Unbleached fibers as a more sustainable replacement for tissue bleached fibers

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Summary

This report presents results from the granted application from ÅForsk Foundation n.24-290. That project aimed to evaluate how much PAE could be decreased in oxygen delignified pulps due to their intrinsic high wet strength, compared to the fully bleached pulps.

Oxygen delignification has been showing several benefits to pulp properties and process sustainability. In a previous project, it was concluded that oxygen delignified pulps achieved similar absorption properties as the fully bleached pulps, but with a much higher wet tensile index. Understanding and investigating the potential of oxygen delignification even further was essential. The project aimed to compare how much wet strength resins could be reduced when used on oxygen delignified fibers compared to fully bleached fibers. Decreasing the requirement of PAE dosage on the oxygen delignified pulps will contribute to an increased sustainability in the tissue process, if the fully bleached fibers are replaced.

Keywords: < less chemicals, oxygen delignification, sustainability, wet strength resins >

RISE Research Institutes of Sweden

Contents

Preface

This report contains the results from the funding obtained from Åforsk foundation.

The author wishes to acknowledge the following colleagues for their contributions to the success of this project:

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- Åsa Blademo, RISE AB

1 Introduction

Previous research concluded that extended oxygen delignification significantly improved both wet and dry strength of pulps compared to commercially available fully bleached pulps. These pulps also demonstrated comparable absorption capacity and softness, indicating their potential to enhance the sustainability of tissue products by reducing energy consumption in both delignification and bleaching stages (Esteves 2024).

With support from the Åforsk grant, we further investigated how oxygen delignified pulps with higher intrinsic wet strength interact with PAE resin incorporation. The project showed that PAE dosage could be reduced by up to five times in oxygen delignified pulps while still achieving the same wet tensile strength as fully bleached pulps.

Project goal

The purpose of this project was to obtain tissue lab handsheets with high wet-strength index and reduced wet strength additives incorporation (such as PAE), leading to better process sustainability.

2 Material and methods

2.1 Raw material

Softwood wood chips and softwood fully bleached fibers, from the same mill, were used in this study.

The Kraft cooking and the oxygen delignification were performed in the laboratory, while the fully bleached pulp was produced industrially.

2.2 Chemicals

A commercial wet-strength resin, polyamidoamine epichlorohydrin (PAE), was kindly provided by Kemira, while a commercial cationic additive, carboxymethyl cellulose (CMC), was supplied by Nouryon for use in the fiber treatment experiments.

2.3 Methodology

Four oxygen delignified pulps, one cooked pulp and one commercial fully bleached pulp were compared - Figure 1.

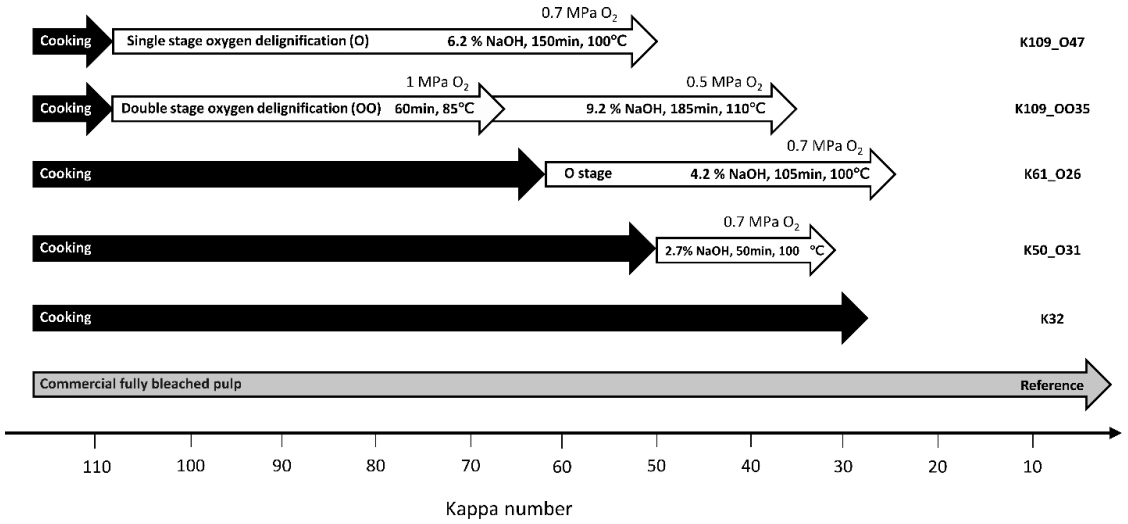

Figure 1: Schematic representation of the kraft cooking and oxygen delignification trials that were performed. Black arrows indicate the progression of kraft cooking, while white arrows represent oxygen delignification stages – the single white arrows represent the single oxygen stage, and overlapping white arrows denote a double oxygen stage. The samples are denominated KX_OY, where X is the kappa number of the cooked pulp and Y the kappa number after oxygen delignification.

2.4 Refining and handsheet preparation

The pulp samples were refined at two intensity levels—500 and 1000 revolutions—using a PFI mill in accordance with ISO 5264-2. Isotropic tissue handsheets were then prepared using deionized water, following ISO 5269-1, to a target grammage of 20 g/m² without any pressing. Sheets were dried under restraint at 23 ºC, 50% RH. Prior to mechanical testing, the handsheets were cured at 105 °C for 15 minutes to ensure proper resin activation and sheet stabilization.

2.5 PAE and CMC incorporation

The pH of the pulp was measured and, if needed, adjusted to 6-8 and the conductivity to 1 mS/cm. When only PAE was used, it was mixed with the pulp suspension for 5 minutes before sheet formation. In cases where both PAE and CMC were applied, CMC was added first and mixed for 5 minutes, followed by the addition of PAE and an additional 5 minutes of mixing. The resulting suspension was then transferred to the sheet former and formed into tissue hand-sheets. Table 1 shows the different dosages used for the PAE and PAE/CMC.

Table 1: PAE and CMC dosages for the different evaluated pulps.

Samples	PAE dosage, weight%				PAE + CMC dosage, weight%	
REF	-	-	0.25	0.5	0.25 + 0.05	0.6 + 0.12
Kraft	-	0.1	0.25	-	0.25 + 0.05	-
K50_O31	-	0.1	0.25	-	-	-
K61_O26	-	0.1	0.25	-	0.25 + 0.05	-
K109_O47	0.05	0.1	0.25	-	0.1 + 0.05	-
K109_OO35	0.05	0.1	-	-	-	-

2.6 Analysis

Table 2 and present the different pulp and paper characterization standards.

Table 2: Standards used for the characterization

Methods	Standards
Kappa number	ISO 302:2004
Water retention value (WRV)	SCAN-C 62:00
Total fiber charge	SCAN-CM 65:02 (Katz et al. (1984))
Schopper-Riegler degree	ISO 5267-1
BDDJ	SCAN-CM 66:05
Fiber morphology*	ISO 16065-2
Grammage	ISO-12625-6:2017
Thickness and bulk	ISO-12625-3:2014
Dry and wet tensile strength	ISO 12625-5:2017

*performed in the FiberTester plus (L&W)

The adsorption was evaluated through streaming potential titration measurements using CAS-II touch, AFG analytics. Pulp samples treated with PAE were filtered and centrifuged to remove all fibres and colloidal fine material. The supernatant was titrated using standard pDADMAC and PVS solutions with known charge density. The increase in cationicity of supernatant samples was used to evaluate the presence of unabsorbed PAE.

3 Results and discussion

The two pulps cooked specifically for this project are presented in Table 3. The other two pulps that were used just for comparison were previously cooked for other purposes.

Table 3: Summary of the kraft cooking and oxygen delignification trials. Cooking temperature was 160 °C, sulfidity 30 %, effective alkali 21 % and liquor-to-wood ratio 4.5 l/kg. For the single oxygen trials the pressure was 0.7 MPa and 100 °C of temperature, while for the double oxygen trials the pressure was 1 MPa and 85 °C of temperature for the first stage and 0.5 MPa and 100 °C for the second stage.

Samples	*H factor*	*-*	*Kappa no.*	*Total yield (cooking stage) (%)*	*Residual alkali (g/l)*	*Fiber charges, meq/kg*
K32	1150	-	32	47.0	8.5	90
K50	780		50	49.4	8.5	124
K61	720	-	61	52.5	12.2	116
K109	420	-	109	54.8	14.5	146
Samples	*Time, min*	*Alkali charge, %*	*Kappa no.*	*Total yield (oxygen stage)(%)*	*End pH*	*Fiber charges, meq/kg*
SK50_O31	50	2.7	30.6	98.0%	11.9	148
SK61_O26	105	4.2	24.5	92.9%	10.3	143
SK109_O47	150	6.2	47.4	90.1%	10.8	159
SK109_OO35	60 / 185	9.2	35.2	89.9%	10.3	130

The pulp with the highest kappa number (K109) was defibrated in a Sprout Waldron refiner before the oxygen delignification.

3.1 Pulp properties

Water retention values, Schopper-Riegler (SR) degree, and fines content were evaluated, as shown in Figure 2. As anticipated, the oxygen-delignified pulps demonstrated the highest water retention and SR values compared to the commercial fully bleached pulp. Upon refining, the pulps with the highest kappa number from the cooking process (K109) exhibited a more significant increase in SR values. Regarding fines content, the results showed considerable variability, particularly for the K109 pulp, which was probably caused by the defibration in the Sprout Waldron.

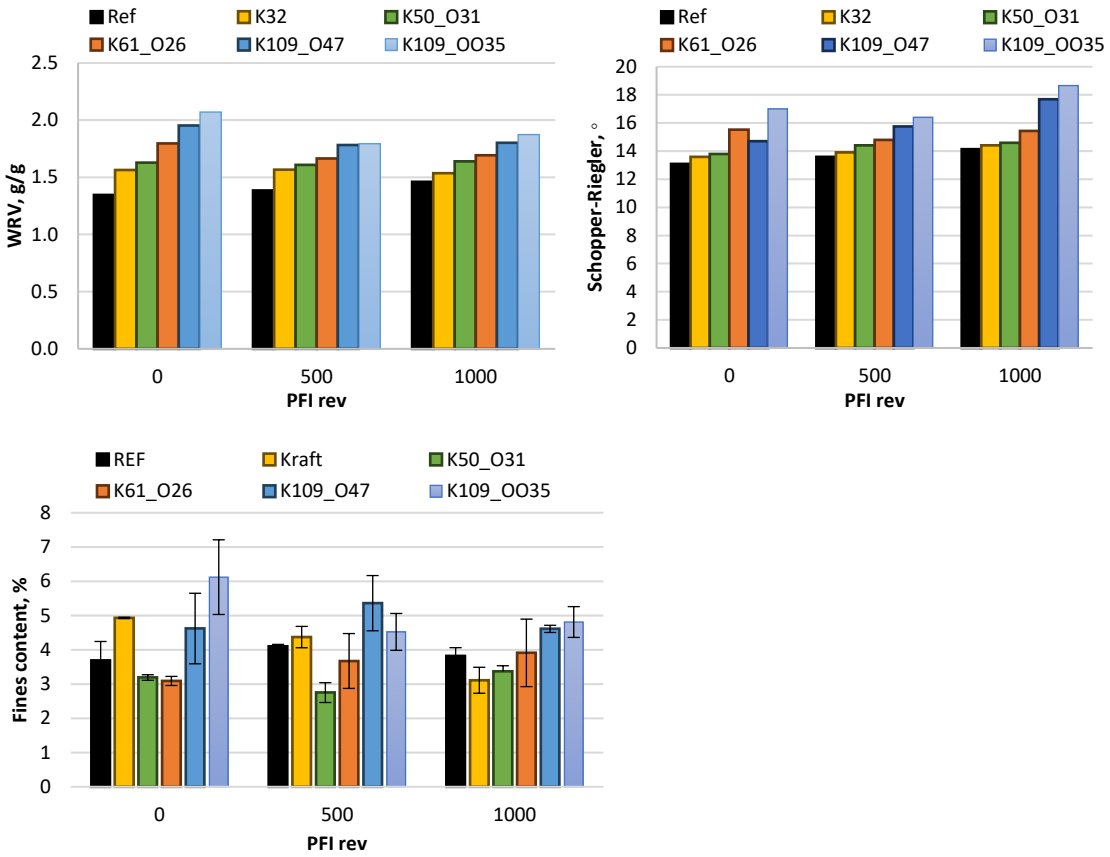

Figure 2: a) WRV, b) Schopper-Riegler degree and c) fines content as a function of the PFI refining, for the evaluated pulps.

3.2 Fiber morphology

The fiber morphology is shown in Figure 3. The fiber length was relatively consistent across all samples (ranging from 2.2 to 2.0 mm), though slightly lower in the commercial fully bleached pulp. The most notable differences were observed in fiber shape and the number of kinks. Fully bleached fibers exhibited a significantly higher number of kinks per fiber compared to the oxygen-delignified pulps, while the kraft-cooked fibers showed the fewest. These findings are consistent with previous studies (Mohlin and Alfredsson 1990, Mohlin et al. 1996, Esteves et al. 2021). Fines content was also evaluated and compared with values obtained from the BDDJ test, revealing minor differences between the methods.

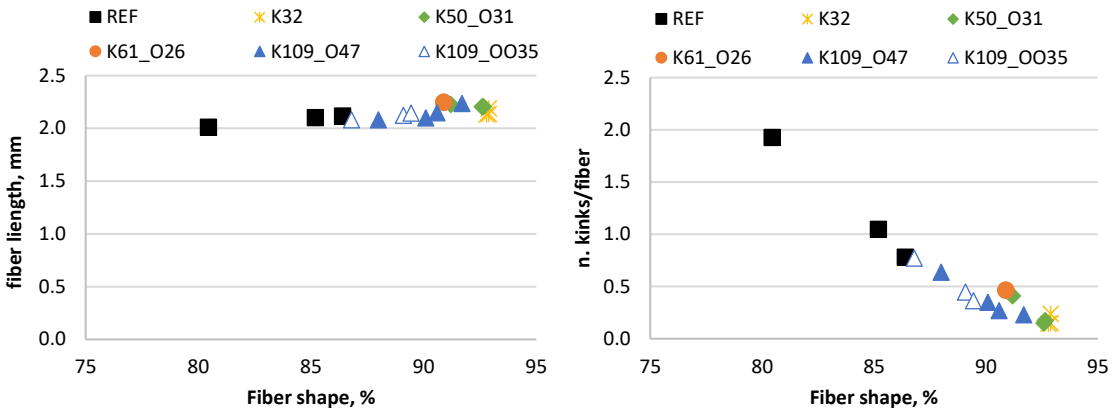

Figure 3: a) fiber length and b) number of kinks per fiber as a function of the fiber shape from the fiber tester.

3.3 Paper properties before PAE addition

Figure 4 presents the dry and wet tensile strength results for all pulp samples in the absence of wet-strength additives. As anticipated, the commercial fully bleached pulp (reference) exhibited the lowest tensile performance under both dry and wet conditions. In fact, the wet tensile strength, for the reference pulp, could not be evaluated due to the weak structure of the sheet (Figure 4b).

The K32 and K50_O31 pulps showed slower strength development and lower overall strength compared to the oxygen delignified pulps K61_O26, K109_O47 and K109_OO35. This difference may be attributed to the varying spruce-to-pine ratios among the samples. When examining wet tensile strength development across PFI revolutions, pulps K32, K60_O31 and K109_OO35 presented very similar development.

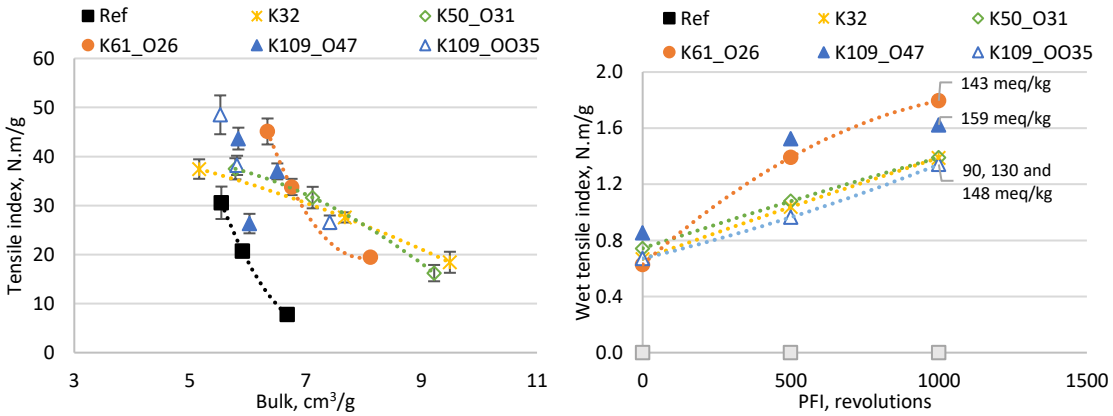

Figure 4: a) Dry tensile index as a function of bulk and b) wet tensile index as a function of PFI revolutions. The increase in tensile strength for each pulp sample is obtained by increased refining. For the wet tensile measurements, it was not possible to obtain values for the reference pulp due to its low strength; therefore, the corresponding data points are shown in grey along the x-axis.

When dry and wet tensile strengths were plotted, all samples—except the reference and K109_OO35—exhibited similar development trends - Figure 5. The oxygen delignified samples, K61_O25 and K109_O47 presented the fastest increase in wet tensile index and in the dry tensile. Especially, the unrefinied K109_OO35 showed significantly higher dry strength but comparatively low wet strength, when compared to the other samples, indicating a divergence in its bonding behavior under wet conditions.

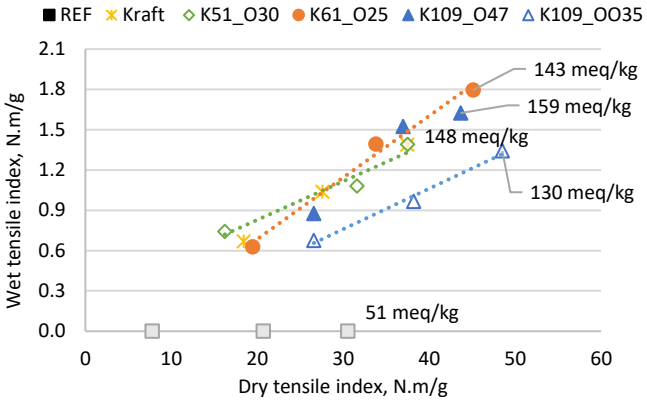

Figure 5: Wet tensile index as a function of the dry tensile index. The increase in tensile strength for each pulp sample is obtained by increased refining. The values shown on the top of the lines, in the graph are relative to the total fiber charge of the samples.

3.4 Paper properties after PAE addition

Refining improved both dry and wet strength for all sheets made with PAE, regardless of which pulp was used. Figure 6a and Figure 7a shows that similar levels of wet strength could be achieved at five times lower PAE dosage for the oxygen delignified pulps when compared to fully bleached pulp at different refining levels.

The strength properties of the unrefined samples varied; however, at the high refining level (1000 revolutions), all samples converged to a similar wet tensile strength. In contrast, slight differences remained in dry tensile strength, with the oxygen-delignified pulps with the highest WRV exhibiting the highest values.

Several mechanisms for how refining improves the performance of wet strength agents have been proposed. In the unrefined state, fibres have low surface area and quickly become saturated with polymer. One explanation is that refining improves PAE performance by fibrillating the fibre surface, which increases the available surface area as well as exposing more carboxylic groups. In this study, there was a robust improvement in wet strength and dry strength with refining for all pulps, despite differences in pulp properties. This indicates that the improved wet strength development with refining could be explained by increased sheet consolidation.

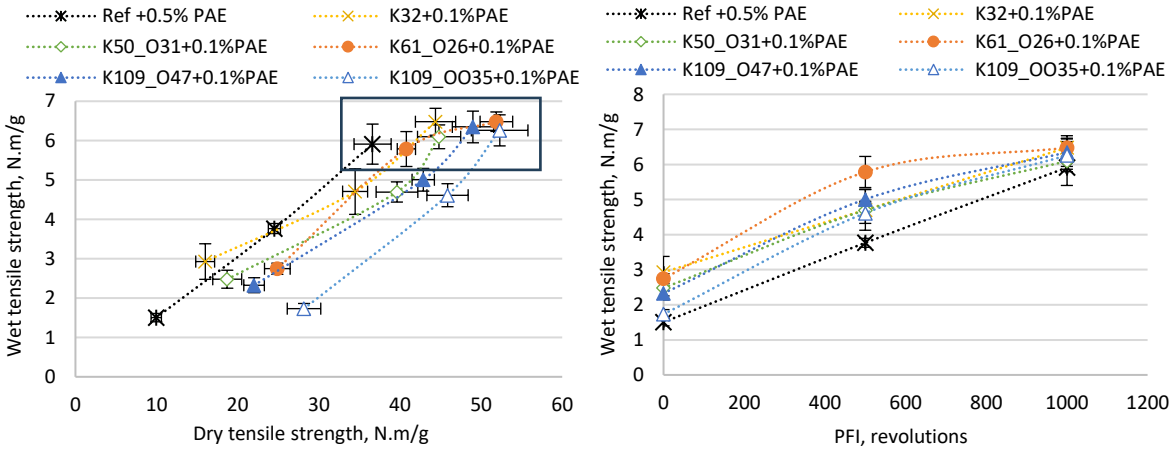

Figure 6: Wet tensile index as a function of the dry tensile index for the reference pulp with 0.5%PAE and for the kraft and oxygen delignified pulps with 0.1% of PAE dosage. The increase in tensile strength for each pulp sample is obtained by increased refining.

Figure 7a shows the lowest PAE dosage, 0.05% for the oxygen delignified pulps K109_O47 and K109_OO35, compared to 0.25% needed for the fully bleached reference pulp. Among these, K109_OO35 consistently exhibited the highest dry tensile strength.

Figure 7b presents results for a fixed PAE dosage applied to both the fully bleached pulp and the unbleached samples (K32, K60_O31, and K61_O26). Notably, the unrefined oxygen-delignified pulp K61_O26 achieved wet and dry tensile strengths comparable to the fully bleached pulp refined to 1000 PFI revolutions. Similarly, the unrefined pulps K32 and K60_O31 reached strength levels equivalent to the fully bleached pulp refined to 500 revolutions. When comparing samples at the same refining level, the oxygen-delignified pulps (K50_O31 and K61_O26) achieved approximately 80% higher wet tensile strength than the fully bleached pulp.

These findings suggest that significant energy savings in refining or cost reductions in PAE dosage may be possible by optimizing pulp selection and processing conditions.

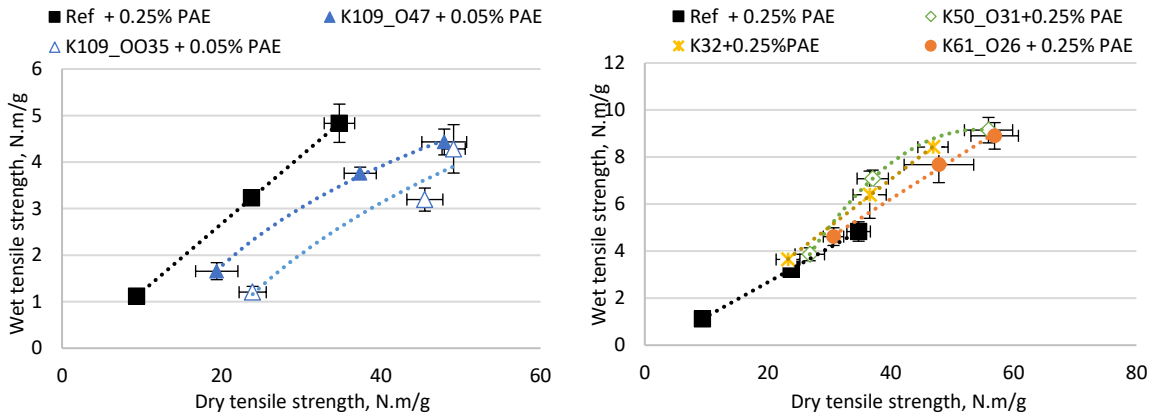

Figure 7: Wet tensile index as a function of the dry tensile index for a) the reference with 0.25%PAE and oxygen delignified pulps with 0.05% PAE dosageb) 0.25% PAE for all pulps. The increase in tensile strength for each pulp sample is obtained by increased refining.

3.5 Pulp and paper properties after PAE and CMC addition

Upon the addition of CMC, a noticeable improvement in wet strength was observed for both the reference and the cooked pulp (K32) - Figure 8 . In contrast, the oxygen delignified pulps showed no measurable improvement upon CMC addition. This highlights the substantial impact of their inherently high fiber charge, which appears sufficient to facilitate effective covalent bond formation with PAE during heat treatment, eliminating the need for supplementary CMC.

This finding is particularly relevant from a process optimization perspective, as it implies that oxygen-delignified pulps can achieve high wet strength without the use of CMC, resulting in chemical savings. Particularly, the oxygen delignified samples reached comparable wet strength levels to the fully bleached pulp, despite using five times less PAE and no CMC, underscoring the efficiency of this approach.

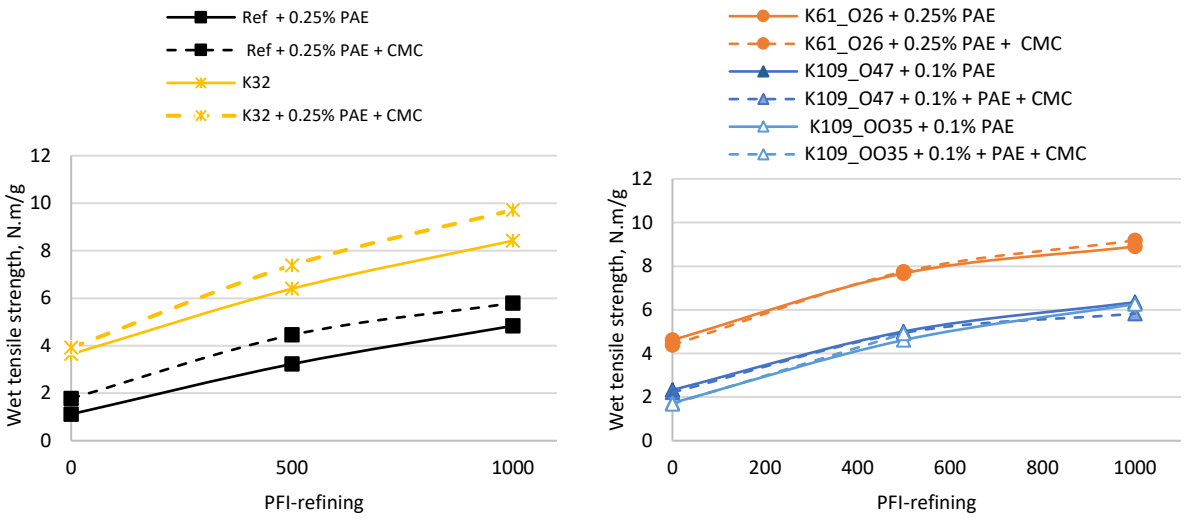

Figure 8: Wet tensile index as a function of the PFI refining for the a) reference and unbleached kraft pulp and b) for the oxygen delignified pulps.

The Schopper-Riegler (SR) degree was also measured following the addition of PAE and CMC. Overall, SR values decreased slightly—by 0 to 1.5 units—across all samples after the incorporation of these additives - Figure 9.

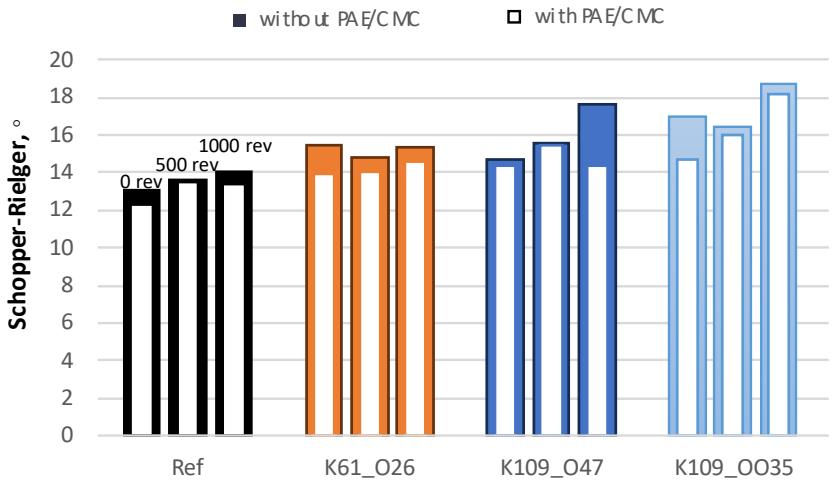

Figure 9: Schopper-Riegler degree for pulps unrefined and 500 and 1000 revolutions, with and without the PAE/CMC addition.

Conclusions

This study highlights the potential of unbleached kraft and oxygen-delignified softwood pulps as efficient and sustainable alternatives to fully bleached fibers in tissue paper production. Oxygen-delignified pulps consistently demonstrated superior wet strength development with up to five times less PAE and no need for CMC, thanks to their high fiber charge and enhanced bonding potential.

Refining improved strength across all pulps, but oxygen-delignified samples achieved comparable performance with reduced refining intensity, offering energy savings. The wet strength development has much faster for the unbleached kraft and oxygen delignified pulps than for the fully bleached pulps.

While high fiber charge in oxygen delignified pulps clearly enhances wet strength and reduces PAE demand, the strong performance of the kraft pulp—despite its lower charge—suggests that other mechanisms may be at play. This highlights the need for further research to better understand the interplay between fiber chemistry, structure, and additive efficiency.

Overall, oxygen delignified pulps offer a promising pathway toward more resource-efficient and environmentally friendly tissue products, enabling reduced use of wet-strength additives and reduce refining energy without compromising product quality.

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