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PROPERTIES OF EUCALYPTUS GLOBULUS FIBERS AFTER HOT WATER EXTRACTION

G. V. Duarte[1*], B.V. Ramarao[1*], T.E. Amidon[1], P. T. Ferreira[2]

[1] Empire State Paper Research Institute, Department of Paper & Bioprocess Engineering, State University of New York College of Environmental Science and Forestry,1 Forestry Drive - Syracuse, NY 13210 USA

[2] Chemical Engineering Department, University of Coimbra, Pólo II, R. Sílvio Lima, 3030-790 Coimbra, PORTUGAL

ABSTRACT

The purpose of this study was to determine the impact of hot water extraction (HWE) on the properties of *Eucalyptus globulus* Kraft pulp, namely in their morphological structure, chemical composition, charge behavior, viscosity and water interaction. Five different HWE were performed - 0, 30, 60, 90 and 120 min - after which the chips were Kraft cooked. As extraction takes place, the hemicelluloses content of the pulps is reduced from a typical of 21-22% to 3-4% and the cellulose fraction increases from 73-75% to 90%. This translates into an increase in the pulps' viscosity. Fiber length decreases for all pulps and both the fine content and kink index increase greatly with extraction. Although there is no significant increase in the pore size, the porosity increases, which may be responsible for the increase of the WRV of the pulps. As for the charge properties, the zeta potential remains unaffected, whereas total cationic demand decreases with extraction. Accordingly with the differences seem, it is expected that papers produced with extracted pulp will tend to give rise to weaker papers, with worse drainability, worse refinability but less consumption of chemicals.

Keywords: FQA, Hot Water Extraction, NMR, Kraft Fiber Properties, Zeta Potential.

INTRODUCTION

The combination of an increasing concern about the environment, especially greenhouse effect and the shortening availability of (cheap and accessible) fossil fuels, which translates into higher costs to the consumer, lead to the first true and serious effort into finding alternative and renewable energy sources. Lignocellulosic materials such as wood constitute an important natural resource for the production of biofuels and biodegradable plastics and can be a component for sustainable industrial development [1]. Biofuels can help alleviate climate change by reducing greenhouse gas emissions while bioresources can substitute for fossil based carbon resources as a raw material for plastics.

Forest biorefineries are expected to process forest biomass feedstock such as wood into a spectrum of fuel and material products, similar to the operation of conventional petroleum refineries [2,3]. Biorefineries will exploit economies of scale to transform these renewable resources into useful energy and materials. Current mills producing papermaking pulps can be converted into integrated biorefineries producing biofuels, acetic acid and bioplastics, while still producing pulp and paper [2,4,]. The idea is to use the hemicellulose present in the wood that are typically dissolved in the black liquor and consequently burned in the recovery process to produce products of higher value.

Several researchers have studied different types of hemicellulose extractions, such as hot-water extraction (autohydrolysis), alkaline and acidic extraction [4-7] on several wood species. Goyal et al [4], studied the effect of hot-water extraction on Sugar Maple pulps and a Brazilian eucalyptus pulps, as a consequence of the application of a biorefinery. Overall they found that the extracted chips are easier to pulp and bleach, but the pulp has worse refinability and strength properties. For their mass removal

[*] Authors for correspondence: bvramara@esf.edu or gvduarte@syr.edu; Phone: (+1) 3154706513; Fax: (+1) 3154706945

of up to 16.5%, they were able to produce sugar maple extracted pulps that exhibit satisfactory strength properties, whereas for eucalyptus they were not. Yoon et al [6,7] studied the properties of loblolly pine extracted kraft pulps and they also found that the extracted pulps exhibit lower refinability hindered tensile strength. However, with the extractions employed, no differences in pulp viscosity, zero span tensile strength (ZSTS) or tear were observed, indicating that the fiber strength remains unaffected, but the inter-fiber bonding decreases with extraction. Al-Dajani et al [5] performed low temperature alkaline extractions on Aspen Chips followed by conventional kraft cook. They reported that it was possible to partially remove hemicellulose from the chips, without detrimentally affecting the pulp's yield or its quality.

Sousa et al [8] investigated the effect of fiber's surface composition on their cationic demand and zeta potential. They observed that a change in hemicellulose content from 20 to 15% decreased the cationic demand but did not affect the zeta potential, whereas the removal of lignin contributes to a decrease of the zeta potential. Since Bhardwaj et al [9] showed that the lignin content does not affect the total fiber charge, Sousa et al [8], attributed the difference in zeta potential of the bleached and unbleached pulps to the hemicellulose content and structure. However, when using other techniques, Bhardwaj [9-11] et al, actually show that different kappa pulps exhibit different fiber charge.

Santos et al, [12] also studied the influence of hemicellulose content in several bleached kraft pulp properties (of E. globulus), namely fiber morphology, pulp composition and viscosity, water retention values (WRV) and paper properties. They noticed that the extracted pulp had slightly smaller fiber length, higher amounts of fines and substantially higher kink when compared to the control These pulps also exhibit higher wet fiber flexibility (WFF) and viscosity, but lower relative bonded area (RBA) than the control. The WRV seems to decrease with the removal of hemicellulose. As for the paper properties, they reported that the removal of hemicelluloses (from approximately 19% to 8.5%) negatively affected tensile and tear indexes as well as zero span tensile strength.

EXPERIMENTAL

The Eucalyptus chips were obtained from Soporcel's mill in Figueira da Foz, Portugal. The chips were air dried upon arrival and screened through a series of screens with circular opening of 9/8, 7/8/ 5/8 and 3/8 inch in diameter. The chips retained in the 7/8 and 5/8 in were considered accepts and used in the laboratorial experiments [13].

The extractions and cooks were carried out in a 4.5 liter M&K Digester, using 500 g of OD chips. DI water was added in order to reach 4:1 liquid to wood ratio. Extractions were carried out at 160 ºC, the heating time was of 30 min and the time at temperature varied from 30, 60, 90 to 120 minutes. The Kraft cooks were performed similarly to the extractions, with the exception of the cooking liquor, the heating time and H-factor. The white liquor was prepared in order to have 16% active alkali (AA) and 25% sulfidity, while maintaining 4:1 L:W ratio. The heating up time was of 60 min and the H-factor varied in order to achieve three different kappa numbers – 15, 25 and 35. Cooks were performed with all of the extracted chips (after 30, 60, 90 and 120 min extraction), as well as with unextracted chips (control) for comparison. When performing a Kraft cook on an extracted chip, the cook was done right after the extraction and therefore the chips were never dried. However, two washes with DI water at 80ºC for 15 min where performed between the extraction and the cook.

The zeta potential was determined using a Brookhaven (BIC) Zeta Potential Analyzer (ZetaPlus®). Since zeta potential is determined by measuring the electrophoretic mobility of particles, these need to be small enough not to be affected by gravity. In other words this instrument can only measure the zeta potential of particles that can be considered in the colloidal range. Therefore, to avoid sedimentation (in the time frame of the measurements) this analysis was only performed with the fine fraction of the pulps.

Lignin was quantified in all the initial chips, extracted chips and pulps. For the chips, both Klason (or Acid Insoluble) Lignin and Acid Soluble Lignin tests were performed, according to the respective TAPPI Standard T222 and TAPPI Useful Method 250. In case of the acid insoluble lignin, the standard was slightly modified since the all the reagent amounts were cut in half. For the acid soluble

lignin, a PerkinElmer Lambda 650 UV/Vis Spectrophotometer was used. For the pulps, the residual lignin was measured via an indirect method, by measuring the Kappa Number of the pulps, according to TAPPI Standard T 236, with the exception that the amounts of chemicals used was cut in half.

^{1}H NMR analysis was used to determine the cellulose and hemicellulose content of wood chips, extracted wood chips and pulp samples. The NMR methods used in this research were developed by Kiemle et al [14] and are commonly used by other researchers [15-17], so further details can be found there. The wood and pulp samples (milled using a Willey Mill with a 60 mesh screen) were first digested to yield sugars and then analyzed using ^{1}H NMR. In a first digestion stage, a 50 mg OD sample (milled wood/pulp) is dispersed in 16 ml of 72% sulfuric acid at room temperature for 2 hours, stirring it every 15 minutes to ensure proper dissolution. In a second stage, 21 ml of DI water are added to the mixture, bringing the acid content down to 40%. This mixture is then placed in a water bath at 80ºC for one hour, being shaken every 15 minutes. The tubes are then cooled down and kept in the refrigerator overnight, for the residual solid matter to precipitate. When necessary the tubes are centrifuged at 2500 rpm for 7 min to further settle the solid matter and allow the collection of 1 ml of the clean supernatant, which is transferred to a NMR tube and mixed with a 0.1 ml of a standard solution. The standard solution is a mixture of known amounts of trimethylamine hydrochloride (TMA) and glucosamine. The NMR spectra were integrated and scaled so that the glucosamine α-peak had an area of 100. All digestions and NMR analyses were done at least in duplicate.

The cationic demand of pulps was measured using a Mütek Particle Charge Detector (PCD-02) with an automatic titrator (PCD-T2). A known amount (approximately 0.8 g) of pulp was dispersed in 100 ml of water and an aliquot of 10 ml was used per test. The pulp was allowed to reach a steady streaming potential for 3 minutes and then it was titrated against a commercial solution of poly-DADMAC with a concentration of 0.001 N.

The fibers pore size distribution and "true" density measurements were done in collaboration with University of Coimbra and the Labgran – Granulometry Laboratory. The pore size distribution and apparent density were performed done using a AutoPore IV Mercury Porosimeter and the "true" density of the fiber was performed using a AccuPyc 1330 both from micromeritics.

The fiber analysis and the Water Retention Value (WRV) measurements were done at the Specialty Minerals Research Center facilities in Allentown, PA. The first was done using their OpTest HiRes Fiber Quality Analyzer (FQA), one of the most modern on-line fiber analysis instruments. The analysis provides a fiber length distribution (different length averages, fines content, among others) as well as fiber curl and kink information. The operating procedure is fairly simple and it basically consists in a series of dilutions in order to obtain a representative sample at very low consistency (0.04%). The methodology used for the WRV was the one in practice there and similar to TAPPI Useful Method T256. 1.94 OD g of pulp where weighed and transferred into the crucibles (forming a 1400 g/m^2 pad), with the assistance of a vacuum to ensure a neat pulp pad at the bottom of the crucible. The crucibles were then placed in the centrifuge for 30 min and 2500 rpm's (900 G's). After the centrifugation the crucibles and pulp were weighed and placed in an oven at 105ºC for drying. Once dried, they were weighed again in order to determine the weight of the dry pulp.

The viscosity of the pulps were determined using TAPPI Standard T230, with the exception that no nitrogen purge was used. Since this method is only valid for lignin amounts below 4%, the pulps with kappa 35 were not tested.

In order to do paper testing, handsheets were prepared accordingly to TAPPI Standard T205. Only non-extracted pulps (control pulps) and 120 minutes extracted pulps (for all kappa levels) were used for paper testing. TAPPI Standards were followed for every property tested.

RESULTS AND DISCUSSION

As we can see in Table 1 as extraction takes place, the amount of hemicelluloses remaining in the fibers after each cook is progressively smaller. This is a consequence of the wood composition after extraction, where the hemicellulose decreases from approximately 26% to 12%. Also, the extent by

which they are removed becomes smaller as extraction carries on. In fact, the difference in xylan content from the 90 min extracted pulp to the 120 min is less than 0.5%. For the control pulp, xylan accounts for 20 to 22% of the pulp's composition and it decreases to 3 – 4% (after 120 min). This necessarily implies that the fraction of other components must increase, and since all the pulps were cooked to the same kappa level (± 1.7) the lignin content is fairly constant. Therefore it is mostly the amount of cellulose that increases with the decrease of the xylan content. It is also worth mentioning that the fraction of other hemicelluloses is virtually insignificant, never surpassing 0.5%. Another interesting aspect is that the amount of unquantifiable material increases with extraction time. Indeed, for the control pulp, a closure of at least 98.3% is achieved, whereas for the extracted pulps the worse closure is of 94.6%. This must mean that as the extraction takes place, there is chemical degradation of the material into components that are not being analyzed. However, the amounts of other materials tend to diminish as the cook progresses.

Table 1 – Pulp's composition for all extraction levels and kappa numbers.

	Components (%)														
	Cellulose			Xylan			Other Hemicellulose			Lignin			Other*		
Kappa / Time (min)	15	25	35	15	25	35	15	25	35	15	25	35	15	25	35
0	74.8	73.0	73.6	20.7	21.4	22.0	0.4	0.2	0.4	2.4	4.1	5.5	1.7	1.3	-
30	87.4	88.5	86.1	8.4	9.3	8.6	0.2	0.1	0.2	2.3	3.7	4.9	1.7	-	0.3
60	89.9	91.5	88.8	4.4	4.4	5.7	0.2	0.3	0.1	2.6	3.6	5.3	2.9	0.2	0.1
90	89.9	87.1	88.4	3.6	3.2	3.4	0.2	0.3	0.5	2.1	4.0	5.1	4.0	5.4	2.6
120	89.9	87.0	85.1	3.1	3.6	3.8	0.2	0.5	0.3	2.2	4.0	5.5	4.6	4.9	5.3

* Calculated by difference. – indicates sum over 100%

Regarding fiber length (Figure 1 A), all pulps show the same behavior, i.e., as extraction takes place, the average fiber length decreases approximately 10, 11 and 15% with increasing kappa. This is in accordance with the trend noticed by Santos et al [12]. Another interesting observation is that at 120 min extraction there is no difference between fiber lengths, whereas for 0 min the fiber length decreases with decreasing kappa (more extended cook), as expected. This is due to the fact that as extraction takes place the fibers become more exposed to the white liquor and therefore what did not harm the fibers at kappa 35 now does. The decrease in fiber length may also be responsible for the decrease in paper strength as discussed later.

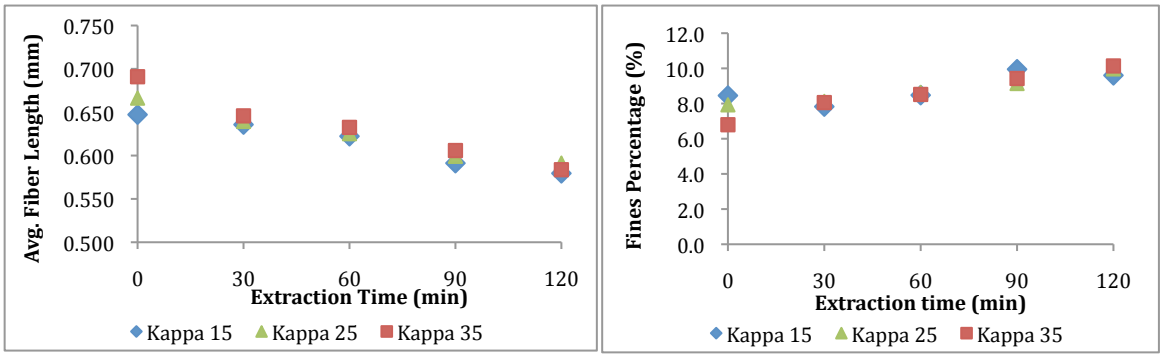

Figure 1 – Eucalyptus' average fiber length and fines percentage versus extraction time, for 3 different kappa numbers.

The amount of fines behaves similarly, with no significant difference between kappa numbers at 120 min extraction, and a higher fine content for lower kappa, at 0 min. The amount of fines increases with increasing extraction, which is also in accordance with Santos et al [12]. There is an increase from the control to the 120 min extracted pulp of 114, 126 and 149%, for kappa numbers 15, 25 and 35 respectively. A possible explanation is that as extraction progresses the fiber length decrease (due to higher exposure to the white liquor), giving rise to the production of fines. Another interesting piece of information is the evolution of the Kink Index with extraction time. As it can be observed in Figure

2, as the extraction takes place, the Kink Index hugely increases (269%). This can be one of the reasons why other authors are observing that these fibers do not refine properly [12].

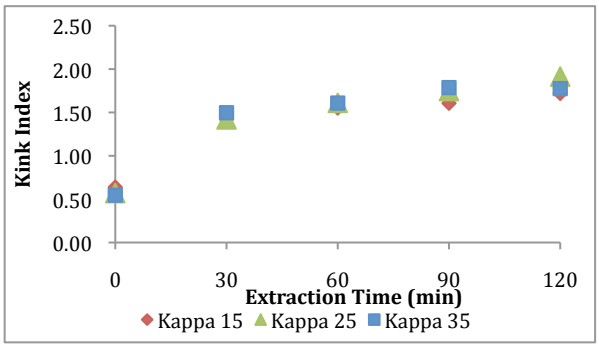

Figure 2 – Effect of Extraction Time on the Kink Index of the Eucalyptus' fibers for all kappa levels.

The zeta potential of the pulps does not show any significant differences between extraction levels and kappa numbers (Figure 3). This was not initially expected but it is in agreement with the results obtained by Sousa et al [8]. It seems that in the ranges studied – lignin content between 2.2 and 5.5% (kappa 15 and 35 respectively) and xylan/cellulose content of 22/73% to 3/90% (control and 120 min respectively), the electrochemical (charge) nature of the fines must be similar in all these pulps. Even though there is a great difference in hemicellulose content, the total polysaccharide fraction remains in the range of 90 to 96%.

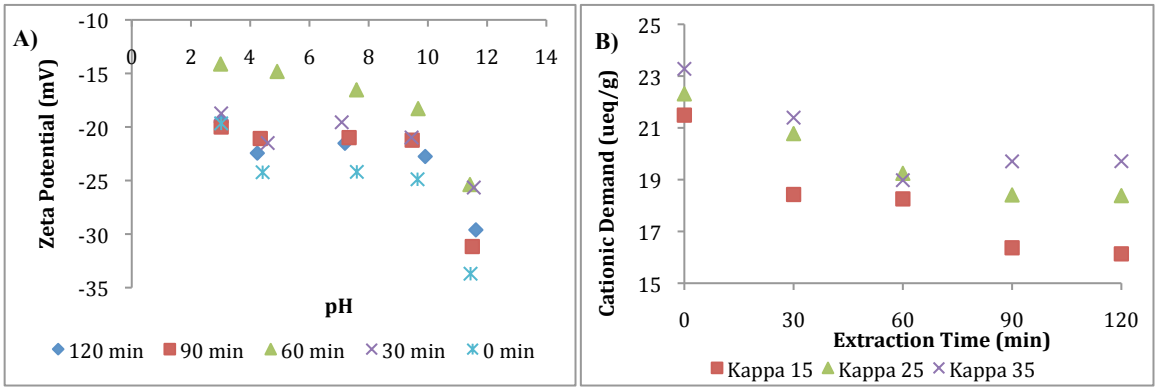

Figure 3 – Zeta Potential (A) and Cationic Demand (B) versus pH.

The cationic demand of the pulps decreases significantly with extraction, which is expected since there is a decrease in the xylan content, which contributes to the total amount of charged groups in the pulp. However, unlike zeta potential, the total charge determination was done using the full furnish, i.e., not just the fine fraction, but also the fibers. Another difference is that the total charge is dependent on the surface area and therefore the fine content and fiber length play an important role in the cationic demand of the pulps. The increase of fines with extraction (see Figure 1), should contribute to an increase of the cationic demand of the pulp. However, the decrease in the cationic demand due to the chemical composition is more significant than the increase of the surface area.

As for the influence of lignin, there is almost a 20% drop at 120 min opposed to 8% for 0 min, which suggests one of two things: either the lignin is altered with extraction (and therefore the same lignin difference in the pulp corresponds to different change in cationic demand) or the removal of hemicellulose makes the contribution of lignin more important for the cationic demand.

As seen in Figure 4, the eucalyptus' pulp viscosity initially increases greatly with extraction (up to 160%), starting to decrease after the 30 min mark. However, even after the 120 min extraction, the viscosity is still 28 to 30% higher (for kappa 25 and 15 respectively) than the control viscosity. Santos et al [12] noticed an increase in viscosity from 950 to 1320 cm^3/g when the hemicellulose content decreased from 19 to 8.5%. In terms of composition these pulps are similar to the control and 30 min extracted pulps at kappa 15. These pulps have viscosities of 1247 and 1443 cm^3/g and therefore are in good agreement with the previously reported values. It is conceivable that with only 30 min extraction the accessibility of the cooking liquor to the chips is increased and the cook (to a given kappa) is

much easier, and therefore gentler to the fiber. As the extraction continues, the accessibility of the liquor to the fibers may be too good therefore harming the fiber. It is possible that for these extraction levels the cooking liquor should be weaker. The increase of the viscosity may be interpreted in two ways, either by the increase of the degree of polymerization (DP) of the pulp (less degraded pulp) or by the removal of the fraction with the lowest degree of polymerization (hemicelluloses). If it was only the latter, than the increase in viscosity could not be more than 27%, which corresponds to the total removal of hemicellulose from the control pulp, (using Eq. 1 - maximum increase possible due to the removal of hemicellulose, with hemicellulose fraction of extracted set to zero). Since the increase is always higher than 27%, this necessarily implies that the degree of polymerization increased. Indeed, at 120 min the removal of hemicellulose alone would explain at best an increase in viscosity of 21.6% and at 30 min it would account for 14.3% increase, not the observed values of 30 and 60% respectively (see Table 2). As seen in Table 2 the increase in the viscosity due to the increase of the DP becomes smaller as extraction takes place, meaning that the fiber are more affected by the chemicals. This is well supported by the decrease in fiber length and increase in fines for these pulps.

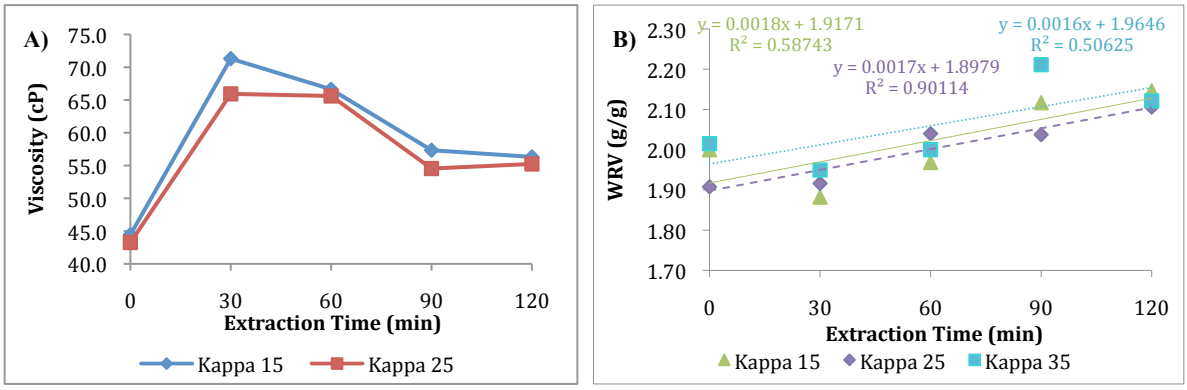

Figure 4 – Effect of Extraction Time in the Eucalyptus Pulp Viscosity (A) and WRV (B).

The WRV (Figure 4) for all the pulps increases with extraction time, unlike what was reported by other authors [12]. This is also an unexpected result, since as extraction takes place more and more xylan is being removed which is a highly hydrophilic component of fibers. On the other hand, the increase of fines content and the increase in porosity could be responsible for the increase in the WRV. The Canadian Standard Freeness (CSF) decreases with extraction, which is in accordance with the behavior of the WRV.

$$\frac{1}{1-\left(hemi_{control}-hemi_{extracted}\right)}\times 100 \qquad (1)$$

Table 2 – Eucalyptus Pulps' viscosity increase – real and maximum expected due to hemicellulose removal.

Extraction Time (min)	Max. Increase due to Hemicellulose removal (%)	Viscosity Real Increase (%)	Increase Difference (%)
120	22	28-30	6-8
90	22	26-29	4-7
60	21	50-52	29-31
30	14	52-60	38-46

From Figure 5 A) it is clear that there is an initial increase in the pulp's porosity, reaching a maximum at 30 min after which, the porosity starts to decrease. For kappa numbers 25 and 35 the same is evident for the pore size, whereas for kappa 15 it does not seem to be affected by the extension of the extraction, which can be due to the fact that at this kappa level, the fibers are collapsed. The "absolute" density of kappa 15 pulps' seems to increase with extraction, however this variation is two minute to state it as real. Therefore, statistically speaking, there does not seem to be a change in the density of these pulps for any given kappa.

The paper properties of the highest extracted pulp (120 min) were compared with the properties of the control pulps for all kappa levels. Figure 6 shows the significant decrease in the tensile index (A)

when the eucalyptus pulp is extracted for 120 minutes. This decrease (55-61%) is in accordance with the results obtained by other authors [12]. As the lignin content of the pulps increases (higher kappa number) the tensile index decreases in a similar fashion, although curiously the extracted pulp loses less tensile index (15%) over the kappa range than the control (19%), as evidenced by the slope of the linear regression.

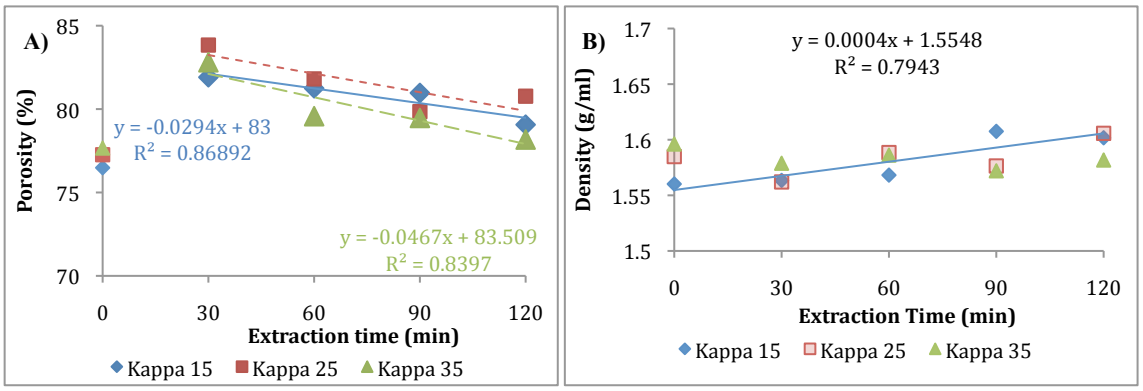

Figure 5 – Effect of Extraction Time in Eucalyptus Pulp's Porosity (A) and Density (B) for all kappa numbers

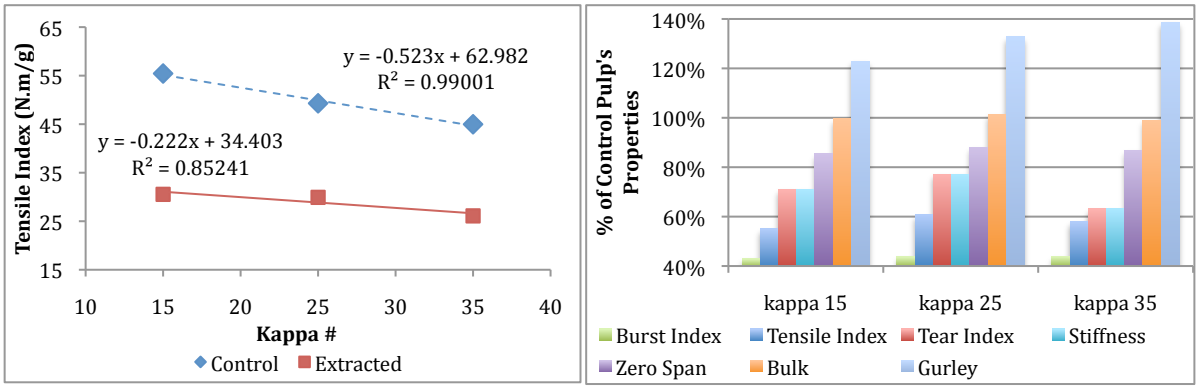

Figure 6 – Effect of Extraction and Kappa in the Tensile Index and remaining properties of Eucalyptus Papers.

Figure 6 B) shows the properties of the extracted pulp as a percentage of the control pulps' properties (extracted pulp was compared with the control at the same kappa). It is evident from this graph that the extracted pulp has weaker properties. The only exceptions are bulk and air resistance. The first remains unaffected, which makes perfect sense since the apparent density of the fibers is unaffected. The second one actually increases and it can be attributed to the increase in fines (Figure 1). However that does not explain the apparent decrease in air resistance's gain with kappa, as the fines content does not varies with kappa. Gurley's absolute value decreases with kappa, as expected.

CONCLUSIONS

It is clear that HWE has a serious affect in several pulp properties and consequently in the paper produced from these pulps. The first and most important parameter that is affect is the pulp composition. As extraction takes place, hemicelluloses are preferentially removed, dropping from 21-22% in the control to 3-4% in the highest extraction level. These differences in composition are very significant and can be responsible for the observed differences in the mechanical properties of the paper, WRV, viscosity and morpholigical properties. In what concerns hemicellulose removal, there is no significant difference in extracting 90 or 120 min, and therefore there is no obvious advantage in extracting eucalyptus pulps for more than 90 min.

The HWE does not seem to have any significant effect on the zeta potential of the pulps. However, the cationic demand of the pulps is, significantly affected by the extraction. The longer the extraction, the lower the cationic demand, which is in accordance with the decrease of hemicellulose content but not the increase of specific surface area (fines and porosity).

The viscosity of the pulps increases and exhibits a maximum at 30 min extraction. Despite the maximum, the 2 hours extraction viscosity is still significantly greater than the control. The existence of a maximum in viscosity suggests that the cook might be too harsh for the higher extraction levels. Therefore reducing the chemical used at higher extracting levels may be recommended. It was also evident that the increase of the viscosity is due to two factors – the removal of the lower degree of polymerization fraction (hemicelluloses) and the increase of the degree of polymerization of cellulose.

The results regarding the WRV are somewhat unexpected. The removal of hemicellulose was expected to decrease the WRV, however, the increase in porosity and fines must have overcame the effect that the removal of hemicellulose should have had.

As for the paper properties, there is a general decrease in the paper properties with the exception of Gurley and Bulk. Therefore, papers produced from these pulps will exhibit weaker properties, unless something is done to compensate the lack of hemicelluloses.

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