

BROWN IS THE NEW GREEN: HIGH CHARGED PULPS FOR TISSUE

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SUMMARY

The present work intended to compare commercial fully bleached pulp for tissue application with high kappa number pulps from oxygen delignification. The goal was to maximize the total fiber charge of the unbleached pulps through oxidation reactions leading to a higher absorption capacity. Single extended oxygen delignification and double stage oxygen delignification were carried out in a softwood kraft cooked pulp. The water retention values and the Schopper-Riegler degrees were significantly higher for the oxygen delignified pulp than for the commercial fully bleached pulp. The higher total fiber charge content obtained from oxygen delignification led to an increase in fiber swelling. The absorption capacity of the evaluated pulps was similar. Unbleached oxygen delignified pulps presented a slightly higher liquid capillarity rate and higher wet tensile strength compared to the commercial bleached pulp.

Keywords: Absorbency, fiber charges, high lignin content, oxygen delignification, swelling.

INTRODUCTION

Tissue products have a great consumption these days which is expected to quickly increase even more in the future. This increase in consumption can lead to some environmental issues. The typical tissue products used nowadays are usually produced from fully bleached fibers to obtain particular properties, such as high softness, high liquid absorption and high brightness [1-3]. The fully bleached fibers are obtained from virgin fibers and they required several delignification and bleaching steps to remove lignin. The typical bleaching processes have a significant environmental footprint, due to the energy and chemicals required and therefore they should be reduced or avoided [4]. Fully bleached products have been preferred, however, consumer awareness for sustainability is becoming more and more important leading to an increase in the preference of products with lower environmental impact, such as unbleached or recycled products. Unbleached fibers are one of the possible candidates to improve sustainability of the tissue products since they have a much lower carbon footprint when compared to fully bleached fibers.

To provide a good water absorption capacity to unbleached fibers, oxygen delignification showed to be an interesting choice. Oxygen delignification is a greener alternative that can contribute to better sustainability and also to interesting pulp properties [5, 6]. The oxidation reactions occurring in the delignification lead to an increase in the carboxylic acid groups in the fibers, increasing their swellability [7, 8]. The increase in fiber swellability can be increased even more when oxygen delignification is performed in pulps with high lignin content [9].

Depending on the intended use, the properties of the tissue products can vary significantly. While toilet or facial paper requires a high softness, for towel papers the absorption capacity and the wet strength are probably more important [10]. The present work intends to evaluate how unbleached fibers with high lignin content can be used in tissue products as a greener alternative to fully bleached fibers, without losing their properties, especially water absorption properties.

EXPERIMENTAL

Materials

A mixture of industrial softwood chips (spruce and pine) was kraft cooked and further delignified with extended oxygen delignification. A fully bleached pulp was also used for the pulp and paper properties comparison.

Kraft cooking

The trials were carried out in a recirculated digester of 2kg capacity with an effective alkali (EA) of 21 % and 30 % sulfidity. The ionic strength was adjusted to 0.1 M with sodium carbonate and the liquor/wood ratio was 4.5 l/kg.

The chips were impregnated with water under a pressure of 5 bars of nitrogen overnight. Subsequently, the water was removed and weighed to have the right amount of liquor added to the cooking step. The impregnation temperature was 100 °C and the cooking temperature was 160 °C.

After the cooking step, the steam flow that was used to control the temperature in the digester was stopped and the spent liquor was drained off the chips and collected for analysis. The delignified chips were washed in deionized water for 10 h in self-emptying metal cylinders and subsequently defibrated and screened in a NAF water jet defibrator (Nordiska Armaturfabriken). The rejects were collected, dried at 105 °C, and weighed.

Oxygen delignification

The trials were carried out in pressurized teflon-coated stainless-steel autoclaves, with 60 g o. d. of pulp and the correct amounts of NaOH, MgSO₄ and water, resulting in a pulp consistency of 12 %. The autoclaves were then pressurized with oxygen and placed in an electrical-heated glycol bath, with rotation and slight inclination. After the trials, the pulps were washed with de-ionized water and filtrated. The oxygen delignification was performed with extended single stage or double oxygen stages with no washing in between. The conditions for each trial are shown in Fig. 1.

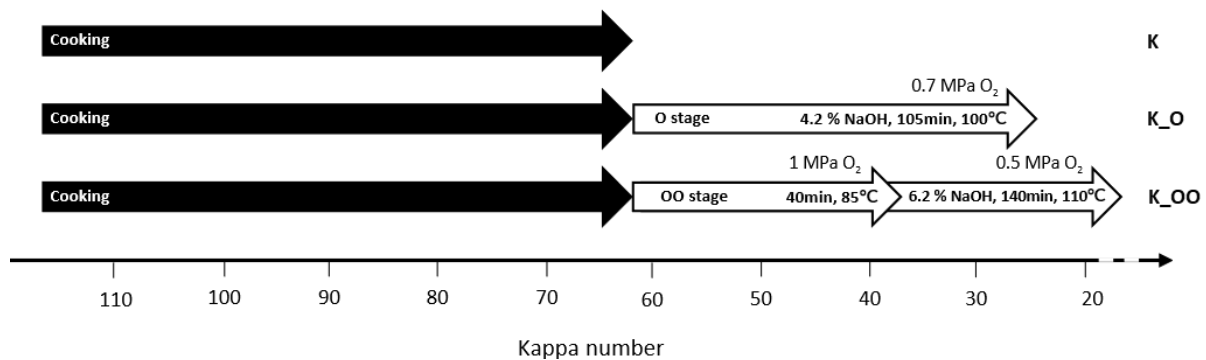


Figure 1. Illustration of the methodology and conditions used for the oxygen delignification trials. The pulps are denominated KX_OY, where X is the kappa number of kraft cooked pulp and Y is the kappa number of oxygen delignified pulp. The oxygen delignification conditions are described in the figure.

Pulp refining and handsheet preparation

Refining was performed in a PFI-mill in accordance with ISO 5264-2. The pulps were beaten with two different degrees (2000, 4000 rpm). The tissue hand sheets were prepared with a grammage of 20 g/m² according to ISO 5269-1 but without pressing. No embossing was performed and the tissue handsheets were conditioned according to ISO 187.

Pulp characterization

Table 1 presents the standards used for the pulp properties and tissue handsheets characterization. All the tests for the pulp characterization were performed in duplicate.

Table 1. Standards used for the pulp and tissue handsheets characterization.

Test	Standard
Kappa number	ISO 302:2015
Water retention value	SCAN-C 62:00
Schopper-Riegler degree	ISO 5267-1
Total fiber charge	SCAN-CM 65:02
Grammage	ISO-12625-6:2017
Thickness and bulk	ISO-12625-3:2014
Basket immersion test	ISO-12625-8:2011
Klemm method	ISO-8787:2022 *

* instead of 10 min the tests were performed with 5min only.

RESULTS AND DISCUSSION

Pulps with high kappa numbers obtained from extended oxygen delignification were compared to a commercial fully bleached pulp typically used for tissue applications. The aim was to investigate if unbleached fibers with highly charged content can be suitable to replace fully bleached pulps used for tissue products. Two oxygen delignified pulps were evaluated by different absorption assessments and compared to a commercial fully bleached pulp.

Table 2 shows the lignin and charge content for the different pulps obtained after kraft cooking and oxygen delignification, as well as the fully bleached reference pulp.

Table 2. Lignin and charge content of the studied pulps.

Pulp samples	Kappa number	Total fiber charge (meq/kg)
K	61	116
K_O	25	145
K_OO	18	131
Commercial fully bleached pulp (REF)	1	55

The oxygen delignification was performed in a single or double stage to maximize the increase in total fiber charge. As also seen in previous studies, the oxygen delignified pulps obtained the highest total charge content (145 and 131 meq/kg) and the fully bleached pulp had the lowest (55 meq/kg). It has been shown that the swelling of the fibers and the total charge content are extremely related [11]. Figure 2 shows the water retention value and the Schopper-Riegler degree for the studied pulps. The higher swellability for the unbleached pulps is clear when compared to the commercial bleached pulp, since the total fiber charge is higher. For the Schopper-Riegler degree, the unbleached pulps presented lower drainability since there is a higher water affinity and also due to higher fibrillation obtained after refining, as it was proposed by Esteves [6].

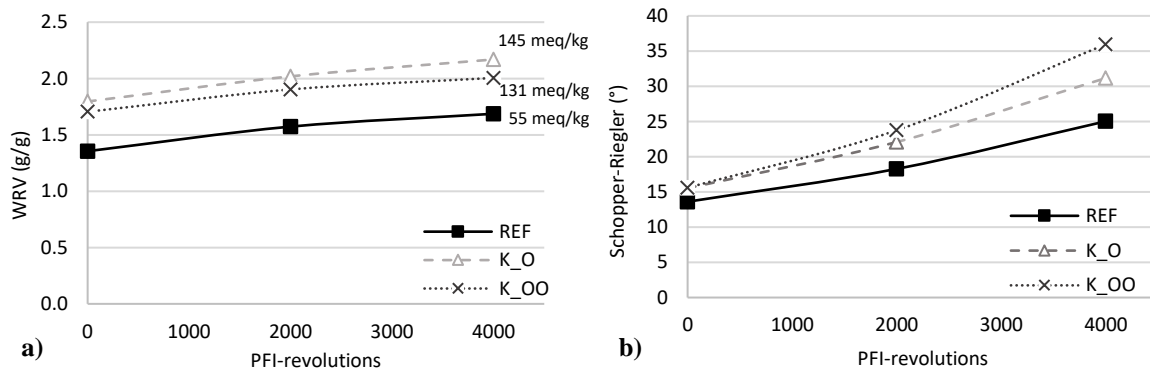


Figure 2. a) Water retention value and b) Schopper-Riegler degree as a function of PFI refining for commercial fully bleached pulp (REF) and oxygen delignified pulps (K_O and K_OO). The total fiber charge is given on the right side of the graph.

Absorbency properties are crucial to be evaluated in tissue papers since one of the main required properties is their ability to absorb and retain liquids. Figure 3a shows the absorption capacity (how much liquid the paper structure can hold) of the unbleached and bleached pulps. The results show that unbleached pulps can achieve similar values of water absorption capacity than commercial pulp. In fact, the unrefined oxygen delignified pulp (K_OO) can have a slightly higher water absorption with higher bulk. This is probably the higher lignin content in the unbleached pulps that can lead to lower fiber conformability, resulting in bulkier paper with high absorption. However, when refining is applied, the bulk values for unbleached and bleached pulps become similar, losing their potential to replace bleached pulps.

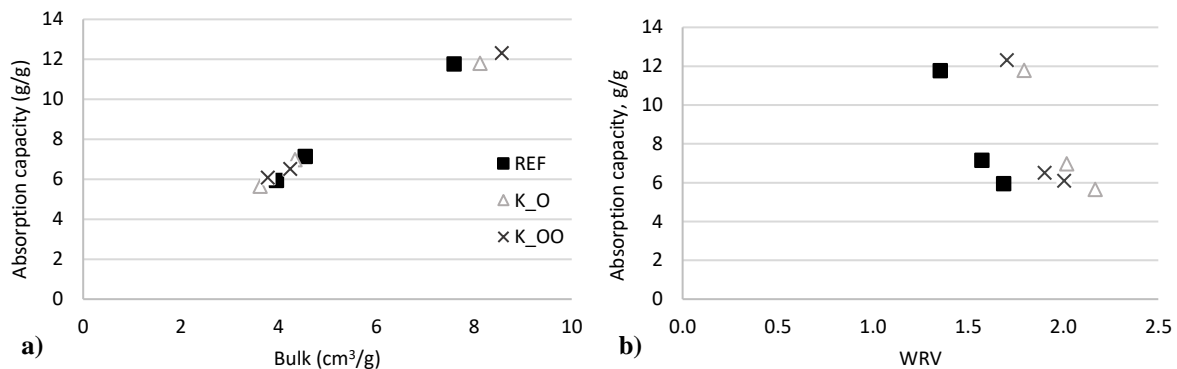


Figure 3. Absorption capacity as a function of a) bulk and b) water retention value for commercial fully bleached pulp (REF) and oxygen delignified pulps (K_O and K_OO).

Is interesting to point out that after refining, even though fibers tend to hold more water as seen with WRV (Fig. 2), the absorption capacity in the paper structure is reduced as shown in Fig. 3b. The water absorption capacity is not dependent on the water retention values obtained in the pulp. This suggests that the water absorbed during the basket method is placed within the spaces in the paper structure instead of the internal structure of the fibers.

Klemm capillary rise method is an additional way to evaluate the absorption properties of the tissue products. Figure 4 shows the different capillary rising obtained from the unbleached and bleached pulps. The Klemm capillary rise method provides information on the absorption rate of the different pulps, which is affected among others by the paper porosity. The higher the capillary pressure in the paper network the higher should be the rising of the liquid in the paper strip [12].

It was seen a slightly higher water rising for the unrefined unbleached pulps than for the bleached pulp, however, when refining is applied the commercial bleached pulp shows a higher capillary rise and

overall the water rising is decreased.

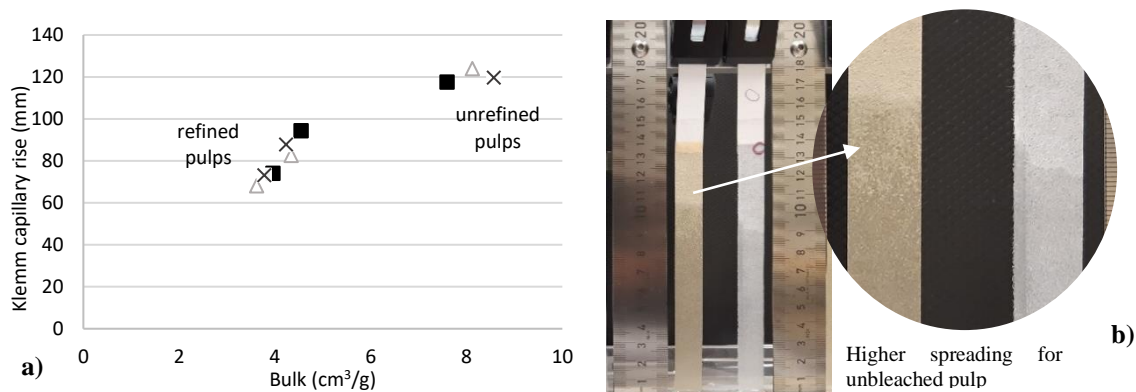


Figure 4. a) Klemm capillary rise as a function of bulk for commercial fully bleached pulp (REF) and oxygen delignified pulps (K_O and K_OO). b) Example of tissue strips with no refining, after the Klemm test.

Unbleached pulps also presented a faster absorption rate than fully bleached pulp when no refining was applied. Besides the higher capillarity rate seen, unbleached pulps showed a higher liquid spreading area when compared to the commercial bleached pulp (Fig. 4b), allowing the liquid to spread in a bigger area instead of being condensed in one place. The spreading behavior is another important property to consider for tissue products.

Figure 5 shows the wet tensile index for unbleached and bleached pulps. The wet tensile for the unrefined commercial fully bleached pulp was not possible to measure due to the lower strength. The commercial bleached pulp did not present an increase in the wet tensile strength with the increase in the refining degree. The unbleached pulps, on the other hand, had an almost linear increase of the wet tensile strength with the refining, obtaining between 200 and 400% higher wet tensile than fully bleached pulp.

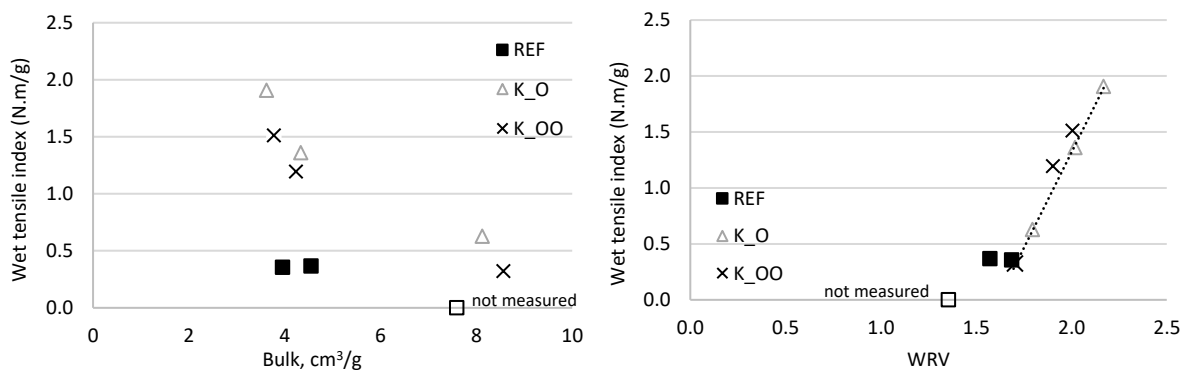


Figure 5. Wet tensile index as a function of a) bulk and b) WRV for commercial fully bleached pulp (REF) and oxygen delignified pulps (K_O and K_OO). The unfilled square means that was not possible to measure the wet tensile index for unrefined pulp.

In Figure 5b the dependency of the fiber swelling with the paper strength is only clear for the unbleached pulps. The increase in fiber fibrillation and fiber bonding that is expected from refining, seems to vanish when the paper is wetted for the fully bleached pulps. It is important to mention that no strength additives were used in this study.

The unrefined unbleached pulps presented the wet tensile strength in the same range as the commercial fully bleached pulp when they were refined with 2000 and 4000 revolutions, with much higher bulk.

The higher wet strength seen for the unbleached pulps shows a great potential for towel papers for example, where they can still have a high absorption capacity and have a higher strength.

CONCLUSIONS

Oxygen delignified pulps presented a great potential to replace fully bleached pulps typically used for tissue application. The oxygen delignified pulps obtained a higher total fiber charge than the commercial bleached pulp which provided a greater swellability of the fibers. The absorbency results were very similar for both unbleached and fully bleached pulps, especially for unrefined pulps. For the water capillary rising, a higher spreading was achieved for unbleached pulps when compared to the reference pulp. The wet tensile strength was found to be much higher for the unbleached pulps than for the fully bleached pulp. The similar absorption values, higher liquid spreading and higher wet strength make the unbleached pulps a greener replacement for some of the tissue papers used nowadays.

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REFERENCES

1. S. M. Rebola, C. A. Azevedo, and D. V. Evtuguin, Effect of cooking and bleaching conditions on the properties of eucalyptus kraft fluff pulps. *Cellulose*. 28(7): p. 4411-4426 (2021).
2. P. D. Beuther, M. W. Veith, and K. J. Zwick, Characterization of absorbent flow rate in towel and tissue. *J. Eng. Fiber Fabr.* 5(2): p. 155892501000500201 (2010).
3. M. Fišerová, J. Gigac, M. Stankovska, and E. Opalena, Influence of bleached softwood and hardwood kraft pulps on tissue paper properties. *Cell. Chem. Technol.* 53(5-6): p. 469-477 (2019).
4. D. W. Reeve, Introduction to the principles and practice of pulp bleaching, in *Pulp bleaching - Principles and practice*, W.D. Carlton and D.W. Reeve, Editors. 1996, Tappi: Atlanta, Georgia. p. 3-24.
5. T. J. McDonough. Oxygen delignification. in *TAPPI Bleach Plant Operations Seminar Charleston*. 1989.
6. C. V. Esteves, E. Brännvall, S. Östlund, and O. Sevastyanova, The effects of high alkali impregnation and oxygen delignification of softwood kraft pulps on the yield and mechanical properties. *Nord. Pulp Pap. Res. J.* 37(2): p. 223-231 (2022).
7. D. Zhang, X.-S. Chai, Q. Hou, and A. Ragauskas, Characterization of fiber carboxylic acid development during one-stage oxygen delignification. *Ind. Eng. Chem. Res.* 44(24): p. 9279-9285 (2005).
8. C. V. Esteves, Pulp strength enhancement by oxygen delignification, in *Fiber and Polymer Technology 2022*, KTH Royal Institute of Technology: Stockholm.
9. J. Mai, Development of pulp fiber charge in oxygen delignification of softwood, in *Fiber and polymer technology 2021*, KTH: Stockholm.
10. J. J. Kim, I. Shalev, and R. L. Barker, Softness properties of paper towels. *Tappi J.* 77(10): p. 83-89 (1994).
11. C. V. Esteves, O. Sevastyanova, S. Östlund, and E. Brännvall, Differences and similarities between kraft and oxygen delignification of softwood fibers: effects on chemical and physical properties. *Cellulose*. 28(5): p. 3149-3167 (2021).
12. T. De Assis, L. W. Reisinger, L. Pal, J. Pawlak, H. Jameel, and R. W. Gonzalez, Understanding the effect of machine technology and cellulosic fibers on tissue properties—A review. *BioResources*. 13(2): p. 4593-4629 (2018).