Evaluating the Potential to Modify Pulp and Paper Properties through Oxygen Delignification

Cláudia S. V. G. Esteves,* Elisabet Brännvall, Sören Östlund, and Olena Sevastyanova

ABSTRACT: The potential to modify pulp and paper properties by oxygen delignification was assessed by looking beyond the ordinary purpose of oxygen delignification. Pulps with the same kappa number were obtained by both pulping and the combination of pulping and oxygen delignification, and the mechanical and chemical properties were compared. The oxidation of pulp components leads to an increase in carboxylic acid groups in the fibers, resulting in a large influence on fiber swelling, seen as an increase in the water retention value and fiber saturation point. The introduction of charged groups appears to replace some of the morphological changes caused by refining and enhance the strength of fiber–fiber joints, generating pulps with better refi nability and higher tensile strength. Oxygen delignification was able to improve the tensile index with 6% at the same sheet density and less refining energy, when the amount of total fiber charges was higher than 140 μeq/g.

1. INTRODUCTION

Oxygen delignification is a well-established technology, widely used in pulping for additional lignin removal before final bleaching. It was first implemented in the 1970s in South Africa at Sappi’s Enstra Mill, and because of its advantages with respect to environment, economy, and energy saving, it was rapidly installed in other pulp mills. Nowadays, to increase efficiency, the industrial process of oxygen delignification is done in two stages. For softwood pulps, the industrial oxygen process is usually performed from an initial kappa number of 22–32 (from the pulping process) to a final kappa number of 8–22. Oxygen delignification is quite a complex chemical process, and to understand it completely is not a trivial task. It starts with lignin degradation through the phenolic radical formation, but the presence of several types of oxidative chemical agents dramatically increases the complexity of the delignification chemistry. One important and limiting factor in the oxygen step is the carbohydrate degradation at extended oxygen delignification due to free radicals, and therefore, delignification is limited to 50% when one oxygen stage is used or delignification is up to 70% when two stages are used. Free radicals attack the cellulose chain randomly, leading to a decrease in the limiting pulp viscosity. However, oxygen delignification is a process with interesting potential to improve the mechanical properties of paper through the increase of charged groups in the fibers. In this study, a new methodology to evaluate if oxygen can have greater potential is proposed in order to assess the potential of oxygen delignification to modify pulp and paper properties.

Carboxylic acid groups are the functional groups with a major influence on the fiber charges present in the pulp. During kraft cooking and oxygen delignification, acid carboxyl groups are formed, degraded, and modified. In the pulping process, the methylglucuronic acid groups (MeGlcA), hexenuronic acids (HexA), and some phenolic hydroxyl groups from residual lignin will contribute to the fiber charges. The HexA are formed from the MeGlcA that are present in the xylan backbone in the early stage of the alkaline pulping
performed in steel autoclaves with a volume of 2.5 dm³, which
were cooled down in a water bath for 10 min, and
the oxidation of the chemical components present in the
wood.
This oxidation occurs mainly in the lignin, but it also
occurs in the carbohydrates, and it will lead to a significant
impact on the fiber properties, such as swelling ability,
conformability, ions interaction, optical properties, and
mechanical properties.
For this reason, the chemical and mechanical properties of the fibers after pulping and oxygen
delignification need to be evaluated in order to understand
their relationship with the final paper properties.

The aim of this study is to assess the potential of oxygen
delignification as a way of modifying the pulp and paper
properties. In order to do this, pulps delignified by either kraft
cooking or kraft cooking combined with a subsequent oxygen
stage to the same kappa number were compared. For the first
time, cook and oxygen delignification will be studied with
pulps with similar chemical compositions, allowing assessment
of the real oxidative potential of oxygen on the final pulp and
paper properties.

2. EXPERIMENTAL SECTION

2.1. Materials. Screened and hand-picked softwood chips
from the BillerudKorsnäs Skärbäck mill [a mixture of 70%
spruce (Picea abies) and 30% pine (Pinus sylvestris)] were used
in this study.

2.2. Methods. 2.2.1. Kraft Cooking. 2.2.1.1. In Auto-
claves. Four series of kraft cooks were done in this study to
obtain pulps with different kappa numbers. The trials were
performed in steel autoclaves with a volume of 2.5 dm³, which
were loaded with 250 g of oven-dried (od) wood chips. With a
vacuum pump, the air inside the vessels was removed for 30
min, and after that time, the cooking liquor was sucked into
the autoclaves. The impregnation was done with 5 bar nitrogen
injection for about 30 min and then released before starting the
cook. The cooking trials were performed with an effective alkali
(EA) of 22%, a sulfidity of 30%, a liquor/water ratio of 4.5 L/
kg, and a temperature of 160 °C.

For the impregnation step, the autoclaves were placed in a
steam-heated glycol bath at 100 °C for 30 min, and at 160 °C
for the cooking step. Rotation and slight inclination of the
autoclaves ensured good mixing inside. The cooking trials were
stopped at different H factors (cooking times) depending on
the desired final kappa number. After the cooking step, the
autoclaves were cooled down in a water bath for 10 min, and
then, the spent liquor was drained off the chips and collected
for analysis. The cooked chips were washed in deionized water
for 10 h in self-emptying metal cylinders and then defibrated
and screened in a NAF water jet defibrator. The shives were
collected, dried at 105 °C, and weighed. Similar to the cooking
trials in autoclaves, the pulp was made more homogeneous by
passing it through a channel with a rotating shaft with horizontal
rods that rip the pulp into smaller dimensions.

2.2.1.2. In a Recirculated Digester. In order to produce a
larger quantity of pulp for the oxygen delignification trials, a
recirculated digester with a dry chip capacity of 2 kg was used.
The temperature in the digester was controlled by a forced
liquor flow. To obtain different kappa numbers, two series of
kraft cooks were performed in a recirculated digester. For these
trials, the impregnation was done with water and 5 bars of
nitrogen overnight. After the impregnation, the water was
removed and weighed to have the right amount of liquor
added in the cooking step. The cooking trials were performed
with an EA of 21%, a sulfidity of 30%, a liquor/water ratio of
4.5 L/kg, and a temperature of 160 °C. The temperature was
raised from 20 °C to an impregnation temperature of 100 °C
in steps of 5 °C/min and raised to a cooking temperature of
160 °C in steps of 3 °C/min.

After the cooking step, the steam flow was stopped, and the
spent liquor was drained off the chips and collected for
analysis. The cooked chips were washed in deionized water for
10 h in self-emptying metal cylinders and then defibrated and
screened in the NAF water jet defibrator. The shives were
collected, dried at 105 °C, and weighed. Similar to the cooking
trials in autoclaves, the pulp was made more homogeneous by
passing it through a channel with a rotating shaft with horizontal
rods that rip the pulp into smaller dimensions.

2.2.2. Oxygen Delignification. Polyethylene bags were filled
with 20–60 g of od pulp, and the appropriate amounts
of NaOH, MgSO₄ and water were added, resulting in a
consistency of 12%. The bags were closed and hand-mixed
to get a uniform action of the chemicals. After the mixing,
the pulp was removed from the bag and placed in pressurized steel
autoclaves coated with Teflon. The autoclaves were closed,
pressurized with 0.7 MPa O₂ and then placed in an electrically
heated glycol bath at 100 °C, with rotation and slight
inclination of the autoclaves. After the oxygen delignification
process, the pulps were washed and filtrated with distilled
water.

2.2.3. Refining. All pulp samples were refined in a PFI mill
according to the standard ISO 5264-2.

2.2.4. Paper Sheet Making. Hand sheets were prepared
according to the standard ISO 5269-1. All sheets were made
with deionized water, and the grammage of the hand sheets for
mechanical testing was 60 g/m².

2.3. Pulp and Paper Analysis. The kappa number of the
resulting pulps was measured according to the standard ISO
302:2004. The intrinsic viscosity was measured according to
the standard ISO 5351:2010. The cellulose viscosity of the
samples was estimated using eq 1.

\[
η_{cellulose} = \frac{η_{pulp} - η_{hemi}x_{hemi}}{x_{cellulose}}
\]

where \(x\) is the mass fraction of the pulp of cellulose (\(x_{cellulose}\)) and hemicellulose (\(x_{hemi}\)). The hemicellulose fraction of the
pulp was calculated by the sum of the glucomannan and xylan
fractions, and the viscosity of hemicellulose was defined as
\(η_{hemicellulose} = 70 \text{ mL/g}\). The xylan, glucomannan,
and cellulose contents were calculated from the monosaccharides
according to Janson, using a glucose/mannose ratio of 4.17.

The carbohydrate composition was determined according to
SCAN-CM 71:09 after the samples were subjected to acetone
e EXTRACTION according to SCAN-CM 49:03 and a subsequent
grinding with a 40-mesh grid. An ion chromatography system
coupled to a pulsed amperometric detector was used to analyze
the soluble monosaccharides, with a Dionex CarboPac PA1
column (4 × 250 mm). The acid-insoluble and the acid-soluble
residue were determined according to TAPPI T 222 om-11 and
TAPPI UM 250, respectively, and their sum was considered to
be the total lignin content.

The water retention value (WRV) tests were performed
according to SCAN-C 62:00. All tests were performed in
duplicate.
For the fiber charge measurements, the pulps were washed with HCl at a concentration of 0.01 M and a pH of 2 for 30 min. Then, the pulps were filtrated and washed again with deionized water until the conductivity was below 5 μS/cm. Thereafter, the pulps were washed in 0.001 M NaHCO₃ with a pH of 9 for 30 min and again filtrated and washed with deionized water until the conductivity was below 5 μS/cm. Half of the pulp was used for the polyelectrolyte titration in the Na⁺ form, and the other half, which was used for the conductometric titration in the H⁺ form, was washed again with 0.01 M HCl using the same procedure as described above.

2.3.1. Total Fiber Charge—Conductometric Titration. The conductometric titration was done according to the method described by Katz. The pulp used (about 0.5–1 g) for the determination of the total fiber charge was in the H⁺ proton form and was dispersed in 500 mL of deionized water with 0.5n mL of 0.01 M HCl and 10 mL of 0.01 M NaCl. The conductometric titration was performed with 0.1n M NaOH in a microprocessor-controlled titrator (Metrohm—Titrino 702SM), and the data were treated in the Tiamo 2.3 software.

2.3.1.2. Surface Fiber Charge—Polyelectrolyte Titration. The polyelectrolyte titration was done according to the method described by Wågberg. The pulp used (about 0.5 g) for the determination of the surface fiber charge was in the Na⁺ proton form and was dispersed in deionized water with 1 mL of 0.001 M NaHCO₃ and a certain amount of PolyDADMAC (M_w > 500k) in a total volume of 100 mL. After 30 min of stirring, the suspension was filtered in a Buchner funnel; the pulp was dried, and the filtrate was used for the titration. The polyelectrolyte titration was performed with the filtrate, with 4.11 × 10⁻⁷ ekv/mL of potassium polyvinyl sulphate (KPVS), in a BASF photoelectric Messkopf 2000 with associated titration equipment (Metrohm—794 Basic Titrino), and the data were treated in the Tiamo 2.4 software.

2.3.2. Fiber Saturation Point. The fiber saturation point (FSP) is a solute exclusion test that measures the water inside the fiber wall that is inaccessible to a dextran solution. About 1 g of od pulp was immersed in the dextran solution of a high molecular weight (2 × 10⁶) and of 1% concentration for at least 3 days. This measurement was made according to Stone and Scallan.

2.3.3. Fiber Morphology. The fiber morphology was evaluated in an L&W Fiber Tester, where the fibers in water suspension are transported by a strong flow, sufficient to orientate them in two dimensions but not cause deformations. A digital imaging system acquires and analyzes the images taken from the fibers, and the software calculates the fiber parameters such as the shape factor that is then used for curl index calculation according to eq 2.

\[
\text{Curl index (\%)} = \frac{1}{\text{shape factor}} - 1
\]

The measurements were made in duplicate for each pulp sample.

2.3.4. Structural and Mechanical Tests. The grammage was determined according to ISO 536, and the structural thickness was determined according to SCAN-P 88:01. Tensile strength tests were done according to ISO 1924-3.

3. RESULTS AND DISCUSSION

The purpose of the investigation was to study the properties of cooked and oxygen-delignified pulps with similar chemical compositions to be able to assess the effect of the oxidative conditions in the oxygen delignification process. Pulps produced by either kraft cooking or kraft cooking combined with subsequent oxygen delignification to the same kappa numbers, 30 and 25, were compared. In Figure 1, the procedure is schematically illustrated. Several pulps with different kappa numbers were produced by kraft cooking in order to perform oxygen delignification afterward. The length of the arrows shows the degree of delignification for each trial.

Cooking conditions and results are shown in Table 1 for pulps produced by kraft cooking, with kappa numbers ranging from 57 to 26. The EA used in the cooking trials was chosen in order to obtain a similar residual alkali level in all trials. As expected, the yield decreased, and the reject content decreased with the delignification degree. The average degree of polymerization of all carbohydrates, measured as the limiting pulp viscosity, was fairly constant until the lowest kappa number was reached, when a significant decrease was seen. There was, however, a drop in the calculated average degree of polymerization of cellulose already at kappa number 31.

The pulps with higher kappa numbers were subsequently oxygen-delignified to kappa number 30 or 25, as shown in
Table 1. Summary of Kraft Cooks\(^a\)

| sample name | cooking equipment | cooking conditions | results |
|-------------|------------------|--------------------|--------|
|             |                  |                    | kappa no. | \(\eta_{\text{pulp}}\) (mL/g) | \(\eta_{\text{cell}}\) (mL/g) | total yield (%) | rejects (%) | residual alkali (g/L) |
| K57        | R.D.             | 21                 | 56.5      | 1226          | 1665          | 50.7            | 6.3       | 9.0 |
| K50        | R.D.             | 21                 | 49.5      | 1247          | 1654          | 49.4            | 3.7       | 8.5 |
| K46        | A                | 22                 | 45.7      | 1290          | 1728          | 50.4            | 1.1       | 10.4 |
| K40        | A                | 22                 | 39.6      | 1288          | 1662          | 48.7            | 0.7       | 10.7 |
| K31        | A                | 22                 | 30.5      | 1236          | 1576          | 48.7            | 0.3       | 9.2  |
| K26        | A                | 22                 | 26.2      | 1150          | 1475          | 47.2            | 0.2       | 8.7  |

\(^a\)Cooking temperature was 160 °C, the sulfidity was 30%, and the liquor-to-wood ratio was 4.5 L/kg. "A" denotes cooking in autoclaves and "R.D." denotes cooking in the recirculated digester. \(\eta_{\text{pulp}}\) is the limiting viscosity measured on the pulp, and \(\eta_{\text{cell}}\) is the calculated viscosity for the cellulose fraction.

Table 2. Summary of the Oxygen Delignification Trials\(^a\)

| sample name | conditions in oxygen delignification | results |
|-------------|--------------------------------------|--------|
|             | NaOH (%) | time (min) | T (°C) | end-pH | kappa no. | \(\eta_{\text{pulp}}\) (mL/g) | \(\eta_{\text{cell}}\) (mL/g) | \(\Delta K\) | screen yield (% on wood) | total yield (% on wood) |
| K57_O30     | 3.2      | 75        | 100    | 10.6   | 29.8      | 1034          | 1312          | 26        | 42.2            | 48.1 |
| K46_O30     | 2.2      | 35        | 100    | 11.7   | 29.8      | 1156          | 1480          | 16        | 47.7            | 48.8 |
| K50_O35     | 3.2      | 72        | 100    | 11.3   | 24.8      | 1027          | 1292          | 25        | 44.2            | 47.7 |
| K40_O26     | 1.7      | 36        | 100    | 11.3   | 26.3      | 1057          | 1331          | 13        | 46.2            | 46.9 |

\(^a\)Pressure was 0.7 MPa, and the temperature was 100 °C. Samples are denominated KX_OY, where X is the kappa number of the cooked pulp and Y is the kappa number of the oxygen-delignified pulps. \(\eta_{\text{pulp}}\) is the limiting viscosity measured on the pulp, and \(\eta_{\text{cell}}\) is the calculated viscosity for the cellulose fraction.

Table 2. The conditions used in the oxygen delignification process were chosen to reach a final pH between 10.5 and 12. A final pH outside this range would result in lower selectivity in the process.\(^22\) Oxygen delignification decreased the average degree of polymerization. Between the cooked pulp and the oxygen-delignified pulp, the decrease in the limiting pulp viscosity was approximately 200 units.

The selectivity of the oxygen delignification process, that is, delignification set against degradation of carbohydrates, can be evaluated in different ways. The extent of random scission of cellulose chains at a given degree of delignification is assessed by the viscosity of the cooked and oxygen-delignified pulps at the same kappa number. According to Tables 1 and 2, oxygen-delignified pulps had 100–200 units lower viscosity, indicating that cleavage of cellulose chains was more pronounced by radical attack in the oxygen stage compared to alkaline hydrolysis in the cooking stage. This is in accordance with previous studies.\(^4,13,21–23\)

The selectivity evaluated as the yield at a given kappa number compares delignification with dissolution of carbohydrates caused mainly by the onset of secondary peeling starting at the reducing end groups formed after chain scission by alkaline hydrolysis or radical attack. According to Tables 1 and 2, the yield was fairly similar whether kappa number 30 or 26 was reached by kraft cooking (total yield was 47.2–48.7%) or by subsequent oxygen delignification (total yield was 46.9–48.8%). However, the gravimetric calculation of the yield in the oxygen stage is not straightforward because chemical components oxidized in the oxygen stage and remaining in the pulp give rise to false yield gains. Nevertheless, there was no indication that oxygen delignification resulted in an improved yield at a given kappa number, when compared to the kraft cook. On the contrary, when the yield, as percent of wood in the oxygen stage, was compared to the screened yield in the cook, a decrease was observed. Large yield gains by oxygen delignification have been claimed in the literature.\(^24,22,26,27\) However, the yield in the cited studies was compared between extended cooking and oxygen delignification, that is, at such low kappa numbers that the kraft cooking has entered the unselective residual phase delignification. On the other hand, when oxygen delignification is introduced after kraft cooking to higher kappa numbers, the yield can be decreased compared to the same final kappa number achieved by kraft cooking alone.\(^23\)

The comparison with the total yield in the present study is however somewhat flawed as oxygen delignification was performed on screened pulp. Because relatively high kappa numbers of 25 and 30 after oxygen delignification were aimed for, the kappa numbers of the cooked pulp were high, ranging between 40 and 57, and thus contained a significant amount of rejects.

The chemical composition for the different pulps is given in Table 3. Apart from lignin, kraft cooking dissolved a significant amount of hemicellulose, mainly glucomannan, which is highly

Table 3. Relative Chemical Composition and Percent of Pulp and Wood Chips

| sample name | cellulose | glucomannan | xylan | lignin | hem/cell |
|-------------|-----------|-------------|-------|--------|---------|
| wood chips  | 43.3      | 18.0        | 9.1   | 31.3   | 0.63    |
| K57        | 72.9      | 8.4         | 8.2   | 10.4   | 0.23    |
| K50        | 74.7      | 8.3         | 8.5   | 8.6    | 0.22    |
| K46        | 73.9      | 8.3         | 8.1   | 8.1    | 0.22    |
| K40        | 76.8      | 8.5         | 8.1   | 6.6    | 0.22    |
| K31        | 77.7      | 8.4         | 8.6   | 5.4    | 0.22    |
| K26        | 77.1      | 8.9         | 8.8   | 5.3    | 0.23    |
| K57_O30    | 77.9      | 8.2         | 8.4   | 5.5    | 0.21    |
| K46_O30    | 77.3      | 8.5         | 8.2   | 5.9    | 0.22    |
| K50_O25    | 78.6      | 8.3         | 8.5   | 4.7    | 0.21    |
| K40_O26    | 78.6      | 8.6         | 8.1   | 4.8    | 0.21    |
susceptible to the peeling reaction. At kappa numbers 25 and 30, the relative amounts of cellulose and hemicellulose in the pulp were similar, indicating that the extent of dissolution of the different carbohydrates was similar whether delignification was achieved by kraft cooking or in the oxygen stage. The ratio of hemicellulose to cellulose was almost constant for all of the trials (0.21−0.23).

3.1. Effect on Mechanical Properties. Mechanical properties are one of the most important aspects to consider in paper production, and pulp refining is used to increase paper strength through both external and internal fibrillation of the fibers. The external fibrillation is related to the release of microfibrils on the fiber, whereas the internal fibrillation is related to the delamination of the pulp fiber wall, resulting in an increase in porosity. With refining, it is possible to improve the fiber flexibility and consequently the bonded area and the number of bonds between the fibers.28−30

To assess the mechanical properties, the pulps were refined by beating in a PFI mill at different degrees. The development of tensile index for pulps at kappa number 30 and 25 is seen in Figure 2a,b, respectively. Interestingly, at both kappa numbers, the oxygen-delignified pulps behaved differently. The pulps K46_O30 and K40_O26 had a similar development in the tensile index as the corresponding cooked pulp, while K57_O30 and K50_O25 had a faster increase in the tensile index. The latter oxygen-delignified pulps were obtained with a higher alkali charge (3.2%) and a larger kappa number reduction (25−26 kappa units). The two oxygen-delignified pulps with a similar tensile index development as the corresponding cooked pulps had a lower alkali charge (2.2 and 1.7%) and a smaller kappa number reduction (13−19 kappa units).

The tensile index as a function of sheet density is given in Figure 3. Oxygen-delignified pulps K46_O30 and K40_O26 had a strength-density correlation similar to that of the corresponding cooked pulps, that is, for a certain tensile index, the same bonded area was needed. On the other hand, pulps K57_O30 and K50_O25 had a slightly higher tensile index at a given sheet density compared to the corresponding cooked pulps. This suggests that the tensile index improvement may have been achieved by increased fiber−fiber joint strength.31−33

![Figure 2. Tensile index at different levels of PFI beating for pulps with kappa number (a) 30 and (b) 25. Error bars show the 95% confidence intervals.](image)

![Figure 3. Tensile index vs structural density for pulps with kappa number (a) 30 and (b) 25. Error bars show the 95% confidence intervals.](image)

![Figure 4. Tensile stiffness index profile along the structural density for pulps with kappa number (a) 30 and (b) 25.](image)
strength was improved by the oxygen delignification process (K57_O30 and K50_O25) for a lower beating energy.

Refining results in densification of the sheet as the number of bonds between fibers increases. This leads to an increased number of activated load-bearing segments, which results in a higher tensile stiffness index of the sheet. As seen in Figure 4, the tensile stiffness index increases with the sheet density similarly for all cooked and oxygen-delignified pulps. Because the tensile stiffness index depends on the axial strength of fibers in the network, the hypothesis that the tensile index improvement was achieved by increased fiber–fiber joint strength is still valid. It has been shown that increased bond strength has a small effect on the tensile stiffness index.28,34

The correlation between elongation and sheet density was also similar for sheets from cooked and oxygen-delignified pulps, as seen in Figure 5. The elongation depends on the single-fiber behavior, the network properties, and the fiber–fiber bonding.35,36 Curled fibers have a stretch potential as stress applied to the fibers will straighten them as well as the fiber network.37 The density of the paper reflects the fiber–fiber contact area and will affect the stress–strain properties. The increase in the number of load-bearing segments leads to increased activation of curled fibers.

Extensibility is an important property for paper-based packaging, such as bag and sack papers. According to the results, oxygen delignification makes it possible to achieve the same elongation at lower refining energy when compared to the cooked pulps.

3.2. Effect on Fiber Deformation. Fiber deformations can affect the stiffness and strength development, and therefore, it is important to evaluate their influence on the mechanical performance of paper.

In Figure 6, the effect of refining on the fiber curl index is shown. Unrefined oxygen-delignified pulps had higher curl indices compared to the corresponding cooked pulps. It has previously been shown that oxygen delignification can introduce some additional curl in the fibers, even when the treatment is performed with a very little inflicted mechanical force as when using autoclaves.3,38 Interestingly, cooked and oxygen-delignified pulps behaved differently when refining. Refining the cooked pulps resulted in an increase in the curl index, while refining of oxygen-delignified pulps resulted in a reduction in the curl index. Generally, PFI refining can remove some fiber deformations, such as curls, making the fibers straighter as previously shown.38–40 However, according to Nordström41 low-consistency refining of unbleached pulp results in an increased curl. Fiber curl affects the tensile stiffness of paper as a higher curl reduces the effective fiber length and thereby the number of load-bearing segments. In Figure 4, it is demonstrated that the tensile stiffness of sheets made from oxygen-delignified pulps increased gradually with refining, and thus, a higher sheet density can be observed. At low refining levels, however, the tensile stiffness of sheets from cooked pulps remained unaffected as the increase in curl caused by refining counteracted the increase in the bonded area.

Interestingly, Figures 5 and 6 show that for a higher curl index, the cooked pulp showed lower elongation values. According to Vishtal and Retulainen, stronger papers exhibit brittle behavior, that is, lower extensibility.35 However, it can be concluded from Figures 3 and 6 that it is possible to increase the paper strength with oxygen delignification without compromising the extensibility properties.

3.3. Effect on the Fiber Charges and Related Properties. As expected, the amount of charged groups increased after oxygen delignification, as seen in Table 4. The increase in the total amount of charged groups (46–88%) was lower than the increase in the surface charge (94–148%), as seen in Table 4. The main increase in charged groups arises from lignin5,11 as the ring opening of an aromatic unit in lignin gives rise to two carboxyl groups. Carbohydrates may be oxidized, introducing a dicarboxylic structure, but the main
charged groups in carbohydrates are HexA and any remaining MeGlcA on the xylan backbone. Oxygen delignification does not directly remove HexA, but some can be removed attached to the xylan in carbohydrate dissolution.\textsuperscript{5,42,43} However, the amount of HexA is affected by pulping. The decrease in the fiber charge with a decreased kappa number for the cooked pulps is mainly due to degradation of HexA that were formed at the early stages.\textsuperscript{44} The lignin content on the fiber surface is usually much higher than that in the bulk of the fiber,\textsuperscript{45-47} and this is probably the reason for the higher increase in the surface charge. In Table 4, a clear correlation can be seen between the water-holding capacity of the fibers and the total amount of charged groups; the higher the amount of charges the higher the WRV and the FSP value. The FSP gives the pore volume within the fiber wall, and as can be seen in Table 4, a higher amount of charges in the fiber wall will increase the repulsion between charged groups, leading to an increased pore volume.\textsuperscript{6,46,49} The WRV was higher than the corresponding FSP value as the WRV measurement probably also includes some water on the fiber surface and maybe also includes some lumen water.

The WRV was higher than the corresponding FSP value as the WRV measurement probably also includes some water on the fiber surface and maybe also includes some lumen water. In Figure 7, the tensile index as a function of WRV is compared. The WRV can provide important information about the swelling capability, and therefore the bonding potential, of the pulps. From the figure, it is apparent that the oxygen-delignified pulps (K46_030 and K40_026) that responded similarly to refining as the cooked pulps also had quite a similar WRV, while the oxygen-delignified pulps with improved refinability (K57_030 and K50_025) had a clearly higher WRV at a given tensile index. Refining pulp fibers improves the strength of the paper formed from the fibers by delamination of the fiber wall (internal fibrillation), which is seen as an increase in swelling (WRV), and results in a more flexible fiber that can conform better to other fibers, and therefore, the bonded area between fibers increases. Introduction of charged groups in the fiber wall has a similar effect because the swelling of the fiber wall is increased by the higher amount of charges. This contributes to the mechanical strength improvement by increasing fiber flexibility and conformability, resulting in a larger surface area for bonding.\textsuperscript{13,35,49,50}

The amount of charges was higher for the oxygen-delignified pulps K46_030 and K40_026 compared to that of the corresponding cooked pulps. However, such an increase was not sufficient to affect the morphology of the fiber wall to such an extent that the tensile index of the paper was affected. The refinability of the oxygen-delignified pulps with the highest amount of charged groups, K57_030 and K50_025, on the other hand, improved as the WRV increased.

The fiber charges must be seen as two parts, surface charge and inner charge, and the sum of both charges is defined as the total fiber charge, which will have different impacts on the fibers and paper properties. The surface charge can be seen as an important player in the bonding strength capacity,\textsuperscript{13} whereas the total charge is highly relevant to the hydrophilicity and swelling ability in the fiber and consequently the fiber flexibility and conformability.\textsuperscript{12,51}

To achieve strength improvements, it seems that the total amount of fiber charges needs to be higher than 140 \(\mu\text{ekv/g}\)—Figure 8. This increase in the fiber charge can be achieved by increasing the delignification time and alkali charge for a larger kappa number reduction. For the surface fiber charge, the increase with oxygen was about 90–150\% for the K57_030 and K46_030 pulps and from 116 to 126\% for the K50_030 and K40_026 pulps. Apparently, the surface charge was not crucial for the improvement of the mechanical behavior of the pulps studied, possibly because of the high lignin content present on the surface, which does not make the bonding sufficiently strong. This leads to the conclusion that the inner charge is the property that mostly contributes to the mechanical improvement — as the fiber gets more swollen, the fibers are more flexible, and the area for bonding increases, leading to stronger fiber–fiber joints.

For lower kappa numbers, Zhang studied the influence of alkali charge on the oxygen delignification between 1.5 and 3.5\%, concluding that the higher increase in fiber charge was with 2.5\%.\textsuperscript{6} In the cited study, the lignin content is lower than that observed in the present study, making the oxidation of lignin possible with a lower alkali charge. A higher alkali charge

### Table 4. Amount of Charged Groups, Total and on the Surface, as Well as the Water Retention Capacity (Water Retention Value, WRV) and the Fiber Wall Volume (Fiber Saturation Point, FSP) of Unrefined Pulps

| Sample Name | Total Fiber Charges (\(\mu\text{ekv/g}\)) | Surface Fiber Charges (\(\mu\text{ekv/g}\)) | WRV (g/g) | FSP (\(\mu\text{ekv/g}\)) |
|-------------|---------------------------------|---------------------------------|-----------|-----------------|
| K57         | 128                             | 4.90                            | 1.68      | 1.46            |
| K50         | 124                             | 4.31                            | 1.67      | 1.40            |
| K46         | 108                             | 4.25                            | n.a.      | n.a.            |
| K40         | 102                             | 3.42                            | n.a.      | 1.45            |
| K31         | 85                              | 3.19                            | 1.59      | 1.23            |
| K26         | 74                              | 2.48                            | 1.58      | 1.27            |
| K57_030     | 160                             | 6.20                            | 1.79      | 1.58            |
| K46_030     | 124                             | 6.84                            | 1.62      | 1.39            |
| K50_025     | 143                             | 6.28                            | 1.76      | 1.44            |
| K40_026     | 111                             | 6.14                            | n.a.      | 1.29            |

n.a.—not analysed.
will introduce much more fiber charges, which will facilitate the lignin solubilization and its removal, leading to a decrease in the fiber charges.

For higher kappa numbers, when the alkali charges 2.2 and 3.2% are compared, it was concluded that higher alkali and a longer time leads to a higher increase in the fiber charge. In this case, a large lignin content is present in the pulp, and therefore more alkali and time are needed in order to oxidize as much lignin and carbohydrates as possible.

Oxygen delignification can be an interesting alternative for semibleached pulps used for sack and bag papers. For fully bleached pulps, the carboxylic acid groups introduced in the oxygen delignification process by lignin oxidation will be removed along the bleaching process, leading to an eventual loss of strength.51–54 However, the charges present in the carbohydrates will not suffer a significant change, and therefore, the improvement in the properties might remain for fully bleached pulps.

For semibleached pulps, this study showed great potential by using oxygen delignification in a way that can modify the fibers, resulting in better mechanical properties.

4. CONCLUSIONS

Pulps at the same kappa number were manufactured either by kraft cooking or by the combination of kraft cooking and oxygen delignification. The study showed that oxygen delignification could be a very useful tool for improving the final paper strength. It was demonstrated that if the oxygen delignification stage introduced sufficiently more charged groups, this could reduce some of the refining energy needed to reach a certain tensile index. An increase in the fiber charges by oxygen delignification led to increased swelling of the fiber wall, which could improve the fiber–fiber joint strength in the paper. A high alkali charge and a larger kappa number reduction in the oxygen delignification stage is favorable for the improvement of the mechanical properties. The increase in the total amount of fiber charges by oxygen delignification is more important for strength improvement than the increase in the surface fiber charge.

■ AUTHOR INFORMATION

Corresponding Author

Cláudia S. V. G. Esteves — RISE INNVENTIA AB, SE-114 28 Stockholm, Sweden; orcid.org/0000-0002-0816-0047;
Phone: 076 876 73 04; Email: claudia.esteves@ri.se

Authors

Elisabet Brännvall — RISE INNVENTIA AB, SE-114 28 Stockholm, Sweden

Sören Östlund — Department of Engineering Mechanics, Solid Mechanics, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Olena Sevastyanova — Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00869

Notes

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Figure 8. Tensile index (y-axis on the left, represented by columns) vs total fiber charge (y-axis on the right, represented by “x”) for approximately the same density (0.79 g/cm³) and different beating levels (K31, K46_O30, K26, and K40_O26 beating of 4000 revolutions, and K57_O30 and K50_O25 beating of 2000 revolutions).
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