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Voltammetric analysis of the bleachability of softwood kraft pulps

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Abstract

Kraft and oxygen delignified pulps with various kappa numbers were prepared from black spruce and western hemlock chips. The bleachability (ratio of kappa number decrease to chlorine dioxide applied) of the different pulps at the same kappa number varied with both wood furnish and delignification process. Thus, unbleached kappa number alone is not a reliable indicator of bleachability for these pulps. This may be due in part to the variable hexenuronic acid content of the pulps; those with higher ratio of hexenuronic acid content to kappa number (HexA/kappa) are harder to bleach. Voltammetric analysis of the same kraft pulps in the presence of redox mediators was found to measure both the content and reactivity of residual lignin. Peak current ratios of redox mediators correlated with pulp bleachability for all pulps. These ratios may therefore provide a more accurate prediction of bleachability than unbleached kappa number.

Keywords: bleachability; ECF bleaching; electrochemical analysis; kappa number; kraft pulp; lignin; reactivity; redox potential; softwood; voltammetry.

Introduction

Kappa number is the most commonly measured parameter to determine the amount of residual lignin in unbleached and semi-bleached kraft pulps. It is currently used to control the kraft cooking and oxygen delignification processes, and as a reference parameter during bleaching sequences to control the addition of bleaching chemicals. Kappa number measures the total amount of material which can be oxidized in pulp with potassium permanganate under standard conditions (Tasman 1959). In unbleached chemical pulps, most permanganate consumption under the conditions of kappa number determination is the sum of contributions from lignin substructures and hexenuronic acid, with a minor contribution from other carbohydrate-derived structures (Li and Gellerstedt 1998a,b; Gellerstedt and Wafa Al-Dajani 2000; Li et al. 2002). The relationship between kappa number and residual lignin content can vary depending on the delignification procedure and wood species. It has been shown that pulps having the same kappa number, but produced under different pulping conditions, behave differently during bleaching (Gustavsson et al. 1999; Gellerstedt and Wafa Al-Dajani 2000). A high content of β-*O*-4 structures in unbleached pulp residual lignin was found to contribute to a better bleachability (Gustavsson et al. 1999). Partial oxidation of aromatic rings during oxidative bleaching stages was reported to produce carboxyl and non-aromatic structures in residual lignin (Li et al. 2002). The presence of quinone structures was found to increase the lignin/kappa ratio from 0.15 to 0.18 and to adversely affect pulp bleachability (Brogdon 2001). In practice, the amount of chlorine dioxide added during ECF (Elemental Chlorine-Free) bleaching stages is based solely on the kappa number (kappa factor), and the reactivity of chlorine dioxide towards the different oxidizable structures in pulp are not taken into account. For mills processing mixtures of wood furnishes, the application of a fixed kappa factor may result in an erroneous estimate of the amount of chlorine dioxide needed to bleach the pulp. To compensate for changes in wood furnishes and processes conditions, mills often use an excess of chlorine dioxide to prevent the production of off-quality pulp which raises bleaching costs.

In the last decade, various on-line kappa analyzers have been developed to improve process control by reducing the time between process variations and kappa determination. They all measure optical properties of pulp fiber suspensions such as UV light absorption and reflection (Kubulnieks et al. 1987; Agnéus and Damlin 1990; Ollila and Erkkilä 1997; Van Fleet and Whalley 1998). In general, the optical-based measurement systems are sensitive to pulp consistency and wood furnish variations. Thus, in order to obtain an accurate kappa number measurement, a strict control of the pulp consistency is required with frequent sensor calibration to account for wood mixture variations and process modification. For mills using mixed wood furnishes or facing frequent process changes, the use of optical sensors for kappa determination may not be feasible. Recently, we developed a new approach to lignin determination in kraft pulps, different to both the established optical on-line methods and the traditional laboratory determinations by permanganate titration (Bourbonnais and Paice 2003). The principle of the method is based on the voltammetric measurement of catalytic reactions between lignin in pulp fiber and a soluble redox mediator. During the voltammetric process, the electrolytically oxidized mediator diffuses into the pulp fiber to react reversibly with lignin. The reaction with lignin regenerates the reduced mediator at the surface of the electrode, resulting in an increase of current when compared to the mediator alone (Figure

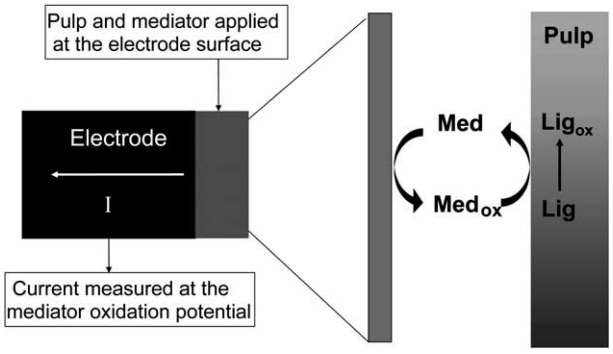

Figure 1 Cyclic voltammetry of pulp in the presence of mediator to measure the content and reactivity of residual lignin in kraft pulp.

1). Using a fixed concentration of mediator, the current measured at the peak potential of the mediator in the presence of pulp (I_k) is proportional to the amount of lignin or the kappa number of the pulp. In this report, we describe the application of this electrochemical method to determine the bleachability of softwood kraft pulps towards chlorine dioxide.

Materials and methods

Preparation of kraft pulps

Eastern Canadian black spruce chips and western Canadian hemlock chips were air-dried and classified within 2–8 mm. Chips were cooked in six 2-l pressure vessels which were rotated in a steam-heated oil bath. Effective impregnation was achieved by adding the white liquor to the chips in the pressure vessels under vacuum (30 mm Hg). For all cooks, the temperature was raised to 170°C in 90 minutes and held at this temperature until the time needed to obtain the target H-factor. After cooling by transferring the cooking vessels to a cold water bath, the pulp was disintegrated for 3 minutes using a Cowles disintegrator. The pulp was well washed and soaked for 18 hours before screening through a laboratory flat screen plate (0.25 mm slots). Kraft cooking conditions and pulp properties are shown in Table 1.

Oxygen delignification

Selected pulps from the previous kraft cooks were further delignified using a lab-scale oxygen pressurized reactor. Fifty grams of kraft pulp were mixed with sodium hydroxide and magnesium sulfate in a Hobart mixer. The pulp slurry was preheated in a plastic bag in a microwave oven before being transferred into the oxygen reactor. Continuous low shear mixing (10 rpm) of pulp during oxygen delignification was done with a pressurized peg-type mixer. Reaction conditions for each pulp are described in Table 2.

D_0E bleaching

Kraft and oxygen delignified pulps were all bleached at a pulp consistency of 3.5% for 45 min at 60°C with chlorine dioxide at a fixed kappa factor of 0.15 (D_0). The kappa factor, also called "active chlorine multiple" (ACM), is defined as the equivalent chlorine charge, expressed as percent on pulp per unit of unbleached pulp kappa number. The alkaline extraction stage (E), was done at 10% pulp consistency with 2% NaOH for 90 min at 75°C.

Pulp testing

Pulp kappa numbers were measured by the permanganate titration method according Paptac Standard Testing Method G18.

Table 1 Kraft cooking conditions and pulp properties.

Wood	Black spruce						Western hemlock					
Cooking conditions	AA[1]: 16.34%; Sulphidity: 29.85% on AA; L/W[2] ratio: 4:1; Temperature: 170°C						AA: 18.0%; Sulphidity: 29.92% on AA; L/W ratio: 4:1; Temperature: 170°C					
Time (min)	165	176	187	207	226	278	164	170	177	190	209	239
H-factor	1250	1427	1598	1904	2199	3004	1250	1349	1447	1655	1951	2404
Kappa	47.6	40.4	36.2	32.5	28.8	23.3	51.5	46.2	43.5	37.0	33.1	29.0
Klason (%)	-	6.8	-	5.6	-	4.2	-	-	6.6	5.7	-	4.6
HexA[3] (mmol kg^{-1})	-	29.1	-	26.6	-	23.6	-	-	24.3	22.9	-	19.7

[1] AA, active alkali.
[2] L/W, liquor to wood ratio.
[3] Hex A, hexenuronic acid.

Table 2 Oxygen delignification conditions and O_2-pulp properties.

	Black spruce kraft pulp with kappa no.			Western hemlock kraft pulp with kappa no.				
	47.6	47.6	40.4	51.5	51.5	46.2	46.2	37.0
O_2 (psi)	100	100	100	100	100	100	100	100
$MgSO_4$ (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
NaOH (%)	2.0	3.5	2.0	2.5	3.5	2.0	2.5	1.25
Temperature (°C)	90	95	90	88	95	85	88	90
Time (min)	45	60	45	45	60	45	45	45
Final kappa	33.2	22.4	28.2	32.5	24.1	32.0	27.9	28.9
Klason (%)	6.0	4.2	4.9	5.8	4.1	-	4.9	-
HexA* (mmol kg^{-1})	33.8	34.2	27.5	25.2	24.9	-	24.6	-

* Hex A, hexenuronic acid.

The acid-insoluble (Klason) lignin was measured accordingly to Paptac Standard Testing Methods G8 and G9. Hexenuronic acid (HexA) groups were quantified by anion-exchange chromatography following acid hydrolysis of pulp samples (Jiang et al. 2001).

Cyclic voltammetry

Cyclic voltammetry determinations were carried out with a BAS CV-50W Voltammetric Analyser (Bioanalytical Systems, Inc., Indiana, USA). The electrochemical cell consisted of a one-compartment cell of 5 ml with an Ag/AgCl reference electrode, a platinum wire counter electrode and a 3-mm diameter glassy carbon working electrode. Two sets of mediators were used in this study: (A) 2,2′-azinobis(3-ethylbenzthiazoline-5-sulphonate) (ABTS) in sodium citrate buffer, 0.1 M, pH 4.5 obtained from Boehringer Mannheim, and (B) an equimolar mixture of transition metal complexes consisting of potassium octacyanomolybdate ($K_4Mo(CN)_8$), potassium octacyanotungstate ($K_4W(CN)_8$) and iron tris (2,2′-bipyridine) $[Fe(bpy)_3](ClO_4)_2$ in sodium acetate buffer, 0.1 M, pH 5 synthesized following the procedures of Leipoldt et al. (1974), Van de Poel and Neumann (1968) and Burstall and Nyholm (1952), respectively.

Cyclic voltammetry of pulp and mediator was performed as follows: after washing the pulp with water, a small sample (equivalent to about 10 mg of oven dried weight pulp) was suspended in 1 ml solution of mediator in buffer. The pulp suspension was centrifuged and the excess liquid discarded. The pulp was then applied to the surface of the working electrode and pressed against the bottom of the electrochemical cell containing the solution of mediator in buffer. This way, the pulp sample formed a small pad at the surface of the working electrode (Figure 1). Cyclic voltammetry was performed at a slow scan rate (2 mV s^{-1}) at room temperature.

Results and discussion

D_0E bleaching of unbleached pulps

Bleachability of kraft and oxygen delignified pulps from black spruce and western hemlock was determined by measuring the change in kappa number per unit of ClO_2 applied after D_0E bleaching. The bleachability is defined as the kappa number decrease per kg of ClO_2 consumed by one ton of pulp. A low kappa factor of 0.15 was chosen to avoid an excess of chlorine dioxide. Table 3 shows that, at the same unbleached kappa number, the brownstock kraft pulps are more effectively delignified than the oxygen delignified pulps. The results also indicate that the brownstock kraft pulps from western hemlock are more reactive towards chlorine dioxide than the brownstock pulps obtained from black spruce. For black spruce pulps, pulps with a higher kappa number are easier to bleach. The difference in bleachability for different pulps at the same kappa number has been observed and discussed in several reports (Halminen et al. 1998; Gustavsson et al. 1999; Gellerstedt and Wafa Al-Dajani 2000; Brogdon 2001). Hexenuronic acid (HexA) content, the presence of lignin-carbohydrate complexes and residual lignin characteristics are among reasons offered to explain differences in pulp bleachability (Lachenal et al. 1999; Costa and Colodette 2002). Recently, it was proposed that the formation of a covalent bond between HexA groups and lignin during oxygen delignification would contribute to lowering the reactivity of pulp to ClO_2 (Jiang et al. 2003). The Klason lignin and HexA contents of selected unbleached kraft (Table 1) and O_2 delignified (Table 2) pulps indicate that oxygen delignified pulps have a higher content of HexA, but similar Klason lignin content as kraft brownstock, when compared at the same kappa number. Figure 2 shows the relationship between bleachability and the ratio of the content of HexA to the kappa number. The general trend, which seems to apply to both kraft and oxygen delignified pulps from the two softwood species, is that a higher ratio of HexA/kappa indicates a lower reactivity of pulp to chlorine dioxide bleaching.

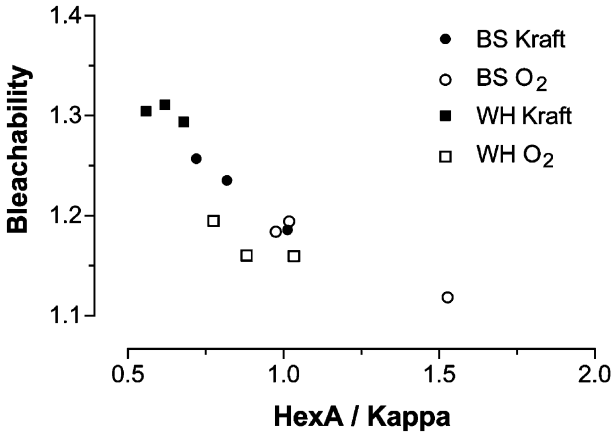

Figure 2 Bleachability [(unbleached kappa–D_0E kappa)/(kg of ClO_2/t of pulp)] of the D_0E stages and ratio of hexenuronic acid (HexA) content to kappa number for kraft brownstock and O_2 delignified pulps from black spruce (BS) and western hemlock (WH).

Table 3 D_0E bleaching of kraft and O_2-delignified pulps at a fixed kappa factor of 0.15.

Pulp	Black spruce kraft					Black spruce O_2		
Unbleached kappa	40.4	36.2	32.4	28.8	23.3	33.2	28.2	22.4
ClO_2 (kg t^{-1})	23.1	20.6	18.5	16.4	13.3	18.9	16.1	12.8
D_0E kappa	11.5	10.6	9.6	8.9	7.6	10.6	9.2	8.1
Bleachability*	1.25	1.24	1.23	1.21	1.18	1.20	1.18	1.12

Pulp	Western hemlock kraft				Western hemlock O_2			
Unbleached kappa	43.5	37.0	33.1	29.0	32.5	32.0	27.9	24.1
ClO_2 (kg t^{-1})	24.8	21.1	18.9	16.5	18.5	18.2	15.9	13.7
D_0E kappa	11.1	9.4	8.7	7.6	10.4	10.2	9.5	8.2
Bleachability*	1.30	1.31	1.29	1.30	1.19	1.20	1.16	1.16

* Bleachability calculation: (unbleached kappa–D_0E kappa)/(kg of ClO_2/t of pulp).

Cyclic voltammetry of ABTS in the presence of kraft pulp

The principle of the voltammetric analysis of lignin in pulp was described in a previous report (Bourbonnais and Paice 2003). The voltammogram of ABTS shows two anodic peaks appearing when the electrode potential reaches 520 mV and 920 mV corresponding to the oxidation of ABTS to its cation radical ($ABTS^{\bullet+}$) and subsequently to its dication ($ABTS^{2+}$). When ABTS is oxidized in the presence of pulp, there is an increase of the two oxidation peaks, reflecting the extent of the reactions taking place between the two oxidized forms of ABTS and the residual lignin in kraft pulp. We have shown in our previous study that the intensities of the catalytic current measured at 520 and 920 mV depend not only on the amount of residual lignin in kraft pulp but also on the reactivity of lignin. Here we test the hypothesis that the peak current ratio for the two oxidation states ABTS (i.e., 520 and 920 mV) can be used as an indicator of the pulp bleachability. The increase of the peak current intensity at 520 mV corresponds to the amount of more easily oxidizable material such as phenolic groups, whereas the increase of the current at 920 mV is more likely related to higher redox potential groups in lignin (Bourbonnais et al. 1998). Thus, a pulp with a high ratio of the peak current intensity at 520 mV to that at 920 mV, should indicate that the pulp can be more easily oxidized than a pulp having a lower ratio. Voltammograms of kraft and oxygen delignified pulps from black spruce and western hemlock are shown in Figure 3 to illustrate the relative differences of the voltammetric signals of ABTS with different pulp types having similar kappa number (28.4 ± 0.5). For all unbleached pulps, there is a strong increase of the catalytic current when compared to the diffusion current measured in the presence of bleached pulp, but their voltammetric traces are not identical even though they all have the same kappa number.

The voltammetric catalytic peak currents measured at 520 and 920 mV and their ratio, I_{p520}/I_{p920}, are shown in Figure 4. The smaller catalytic current at low potential (520 mV) for the O_2 pulps indicates that there is less easily oxidizable lignin structures in O_2 pulps than in kraft pulps. These results support the hypothesis proposed by

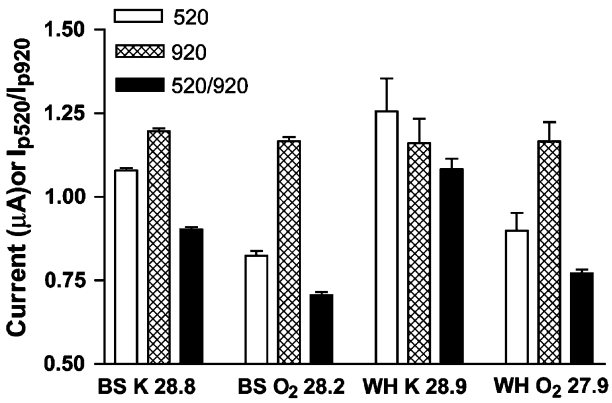

Figure 4 Voltammetric peak currents measured at 520 and 920 mV and the signal ratios, I_{p520}/I_{p920}, for similar kappa number pulps.

Jiang et al. (2003) that the formation of covalent bonds between HexA groups and lignin during oxygen delignification contributes to lowering the reactivity of pulp to bleaching reactions. The 520 mV currents in Figure 4 also indicate that the residual lignin in kraft pulp from western hemlock is more reactive than from black spruce. However, the intensities of the current measured at higher redox potential (920 mV) are similar for all pulps at the same kappa number. Thus, the measurement at high potential correlates with the kappa number or the total amount of the oxidizable material in pulp, whereas the measurement at 520 mV corresponds to the portion of material that can be oxidized at lower potential.

In Figure 5 we have compared the bleachability (reduction of kappa number after D_0E from Table 3) for all series of pulps as a function of their kappa number (left), Klason lignin content (middle), and their voltammetric signal ratio I_{p520}/I_{p920} measured in the presence of ABTS (right). The results show that pulp bleachability toward ClO_2, varies with the nature of pulp when compared at the same unbleached kappa number or lignin content (Figure 5 left and middle) and increases with the voltammetric signal ratio (Figure 5 right). Bleachabilities for all western hemlock kraft pulps were the highest and range from 1.29 to 1.31, followed by black spruce kraft with a wider efficiency range, going from 1.19 to 1.26. The two oxygen delignified pulps had lower bleachability with similar val-

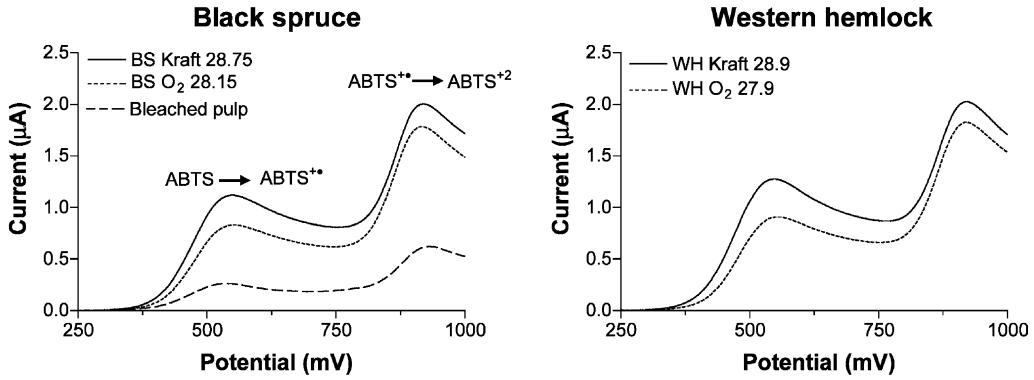

Figure 3 Voltammograms of ABTS (0.2 mM) in the presence of fully bleached pulp and with kraft and oxygen delignified pulps from black spruce and western hemlock with similar kappa number: 28.4 ± 0.5.

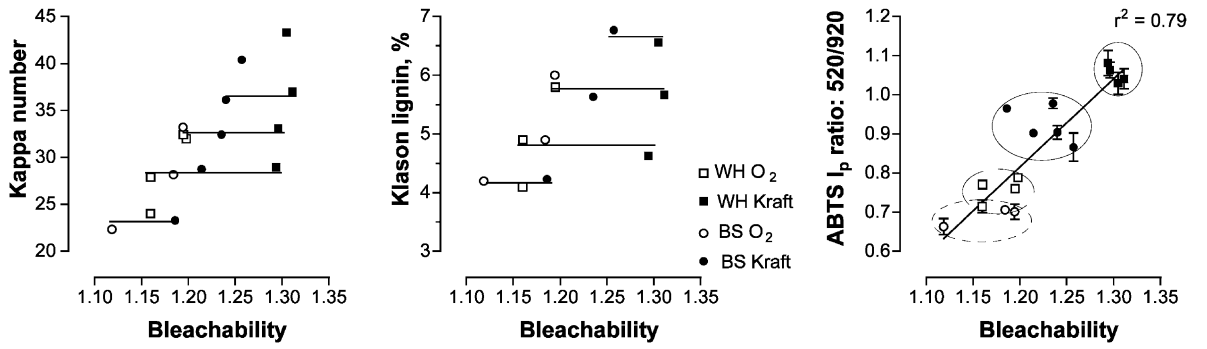

Figure 5 Variation of the bleachability of D_0E stages for different types of pulp at various kappa numbers (left) or Klason lignin contents (middle) and relationship between pulp bleachability and voltammetric signal ratio I_{p520}/I_{p920} of ABTS with the same series of pulps (right).

ues ranging from 1.16 to 1.19 for hemlock and 1.12 to 1.19 for spruce. The signal ratios for western hemlock were always higher than the corresponding ratios for black spruce.

Voltammetry of pulps with a mixture of transition metal mediators

We have tried the same approach as with ABTS but using a mixture of three inorganic redox mediators, each of which has a distinct redox potential and reversible redox couple. These transition metal complexes were shown to react with lignin in pulp by a mechanism involving only electron transfer without formation of coupling reactions (Bourbonnais et al. 2000, 2001). Figure 6 shows separate cyclic voltammograms (left) of each transition metals complex: $K_4W(CN)_8$, $K_4Mo(CN)_8$ and $[Fe(bpy)_3](ClO_4)_2$ and the voltammogram of an equimolar mixture of each (right). The typical reversible voltammetric curves for these metal complexes indicate that they form stable redox couples. Thus, both their reduced and oxidized forms (i.e. $W^{4+/5+}$, $Mo^{4+/5+}$ and $Fe^{2+/3+}$) are stable enough to exist in aqueous solution and are available to undergo reversible redox reactions with lignin. The redox potentials (E_0) of the complexes measured at the mid-point between their oxidation and reduction peaks are: $K_4W(CN)_8$: 285 mV; $K_4Mo(CN)_8$: 550 mV; $[Fe(bpy)_3](ClO_4)_2$: 880 mV.

Voltammograms of black spruce and western hemlock kraft and oxygen delignified pulps in the presence of an equimolar mixture of the three metal complexes (0.5 mM each) are illustrated in Figure 7. For the molybdenum (I_{p600}) and iron (I_{p900}) complexes, there is strong increase of the catalytic current when compared to the diffusion current measured in the presence of bleached pulp. However, for the tungsten complex (I_{p300}), the catalytic signals obtained with the unbleached kraft and the O_2-delignified pulps are slightly higher or equal to the signal obtained with the bleached pulp. These results indicate that a very small proportion of the lignin in kraft pulp can be oxidized at a potential of around 300 mV and that it disappeared completely after oxygen delignification. The amount of structures in lignin oxidized at 600 mV and 900 mV are much more important and also varied with the nature of pulps, even at the same kappa number. The current signal ratios of each metal over the total current and the bleachability for all kraft and O_2-delignified pulps are shown in Figure 8. As expected the ratios measured at 300 mV (W peak) are very small for all type of pulps. The ratios at 600 mV (M_0 peak) are much higher and show some similarity with the ABTS 520/920 ratios previously shown in Figure 5. Thus, the current ratio at 600 mV increases with pulp bleachability. Ratios obtained with the oxygen delignified pulps are lower than those from kraft brownstocks, and pulps from hemlock are slightly more reactive than pulps from spruce. The inverse situation is observed when we compare the signal ratios at 900 mV (Fe peak). The signal ratio at 900 mV varies inversely with pulp bleachability. Thus the fraction of lignin being reversibly oxidized at high redox potential is higher for all oxygen delignified pulps than the corresponding kraft pulps.

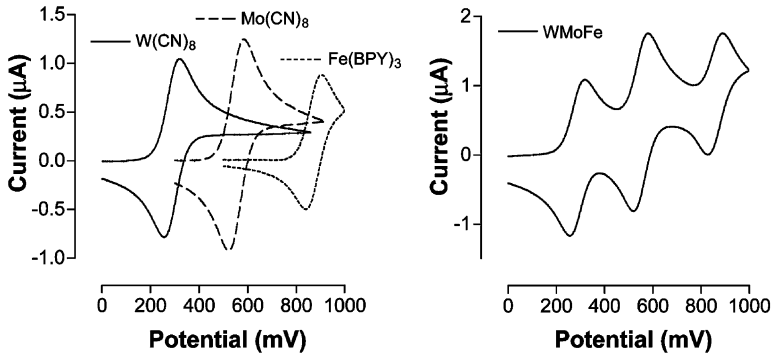

Figure 6 Cyclic voltammograms of transition metal redox complexes separately (left) and mixed together (right).

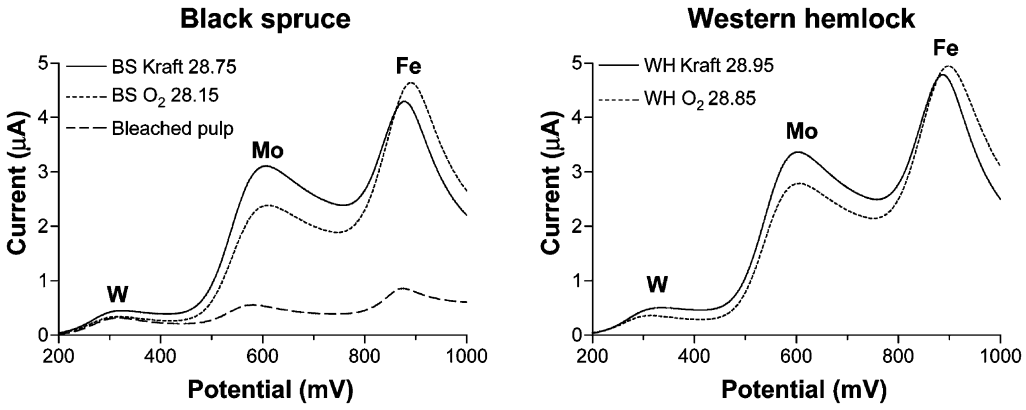

Figure 7 Voltammograms of equimolar mixture of transition metals mediators (0.5 mM each) with brownstock kraft and O_2-delignified pulps from black spruce (left) and western hemlock (right). A voltammogram of mediators with fully bleached pulp is also shown (left).

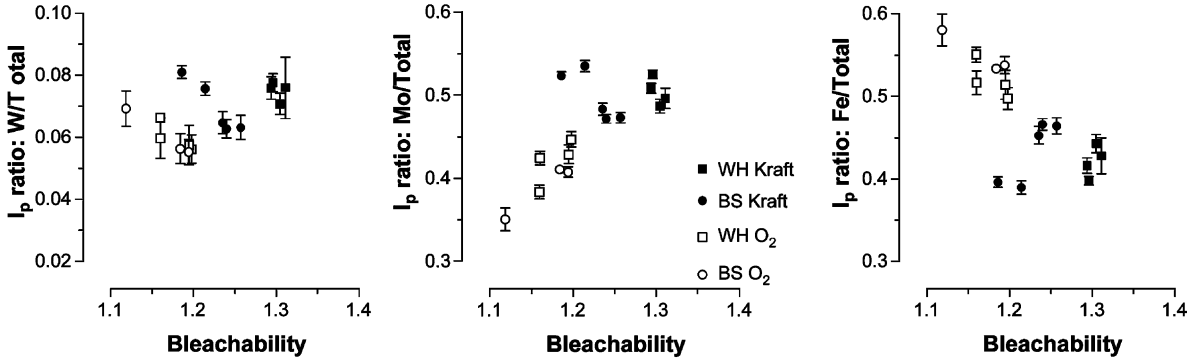

Figure 8 The current peak signal ratios of each metal complex over the total current of all three mediators in the presence of kraft and O_2-delignified pulps from black spruce and western hemlock as a function of pulp bleachability.

Conclusions

The ECF bleachability of different softwood pulps having the same kappa number varied with the wood furnish and delignification process. Western hemlock kraft pulps are more reactive towards chlorine dioxide bleaching then black spruce pulps, and oxygen delignification makes the pulps less reactive to D_0E bleaching. Thus kappa number is not a reliable indicator of bleachability for these pulps. This is due in part to the variable hexenuronic acid contents of the pulps. Those with higher ratio of hexenuronic acid content to kappa number (HexA/kappa) are harder to bleach.

Linear sweep voltammetry of unbleached pulps in the presence of redox mediators can be used to measure the reactivity of residual lignin in pulp. Peak current ratios at two voltages with ABTS (520 mV/920mV) and at each respective peak potential for a mixture of three transition metal mediators (W_{300mV}, Mo_{600mV} and Fe_{900mV} / total catalytic current) were shown to correlate with bleachability. The voltammetric signal ratios provide a more accurate prediction of bleachability than unbleached kappa number.

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