

Kraft Pulping of Reduced Metal Content Eucalyptus Wood: Process Impacts

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The effect of using acid pretreated eucalyptus wood chips in the Lo-Solids® pulping process was evaluated in the laboratory. Lo-Solids® cooking technology was chosen to evaluate the impact of acid pretreatments on the cooking performance, brown stock chemical composition, and black liquor heating value. The acid leaching stage reduced the contents of transition metals and other non-process elements in the wood chips and in the pulps produced. Benefits were detected in terms of the reduction in white liquor charge, increase in pulp yield, as well as pulp viscosity and black liquor heating value. Carbohydrate content and other wood/pulp constituents were not affected by the acid leaching pretreatments.

Keywords: Acid leaching; Eucalyptus; Lo-solids; Kraft pulping; Non-process elements

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INTRODUCTION

The kraft pulping process is the main chemical pulping method for producing high-quality wood-based fibers. Chemical pulping is a means of removing lignin from wood by chemical alteration to produce soluble lignin fragments. The removal of lignin liberates individual fibers from the wood matrix with mild mechanical treatment. Pulping must be able to selectively remove lignin from the fibers through chemical degradation, while minimizing damage to the cellulosic portion of the fibers, to preserve pulp strength. In comparison to other pulping processes, the kraft pulping process does an excellent job of producing stronger pulps. In addition, it is reasonably insensitive to the presence of bark and extractives. The kraft pulping process is adaptable to both hardwood and softwood tree species. In addition, it requires shorter cooking times, thus reducing some of the capital costs associated with the pulping process. Finally, the efficient recovery of pulping chemicals, the production of heat, and the valuable materials that can be produced from by-products, such as tall oil and turpentine from pine species, are strong assets of the kraft pulping process (Fuller 1987).

Several improvements have been made to the kraft pulping process over the years. Initially, pulping was performed in batch digesters. Since the 1960s, continuous pulping digesters have been developed. Improvements in continuous digester pulping technology have resulted in pulping processes that enhance liquor impregnation and level out the alkali profile throughout the cooking process, which results in a greater pulp yield and improves the pulp strength (Andersson *et al.* 2002; Hart and Connell 2006). Other operational changes in continuous digesters, such as downflow, Lo-solids, or compact cooking technologies, have been developed to make continuous digesters easier to

operate while retaining pulp strength and yield benefits (Marcoccia *et al.* 1996; Rantanen *et al.* 2005; Hart *et al.* 2011).

One area of potential concern in the kraft pulping process that has not been successfully improved, even with the benefits of continuous cooking technologies, is the presence of transition metals in the raw materials (mostly from wood) employed in the process. Negative impacts from these metals are common and can influence chemical reaction rates, process efficiency, and pulp properties. Wood chips are considered to be the main source of these metal ions, which are typically referred to as non-process elements (NPE) (Lundqvist *et al.* 2006; Doldán *et al.* 2011). Incoming NPEs such as Ca, Al, Si, Ba, K, Cl, Mg, Cu, Fe, and P present the potential opportunity for mineral scale and deposit formation, pulp quality concerns, potential process equipment corrosion, recovery boiler plugging, increases in lime kiln fuel consumption (Taylor and McGuffie 2007), and loss of pulp quality (Svensson 2012).

Transition metal ions have generally been identified as having deleterious effects in bleaching stages that use hydrogen peroxide, as those metal ions are known to catalyze hydrogen decomposition; the result is reagent waste and the formation of radicals, which degrade pulp fiber. Metals such as Fe and Al limit brightness through bleaching and intensify bleached pulp brightness reversion (Gupta 1970; Gilbert *et al.* 1973; Ali *et al.* 1986; Lapierre *et al.* 1995; Basta *et al.* 1994; Lachenal *et al.* 1997; Yuan *et al.* 1997; Forsskahl *et al.* 2000). From the pulp mill aspect, Ca has been recognized to reduce the rate of wood delignification in the digester. This same study showed increasing pulp yield and viscosity when Ca was removed prior to pulping (Lundqvist *et al.* 2006).

In recovery, the buildup from K and Cl produces fouling and corrosion problems. In addition, the presence of Si, Al, Ca, and Fe intensifies evaporator fouling. Magnesium, Si, P, S, Mn, Fe, and Al, when present in high concentrations, add to the causticizing effect of poor lime settling and low lime reactivity (Crouse and Stapley 1979; Ulmgren and Raadestrom 1997; Taylor and Bossons 2006; McGuffie and Taylor 2007; Tran and Vakkilainen 2008). This negative impact on processing because of these NPEs in wood motivates the development of a removal process that will be both desirable and economically attractive. Such a removal system should improve the pulping process, pulp bleachability, filtrate recirculation systems, and the chemical recovery cycle. A technique that is promising for the removal of these elements is acid leaching. Such a process can be applied as a pretreatment to the chips prior to pulping. This approach has the potential to reduce the damage caused by NPEs, without sacrificing pulp quality.

The current study was designed to identify the impact of acid leaching pretreatment on NPEs removal and its impact on the Lo-Solids® pulping process.

EXPERIMENTAL

Materials

Two different, 7-year-old, eucalyptus woods (A and B), pretreated with different filtrates (acid sources), were used. Wood A (*Eucalyptus grandis*) was an industrial eucalyptus clone, recognized for exhibiting high performance in the pulping process. Wood B (*Eucalyptus urograndis*) was a mix of industrial clones, possessing inferior pulping performance. The pretreatments were acidified water (Leach 1) and acidic filtrate obtained from an AHT (hot acid) bleaching stage (O-AHT(PO)DP sequence; Leach 2). Non-treated chips (original) were used as a reference. The conditions used for chip

leaching were pH 2, 70 °C, 4/1 liquor/wood ratio, and a 1-h treatment time. Details associated with the chip pretreatment results were presented in a previous study by Santos *et al.* (2015).

All wood samples were characterized for carbohydrate, extractives, and lignin contents, S/G ratio, and NPE content (Table 1 and 2). Total lignin showed a tendency to increase with the application of acid treatments. This increase in lignin, particularly leach 2, may be explained by the presence of dissolved lignin in the acidic filtrate where the low pH could have precipitated some of the lignin onto the fiber. It could also be explained by nondetectable yield losses occurring during leaching pretreatment. A detailed explanation for this characterization is also found in our previous publication (Santos *et al.* 2015).

Table 1. Wood Sample Composition

Sample	Pre treatment	Wood composition (% original)									
		S/G	Glc	Xyl	Gal	Ara	Man	Extr.	Total lignin	Uronic acid	Acetyl
Wood A	Original	2.8	48.6	11.5	0.9	0.2	0.9	0.6	28.9	4.7	2.7
	Leach 1	2.7	49.6	12.1	0.8	0.3	1.2	0.5	29.2	4.1	2.7
	Leach 2	2.8	48.3	11.5	0.9	0.3	0.9	0.6	29.8	4.5	2.7
Wood B	Original	2.2	45.9	12.8	1.0	0.2	1.1	1.7	29.5	5.0	2.7
	Leach 1	2.2	46.4	12.4	1.1	0.3	0.8	1.4	29.7	5.2	2.7
	Leach 2	2.2	45.7	12.5	1.0	0.2	0.9	1.4	30.1	4.8	2.7

S/G: siringyl/guaiacyl; Glc: glucan; Xyl: xylan; Gal: galactose; Ara:arabinan; Man: mannan; Extr: extractives

Table 2. Non-Process Elements (NPEs) in the Wood Samples

Sample	Pretreatment	NPE concentration (mg/Kg)						
		Cu	Mg	Fe	Ca	Mn	K	Cl
Wood A	Original	3.3	96.8	37.6	883.0	33.0	430.9	318.6
	Leach 1	2.6	57.0	27.5	574.0	22.4	77.1	58.6
	Leach 2	3.1	60.8	28.1	593.4	22.4	137.0	50.0
Wood B	Original	3.4	84.5	38.7	513.0	52.5	254.0	221.0
	Leach 1	3.0	48.9	28.4	346.3	27.0	81.0	44.9
	Leach 2	3.3	45.9	30.8	346.8	26.1	73.7	30.1

Wood Chip Pulping and Process Stream Characterization

Lo-Solids® cooking technology was chosen to evaluate the impact of acid pretreatments on cooking performance, brown stock chemical composition, and black liquor heating value. Lo-Solids® cooks were performed in triplicate, with a target Kappa number of 17 ± 0.5 . The system used for Lo-Solids® technology was an MK digester (1/K409, MK Systems Inc., Peabody, MA, USA) with a 7.0-L capacity and electrically heated controls containing peripheral equipment, such as a pressure gauge, heat exchanger, and circulation pump. To allow continuous digester simulation, white liquor

was injected/extracted utilizing pressurized heated liquor tanks connected to the digester. Cooking conditions are described in Table 3. A list of analyses and their respective methodologies for process stream characterization are shown in Table 4.

Table 3. Cooking Conditions

Parameter	Impregnation zone	Upper cooking zone	Lower cooking zone
Time to temperature (min)	15	15	-
Time at temperature (min)	30	60	120
Temperature (°C)	110	155	156
Alkali charge (% total EA)	50	30	20
Liquor/wood ratio	4/1	4/1	4/1

Table 4. Methodologies for Process Stream Characterization

Analysis	Methodology
Metals	TAPPI T244 om-88
Chloride	TAPPI T700 om-93
Carbohydrates	Santos <i>et al.</i> 2011
Hexenuronic acids	Vuorinem <i>et al.</i> 1996
Kappa number	TAPPI T236 cm-85
Pulp viscosity	TAPPI T230 om-94
Heating value	ASTM D-2015-96

RESULTS AND DISCUSSION

Lo-Solids® Kraft Pulping Process

The kraft pulping process was performed under the same conditions for all the samples, with adjustments made only for effective alkali charge. The goal of the variation in charge was to achieve the target Kappa number of 17 ± 0.5 . The effective alkali charges and corresponding Kappa numbers are shown in Table 5. The alkali demand for wood B without pretreatment (original) was higher than wood A by 2.5%. This increase in alkali demand was expected, as the S/G ratio for wood B was lower than that for wood A. As shown in the literature (Santos *et al.* 2011), the S/G ratio is an important wood feature used for determining the delignification rate. A higher S/G ratio indicates a more easily delignified wood, which consequently requires less aggressive cooking conditions, resulting in carbohydrate preservation. Pretreatment of wood chips, with either Leach 1 or Leach 2, was shown to be beneficial for lowering alkali demand, although Leach 2 was

found to be slightly more effective (Table 5). The lower alkali demand of the chips subjected to acid leaching could be related to a reduction in extractive content or free calcium, where the latter has been shown to negatively impact delignification of wood during kraft pulping (Lundqvist 2006).

Table 5. Effective Alkaline Charge and Kappa Number

Sample	Pretreatment	Effective alkali (%)	Kappa number
Wood A	Original	16.7	16.6
	Leach 1	16.0	16.8
	Leach 2	15.3	17.4
Wood B	Original	19.2	17.0
	Leach 1	18.7	16.9
	Leach 2	17.9	16.8

The pulping yield superiority of wood A was maintained with Leach 1 and Leach 2 (Fig. 1). The acid pretreatment in wood B resulted in a 0.5% increase in pulping yield, indicating that the pretreatment did not negatively impact the carbohydrate composition or content. This finding was of great importance, as acid treatments may potentially degrade carbohydrates. As reported earlier (Santos *et al.* 2015), the pretreatment conditions applied in this study are confirmed to be mild enough to not cause significant carbohydrate damage that could result in yield loss.

Pulp viscosity (Fig. 2) was also measured to confirm the impact of NPEs and the benefit of the acid treatment on pulp strength. Surprisingly, pulp A exhibited an increase of 30.6 cP viscosity points and pulp B was increased by 39.4 cP when leaching pretreatments were applied. This represented more than a 60% viscosity gain for the treated pulps (Fig. 2) in comparison to the original, non-treated pulp.

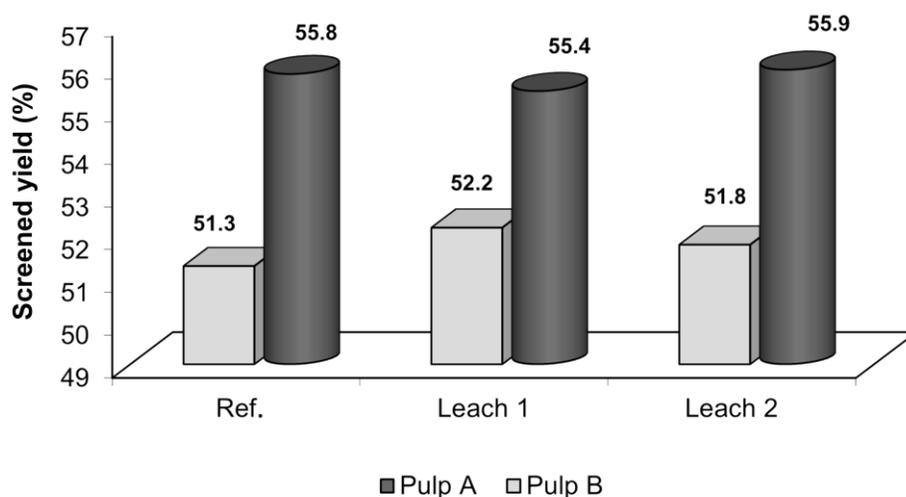


Fig. 1. Screened yield

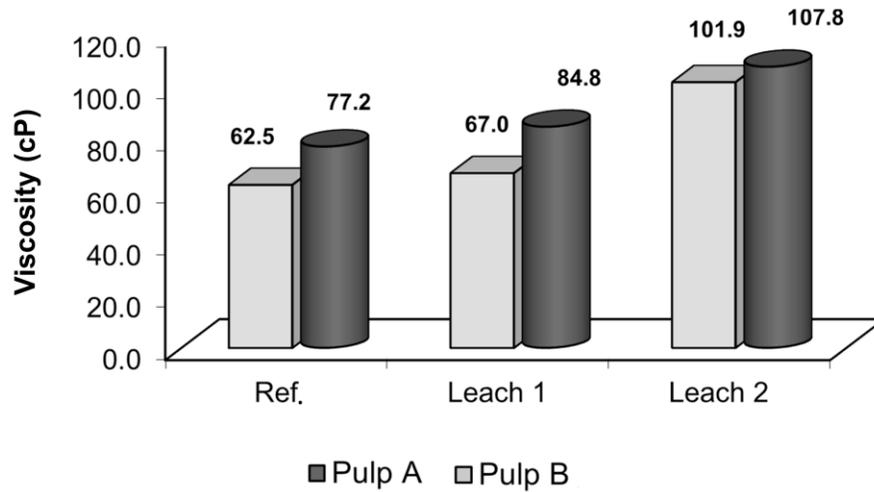


Fig. 2. Pulp viscosity

Brown Stock and Black Liquor Chemical Analyses

The impacts of acidic pretreatments on brown stock pulps and black liquors were investigated. The levels of glucan, xylan, hexenuronic acid, uronic acid, and NPEs of original and pretreated samples were analyzed (Fig. 3).

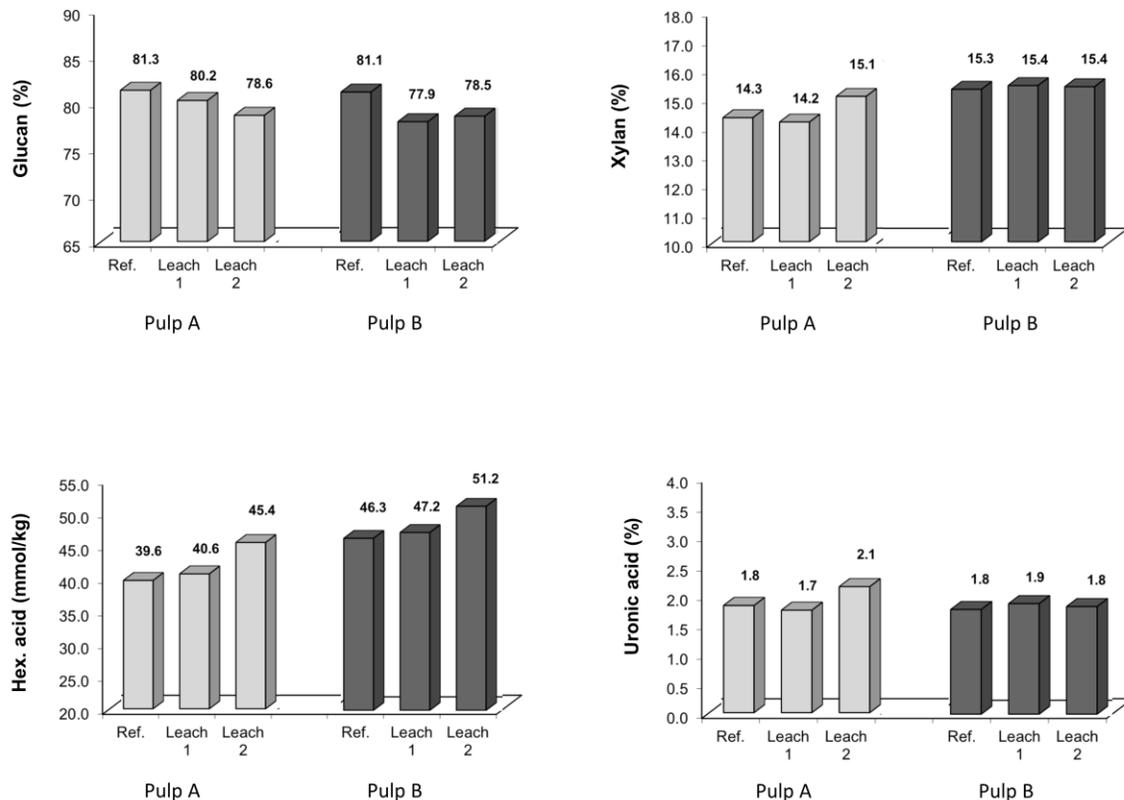


Fig. 3. Pulp characterization for glucan, xylan, hexenuronic acid, and uronic acid contents

Both acid treatments resulted in a small decrease in the glucan level. The decrease in glucan level was not pronounced and was within analysis error. Xylan and uronic acid contents for all pulps were maintained and were comparable to that of the original, non-treated pulp. Although pretreatment favored the formation of hexenuronic acid in both pulps, the highest levels of hexenuronic acid were detected in the pulps produced with Leach 2. This finding was explained by the reduced alkali charges; lower alkali charges resulted in less drastic cooking conditions and a resulting increase in hexenuronic acid levels during the cooking process (Gustavsson and Al-Dajani 2000).

To investigate the effectiveness of NPE removal by acidic pretreatment, all pulp samples were analyzed for NPE content. The NPE removal data were reported relative to the original pulp (no pretreatment) and are shown in Fig. 4. Pulp A, which initially had the highest NPE content (Table 2), was found to have the lowest NPE percent removal after cooking. Calcium removal in pulp A was the highest, achieving up to 35%. The removal order (from highest to lowest) was Mn, Fe, K, Mg, and Cu. For pulp B, Mn and Mg were the metals with the highest percent removal, followed by K, Ca, Fe, and Cu.

No apparent explanation of what determines the amount of NPEs left in the pulp is clear at this moment. Nevertheless, NPE reduction was achieved when wood chips were pretreated with acidic solutions. The removal of the NPEs resulted in a lower concentration of process liquors and a diminished process deposition that could reduce corrosion and mineral scale problems. The reduction in NPE also allowed for increased pulp quality because higher viscosity was achieved for the pretreated samples (Fig. 2) (Wathen 2006).

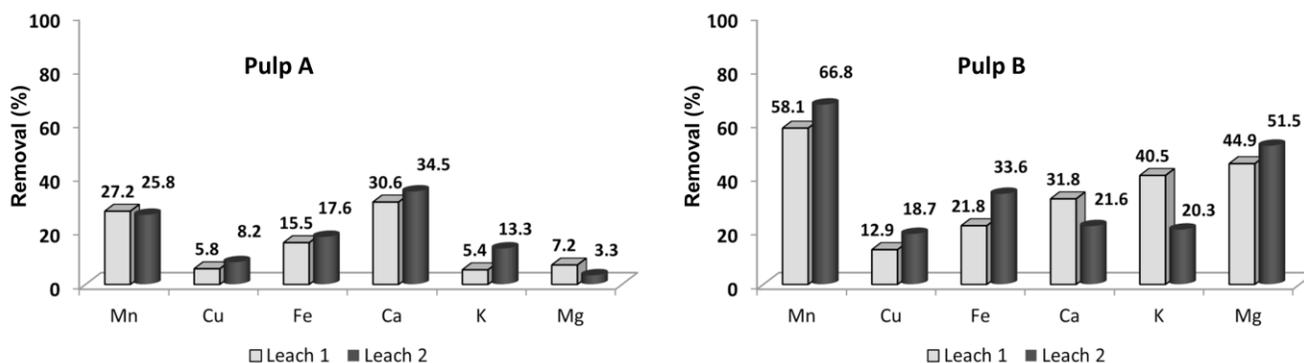


Fig. 4. The % removal of NPEs

To confirm the lower input of NPE to the process, black liquor samples were collected after cooking and analyzed for their elemental composition and heating value. The organic, inorganic, and total solids content for each sample are shown in Table 6. The elemental analysis showed no apparent change in liquor composition, and the differences observed were within the experimental error ($\pm 3\%$ error for black liquor solids and $\pm 3.5\%$ error for elemental analysis).

On the other hand, the black liquor heating value analysis revealed a clear tendency of an increased heating value in the pretreated wood samples, especially for Leach 2 samples (Fig. 5). This increase was associated with higher pulp yields and the reduction of inorganic matter in the black liquor. The pulp yield increase resulted in there being less carbohydrate present in the black liquor, which had a lower heating value than lignin. The reduction in alkali charge, in association with the leaching pretreatments,

reduced the amount of inorganic matter present in the black liquor. Inorganic matter does not strongly contribute to the heating value (Hart 2011). The reported reduction in NPE levels clearly showed a benefit to acid pretreatment prior to pulping, and its positive effects can be observed in the black liquor properties (Table 6).

Table 6. Black Liquor Elemental Analysis

Sample	Pretreatment	Organic solids (%)	Inorganic solids (%)	Total solids (%)	C (%)	O (%)	N (%)	H (%)
Wood A	Original	7.7	5.2	12.9	38.7	57.0	0.1	4.2
	Leach 1	7.9	4.9	12.8	39.1	56.7	0.1	4.1
	Leach 2	8.0	4.7	13.7	37.1	58.6	0.3	3.9
Wood B	Original	8.0	5.7	13.7	35.8	60.6	0.1	3.5
	Leach 1	8.4	5.7	14.0	37.6	58.4	0.4	3.7
	Leach 2	8.0	5.7	13.7	37.1	58.6	0.5	3.9

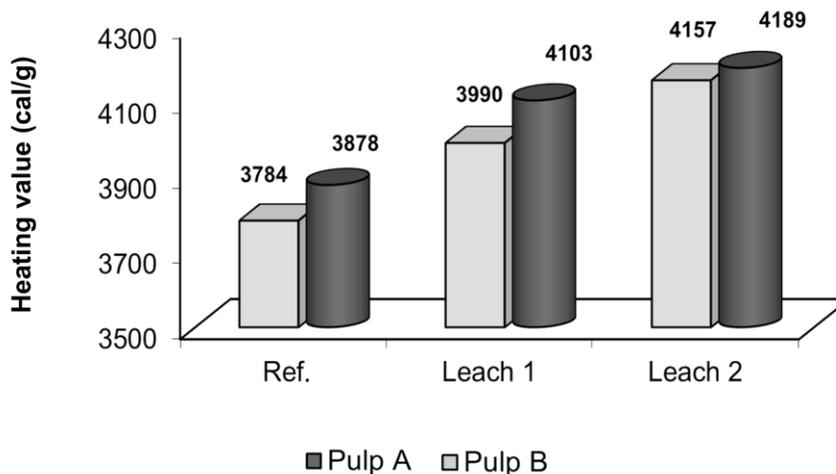


Fig. 5. Black liquor heating value

CONCLUSIONS

1. Acid leaching of wood chips resulted in a 0.9% increase in pulp yield for wood B produced from the Lo-Solids® cooking process. Wood A showed no positive or negative yield impacts associated with the acid leaching pretreatment. For the same Kappa number, effective alkali demand for pretreated wood chips was lower, providing higher viscosity for the resulting pulp.
2. Leaching of wood chips with acidic bleaching effluent obtained from an AHT stage exhibited the best results in alkali demand reduction and pulp viscosity improvement. No influence on the black liquor composition was detected. Increases in the heating values of these liquors were observed for samples pretreated with acid.
3. There were no significant differences in the carbohydrate content of pretreated wood and the resulting pulps.

REFERENCES CITED

- Ali, T., McArthur, D., Stott, D., Fairbank, M., and Whiting, P. (1986). "The role of silicate in peroxide brightening of mechanical pulp. I: The effects of alkalinity pH, pre-treatment with chelating agent and consistency," *Journal of Pulp and Paper Science* 12(6), 166-172.
- Andersson, N., Wilson, D. I., and Germgard, U. (2002). "Validating continuous kraft digester kinetic models with online NIR measurements," *Proceedings of the American Control Conference* 5, 3783-3787. DOI: 10.1109/ACC.2002.1024516
- ASTM D-2015-96 (1996). "Gross calorific value of solid fuel by the adiabatic bomb calorimeter," ASTM International, West Conshohocken, PA.
- Basta, J., Holtinger, L., Hermansson, W., and Lundgren, P. (1994). "Metal management in TCF/ECF bleaching," in *Proceedings from the International Pulp Bleaching Conference*, pp. 29-32.
- Crouse, N. E., and Stapley, C. E. (1979). "Dregs – Their cause and effect," *Pulp & Paper-Canada* 80(NC), 78.
- Doldán, J., Poukka, O., Salmenoja, K., Battegazzore, M., Fernandez, V., and Eluén, I. (2011). "Evaluation of sources and routes of non-process elements in a modern eucalyptus kraft pulp mill," *O PAPEL* 72(7), 47-52.
- Forsskåhl, I., Gullichsen, J., and Paulapuro, H. (2000). "Brightness reversion," in: *Forest Products Chemistry*, P. Stenius (ed.), TAPPI Press, Atlanta, GA, pp. 279-332.
- Fuller, W. S. (1987). "Kraft pulping: New developments in an old technology," Weyerhaeuser Paper Company, Tacoma, WA.
- Gilbert, A. F., Pavlovova, E., and Rapson, W. H. (1973). "Mechanism of magnesium retardation of cellulose degradation during oxygen bleaching," *TAPPI Journal* 56(6), 95-99.
- Gupta, V. N. (1970). "Effect of metal ions on brightness, bleachability and colour reversion of groundwood," *Pulp & Paper-Canada* 71(18), 69.
- Gustavsson, C., and Al-Dajani, W. (2000). "The influence of cooking conditions on the degradation of hexenuronic acid, xylan, glucomannan and cellulose during kraft cooking of softwood," *Nordic Pulp and Paper Research Journal* 15(2), 160-167.
- Hart, P. W. (2011). "Production of high yield bleached hardwood kraft pulp: Breaking the kraft pulp yield barrier," *TAPPI Journal* 10(9), 37-41.
- Hart, P. W., and Connell, D. (2006). "The effect of digester kappa on the bleachability and yield of EMCCTM softwood kraft pulp," *TAPPI Journal* 5(4), 23-27.
- Hart, P. W., Colson, G. W., Antonsson, S., and Hjort, A. (2011). "Impact of impregnation on high kappa number hardwood pulps," *BioResources* 6(4), 5139-5150. DOI: 10.15376/biores.6.4.5139-5150
- Lachenal, D., Nguyen Thi, N. B., Chirat, C., and Soria, L. (1997). "Optimum use of H₂O₂ in kraft pulp delignification," *Paperi ja Puu-Paper and Timber* 79(4), 252-256.
- Lapierre, L., Bouchard, J., Berry, R. M., and Van Lierop, B. (1995). "Chelation prior to hydrogen peroxide bleaching of kraft pulps: An overview," *Journal of Pulp and Paper Science* 21(8), 268-273.
- Lundqvist, F., Breid, H., Saltberg, A., Gellerstedt, G., and Tomani, P. (2006). "Removal of non-process elements from hardwood chips prior to kraft cooking," *Appita Journal* 59(6), 493-499.
- Marcoccia, B. S., Laakso, R., and McClain, G. (1996). "Lo-Solids pulping: Principles and applications," *Tappi Journal* 79(6), 179-188.

- McGuffie, B., and Taylor, K. (2007). "Non-process element mass balance improves recaust and lime kiln efficiency at Elk Falls mill," *Pulp & Paper-Canada* 108(3), 49-55.
- Rantanen, R., Simila, E., and Ahvenlampi, T. (2005). "Modeling of kappa number in Downflow Lo Solids cooking using Gustavson's model," *Pulp & Paper-Canada* 106(5), 31-34.
- Santos, R. B., Capanema, E. A., Balakshin, M. Y., Chang, H. M., and Jameel, H. (2011). "Effect of hardwoods characteristics on kraft pulping process: Emphasis on lignin structure," *BioResources* 6(4), 3623-3637. DOI: 10.15376/biores.6.4.3623-3637
- Santos, R. B., Gomide, J. L., and Hart, P. W. (2015). "Impact of wood chips leaching pretreatment on wood chemical composition," *TAPPI Journal* 14(1), 9-14.
- Svensson, J. (2012). *Non-Process Elements in the Green Liquor System*, Department of Chemical Engineering, Lund University, Sweden.
- TAPPI T230 cm-94 (1994). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA.
- TAPPI T236 cm-85 (1985). "Kappa number of pulp," TAPPI Press, Atlanta, GA.
- TAPPI T244 om-88 (1988). "Acid-insoluble ash in pulp," TAPPI Press, Atlanta, GA.
- TAPPI T700 om-93 (1993). "Analysis of bleaching liquors by suppressed ion chromatography," TAPPI Press, Atlanta, GA.
- Taylor, K., and Bossons, D. (2006). "Investigation of green lime mud at Harmac mill," *Pulp & Paper-Canada* 107(3), 63-66.
- Taylor, K., and McGuffie, B. (2007). "Investigation of non-process element chemistry at Elk Falls mill - Green liquor clarifier and lime cycle," *Pulp & Paper-Canada* 108(2), 27-32.
- Tran, H., and Vakkilainen, E. K. (2008). "The kraft chemical recovery process," *TAPPI*, (<http://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf>).
- Ulmgren, P., and Raadstroem, R. (1997). "The composition of calcium phosphates precipitated from green and white liquors," *Nordic Pulp and Paper Research Journal* 12(3), 167. DOI: 10.3183/NPPRJ-1997-12-03-p167-174
- Wathen, R. (2006). *Studies on fiber strength and its effect on paper properties*. KCL Communications 11, KCL, Espoo, Finland, 98 p.
- Yuan, Z., d'Entremont, M., Ni, Y., and Van Heiningen, A. R. P. (1997). "The role of transition metal ions during peracetic acid bleaching of chemical pulps: They may waste a significant amount of the bleaching chemical," *Pulp & Paper-Canada* 98(11), 24-29.
- Vuorinen, T., Teleman, A., Fagerstrom, P., Buchert, J., and Tenkanen, M. (1996). "Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps", In *Proc. Int. Pulp Bleaching Conf.*, Atlanta: TAPPI Press, Vol. 1, 43-51.

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