of $Mg(OH)_2$ slurry.

Another question is whether the $Mg(OH)_2$-based peroxide bleaching process produces less oxalate than the NaOH-based process for a given brightness of a pulp. Figure 8 shows that in the brightness range of 68-78% ISO, the amount of oxalate formed from the softwood TMP was similar in the two peroxide bleaching processes for a given brightness target. For the maple CTMP, however, slightly more oxalate formation was observed from the

$Mg(OH)_2$-based process than from the NaOH-based process at the same brightness target in the range of 65-80% ISO, as shown in Figure 9. These results are in general agreement with those from a previous study [7]. This can be explained by the kinetic difference of oxalate formation between the two bleaching processes. In the $Mg(OH)_2$-based process, oxalate is formed at a slower but more steady rate due to the buffering effect of $Mg(OH)_2$, while in the NaOH-based process, oxalate is formed quickly in the initial bleaching phase and only a small portion of oxalate was produced during the later bleaching phase [7].

Kinetic Models for the Brightening and Oxalate Formation

The brightening process. A general rate equation for the brightening reaction of peroxide bleaching of mechanical pulps may be in the following form [14-16].

$$-\frac{dk}{dt} = K[H_2O_2]^a[OH^-]^b[k]^n \tag{1}$$

K: rate constant
$[H_2O_2]$: concentration of hydrogen peroxide, mol/l
$[OH^-]$: concentration of hydroxyl ions, mol/l
k: light absorption coefficient of pulp, m^2/kg

The reaction orders may depend on the type of pulp, reaction conditions and the method for model development [15]. In this paper, a differential method was adopted for the development of the brightening kinetic models [15]. Bleaching experiments was carried out under the normal conditions encountered in mill practice, and pulp was sampled at a series of reaction time to obtain data of peroxide concentration, alkalinity and light absorption coefficient as functions of time. The reaction rate (-dk/dt) was obtained by differentiating the function of light absorption coefficient with respect to time t. Then the model was fit into the experimental data for best *a, b, n,* and *K.* The kinetic models for the spruce TMP and eucalyptus CTMP were found to be as follows.

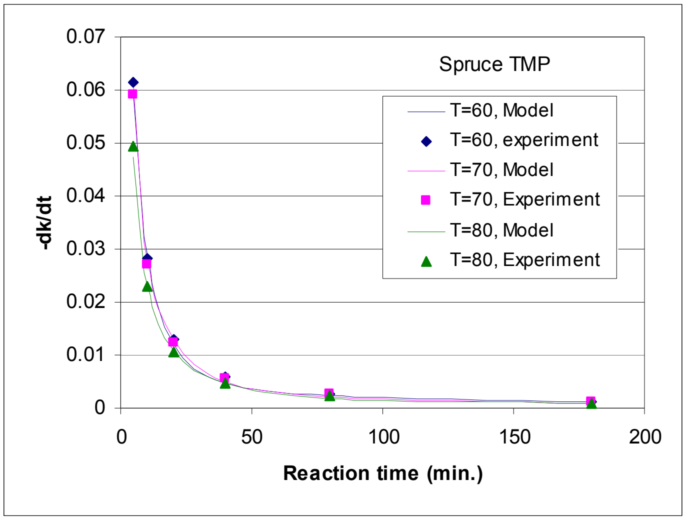
For the spruce TMP

$$-\frac{dk}{dt} = 6.67\times 10^6 \cdot e^{\frac{-25900}{RT}}[H_2O_2]^{0.3}[OH^-]^{1.2}[k]^{2.2} \tag{2}$$

For the eucalyptus CTMP:

$$-\frac{dk}{dt} = 2.59\times 10^7 \cdot e^{\frac{-43040}{RT}}[H_2O_2]^{0.25}[OH^-]^{0.75}[k]^{2} \tag{3}$$

As shown in Figure 10, for both pulps, the reaction rate of chromophore removal (dk/dt) predicted by the models agree well with those obtained from the experimental data. The reaction rate for the eucalyptus CTMP is much higher than that for the spruce TMP during the whole bleaching process. Figure 10 also shows that the brightening rate is more temperature-sensitive for the eucalyptus CTMP than for the spruce TMP. This can be explained by the difference of the Arrhenius' activation energy (E_a) that is indicated in the rate equations (2) and (3): 25.9 kJ/mol for the spruce TMP, and 43.0 kJ/mol for the eucalyptus CTMP. The light absorption coefficient (k) of pulp can be predicted as the function of time (t) by the model by the integration of the reaction rate (dk/dt). As shown in Figure 11, both kinetic models give good prediction of k during the bleaching period from 5 min to 180 min.



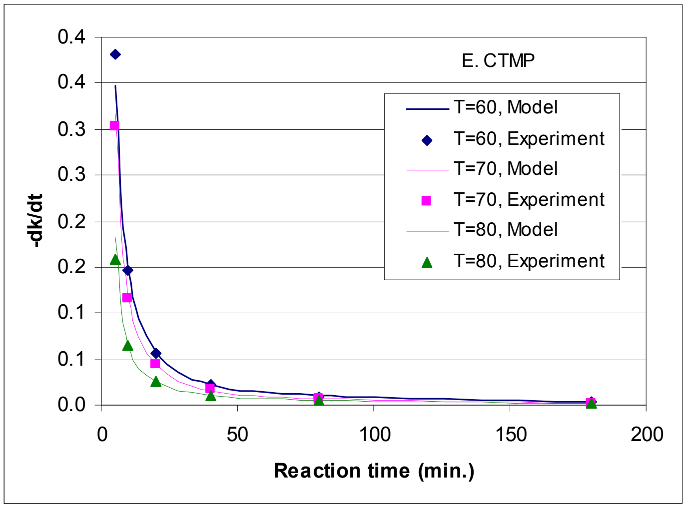


Figure 10. Reaction rate of chromophore destruction as the function of time in peroxide bleaching of the spruce TMP (upper) and eucalyptus CTMP (lower). (Other bleaching conditions: 5.5% H_2O_2, 3.8% NaOH, 2.45% silicate (40 Bé), 0.12% Epsom salt, 16% pulp consistency, 80°C).

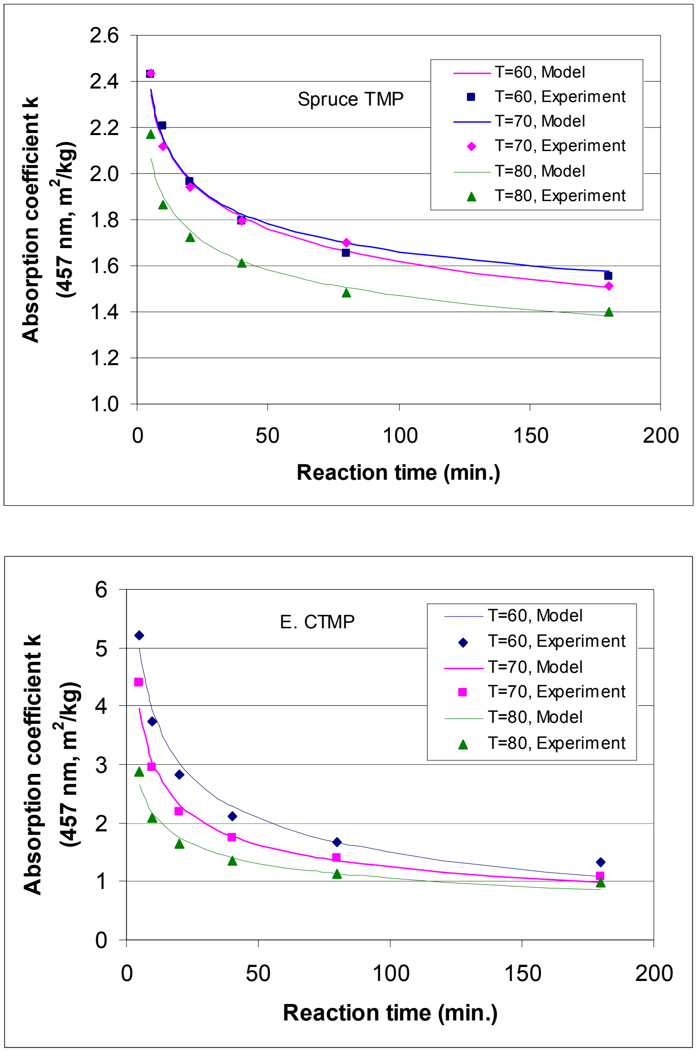


Figure 11. Prediction of the light absorption coefficient of pulp at 457 nm by the kinetic models as the function of time in peroxide bleaching of the spruce TMP (upper) and eucalyptus CTMP (lower). (Bleaching conditions were the same as in Figure 10).

The oxalate formation process. Based on the fact that the development of oxalate formation reaction is similar to that of brightness we adopted the kinetic models for the brightness development in the literature [11-13], for the oxalate formation, during peroxide bleaching of mechanical pulps, as

$$\frac{d[oxalate]}{dt} = k[H_2O_2]^a[OH^-]^b[precursor]^n \qquad \textbf{(4)}$$

Where k is the rate constant that is temperature dependant, and a, b and n are the reaction orders. The precursor concentration: [*precursor*], represents the amount of lignin precursors that can be converted to oxalate when reacting with peroxide. During peroxide bleaching of mechanical pulps, chromophores, such as quinones, react with hydroperoxyl anions to form muconic acid structure to give the brightening effect, and the muconic acid can further react with hydroperoxyl anions to form oxalate [10]. The muconic acid structures are therefore the precursor for oxalate formation during peroxide bleaching of mechanical pulps. The amount of oxalate precursor in the system is continuously generated through the brightening reactions and consumed by the oxalate formation reactions.

$$[precursor] = A[\Delta k] - B[oxalate] \quad \textbf{(5)}$$

$$\Delta k = k_0 - k_t \quad \textbf{(6)}$$

k_0 and k_t are the light absorption coefficients at 457 nm of pulp at the bleaching time of 0 and t, and Δk is the change of light absorption coefficient of pulp due to bleaching. [*oxalate*] is the total amount of oxalate formed by time t, measured as mg/kg of pulp. *A* and *B* are two constants to relate the precursor concentration in the system at time t to the amount of chromophore destroyed as measured by Δk (generation of oxalate precursors) and the amount of oxalate already formed (consumption of oxalate precursors). It was assumed that the unbleached pulp contained a negligible amount of oxalate precursors. Therefore, at t=0, the initial reaction rate of oxalate formation is zero.

Substituting Equation (5) to (4) yields:

$$\frac{d[oxalate]}{dt} = K[H_2O_2]^a[OH^-]^b[A \cdot \Delta k - B \cdot [oxalate]]^n \quad \textbf{(7)}$$

$$\frac{d[oxalate]}{dt} = KA^n \cdot [H_2O_2]^a[OH^-]^b[\Delta k - \frac{B}{A} \cdot [oxalate]]^n \quad \textbf{(8)}$$

Let $KA^n = K'$, and $B/A = C$,

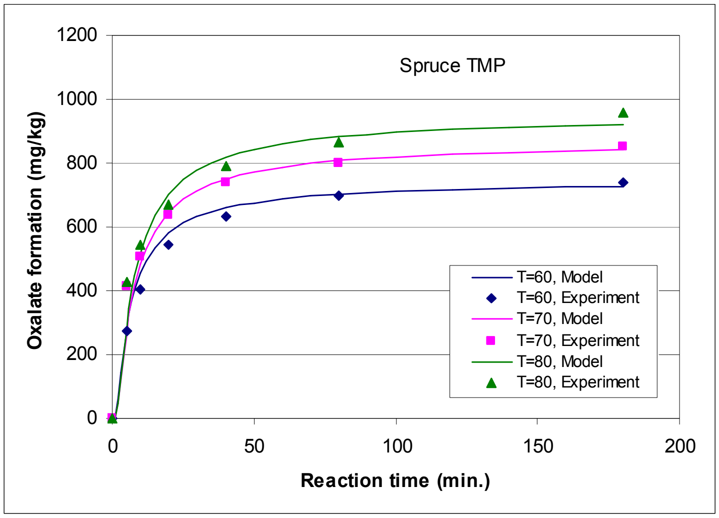
$$\frac{d[oxalate]}{dt} = K'[H_2O_2]^a[OH^-]^b[\Delta k - C \cdot [oxalate]]^n \quad \textbf{(9)}$$

The kinetic parameters of the oxalate formation were obtained based on the experimental data, by fitting the model to solve for the best values of *a, b, n, C* and *K′* in a Maple software package. For the same pulp, we assumed that *a, b* and *n* were constant for different temperatures. The results were summarized in Table II.

Table II. Constants found for the kinetic model of oxalate formation (Equation (9))

Pulp	Temperature °C	*a*	*b*	*n*	*C*	*K′*	E_a kJ/mol
Softwood TMP	60	1.80	1.70	1.65	0.0038	3.88×10^8	56.3
	70	1.80	1.70	1.65	0.00375	7.48×10^8	
	80	1.80	1.70	1.65	0.0037	1.22×10^9	
Eucalyptus CTMP	60	2.20	0.95	1.60	0.0112	3.00×10^4	47.8
	70	2.20	0.95	1.60	0.0047	4.28×10^4	
	80	2.20	0.95	1.60	0.0029	8.00×10^4	

It is noted in Table II that the constant *c*, decreased with the increase of temperature for the eucalyptus CTMP, but it was relatively stable for the softwood TMP (Table II). This is probably due to the difference in the reactivity of the oxalate precursors produced from the brightening reactions.



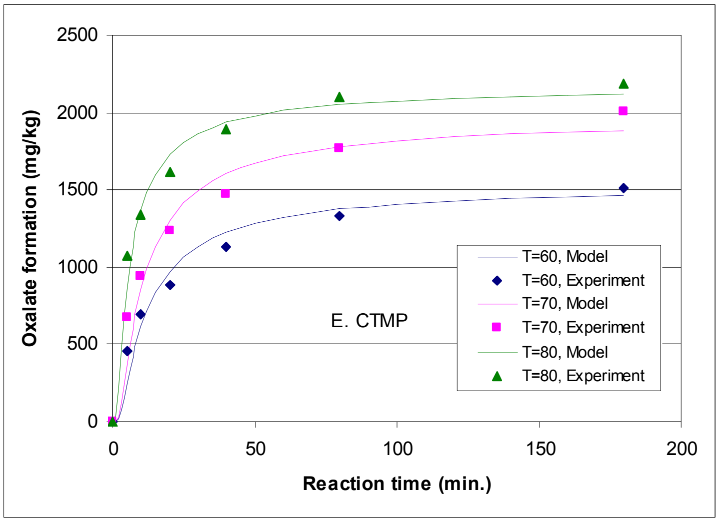


Figure 12. Prediction of oxalate formation by the kinetic models as the function of time in peroxide bleaching of the spruce TMP (top) and eucalyptus CTMP (bottom). (Bleaching conditions were the same as in Figure 10).

Figure 12 shows the prediction of oxalate formation by the kinetic models during peroxide bleaching and the predicted results are in good agreement with those obtained experimentally. Oxalate is formed at a much faster rate in the case of eucalyptus CTMP than in the case of spruce TMP. Apparently, this is due to the faster brightening process for the eucalyptus CTMP. A faster destruction of chromophores generates more precursors, leading to a faster oxalate formation. The difference in oxalate formation between the two pulps was more pronounced at higher temperatures. The kinetic models show that the reaction rate of oxalate formation has a higher E_a, therefore is more temperature-dependent than the brightening process. The implication is that the oxalate formation can be reduced by using a lower bleaching temperature for a given brightness target.

Conclusions

Under similar alkaline peroxide bleaching conditions the softwood TMP always produced less oxalate than the other three hardwood CTMP pulps. This is also true if the oxalate formation is based on peroxide consumption during peroxide bleaching. However, the oxalate formation at a given brightness gain depends on the unbleached pulp brightness, and pulps with higher original brightness produced less oxalate for a given brightness target. The difference in the amount of oxalate formed per unit of brightness gain was small between the spruce TMP, maple CTMP and eucalyptus CTMP.

The same conclusions also apply to the $Mg(OH)_2$-based peroxide bleaching process in the comparison of oxalate formation between different mechanical pulps. For the same pulp, the $Mg(OH)_2$-based process produced similar or slightly more oxalate than the NaOH-based process for a given brightness target.

Kinetic models show that the oxalate formation process has higher reaction orders with respect to peroxide concentration and alkalinity and is more temperature-dependant, in comparison with the brightening process during the alkaline peroxide bleaching of mechanical pulps. The reaction rate of oxalate formation for the spruce TMP has a higher activation energy and is more sensitive to alkalinity but less sensitive to peroxide concentration than that for the eucalyptus CTMP.

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