Using online bubble size and total dissolved solids measurements to investigate the performance of oxygen delignification

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ABSTRACT: The main target of oxygen delignification is to continue delignification that started in cooking in a more selective manner than occurs in the digester (i.e., remove a substantial fraction of the residual lignin using oxygen and alkali at a moderate temperature). Delignification with oxygen is a gentler way of reducing the kappa number than extended cooking. Lowering inlet kappa to bleaching also decreases bleaching chemicals consumption and, because of this, reduces organic wastewater load from bleaching.

We studied the performance of oxygen delignification by installing bubble size imaging systems and refractometers, which measure dissolved dry solids in the oxygen stage feed. Based on these measurements, we gathered information about gas dispersion (bubble size distribution) and the behavior of dissolved matter in the hardwood mill's oxygen delignification stage. Our goal was to investigate the effects of different variables on the oxygen stage's gas dispersion, kappa reduction, yield, and pulp quality. Gas dispersion improved (i.e., average bubble size decreased) when the chemical mixer speed increased. Increasing the mixer speed and the amount of oxygen yielded higher kappa number reductions and increased the amount of dissolved organic matter.

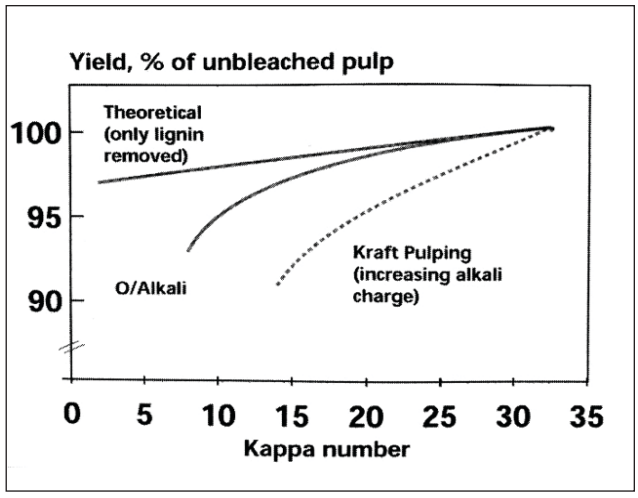
Application: Methods described here could help mills adjust the oxygen charge and gas dispersion in delignification processes and allow for future monitoring and controlling of the oxygen process.

In the late 1970s, medium-consistency mixing technology became available and the new high-shear mixing devices made it possible to efficiently disperse oxygen as very small bubbles in 10%–14% consistency pulp. Thus, most of the oxygen delignification systems installed today are medium-consistency ones. The main reasons for the interest in medium-consistency applications are lower capital costs, greater ease of stock handling with medium-consistency mixing and pumping technology, and improved selectivity in the presence of appreciable amounts of black liquor solids [1].

The process is very flexible, and is best viewed as a "bridging strategy" between cooking and final bleaching. The method and degree to which oxygen delignification is applied involves a comprehensive optimization of the fiber line process, considering total cost, pulp quality, and environmental impacts.

Process variables, such as the consistency of pulp, temperature, pressure, amount of alkali, amount of oxygen, and washer losses, and inhibitors, such as magnesium salts, influence the performance of oxygen delignification. Agarwal et al. in 1999 [2] stated that consistency has no major effect on kappa reduction if mixing is sufficient. However, in an industrial environment, neither mixing nor mass transfer is perfect. Elton et al. in 1980 [3] showed that higher consistency results in lower diffusion distance and higher alkali concentration at a given alkali charge.

Alkalinity and temperature are the most important factors affecting delignification during the oxygen delignification process. Although molecular oxygen has high electronegativity, it is a mild oxidizing agent for lignin because of its normal electronic configuration (i.e., its triplet state). Therefore, the reactivity of oxygen for delignification is intensified by increasing the reaction temperature or the alkali dosage. The limitation of oxygen is actually a diffusion limitation from the gas into the fiber. In addition, decreasing bubble size actually increases the surface area available for diffusion. The oxygen charge has a less important role than the alkali charge and temperature. Even so, a sufficient amount of oxygen must be present during the process to achieve a decent degree of delignification. However, increasing the oxygen charge too much can provoke the formation of larger gas bubbles and channeling through the tower, which again decreases the effectiveness of the oxygen delignification. Higher pressure helps diffuse the oxygen, and only the dissolved oxygen can react with the phenol groups of the lignin. The organic substances dissolved in cooking create side reactions during the oxygen stage. This causes additional oxygen consumption and degra-



1. Comparison of yield selectivity between extended cooking and oxygen delignification [4].

dation of cellulose chains. An increase in washing loss before the oxygen stage causes reductions in pulp viscosity, strength, and yield. Correspondingly, efficient post-oxygen washing is the key for low-cost bleaching. Magnesium salts in the softwood process improve the selectivity of the oxygen delignification and result in higher viscosity at a given kappa number.

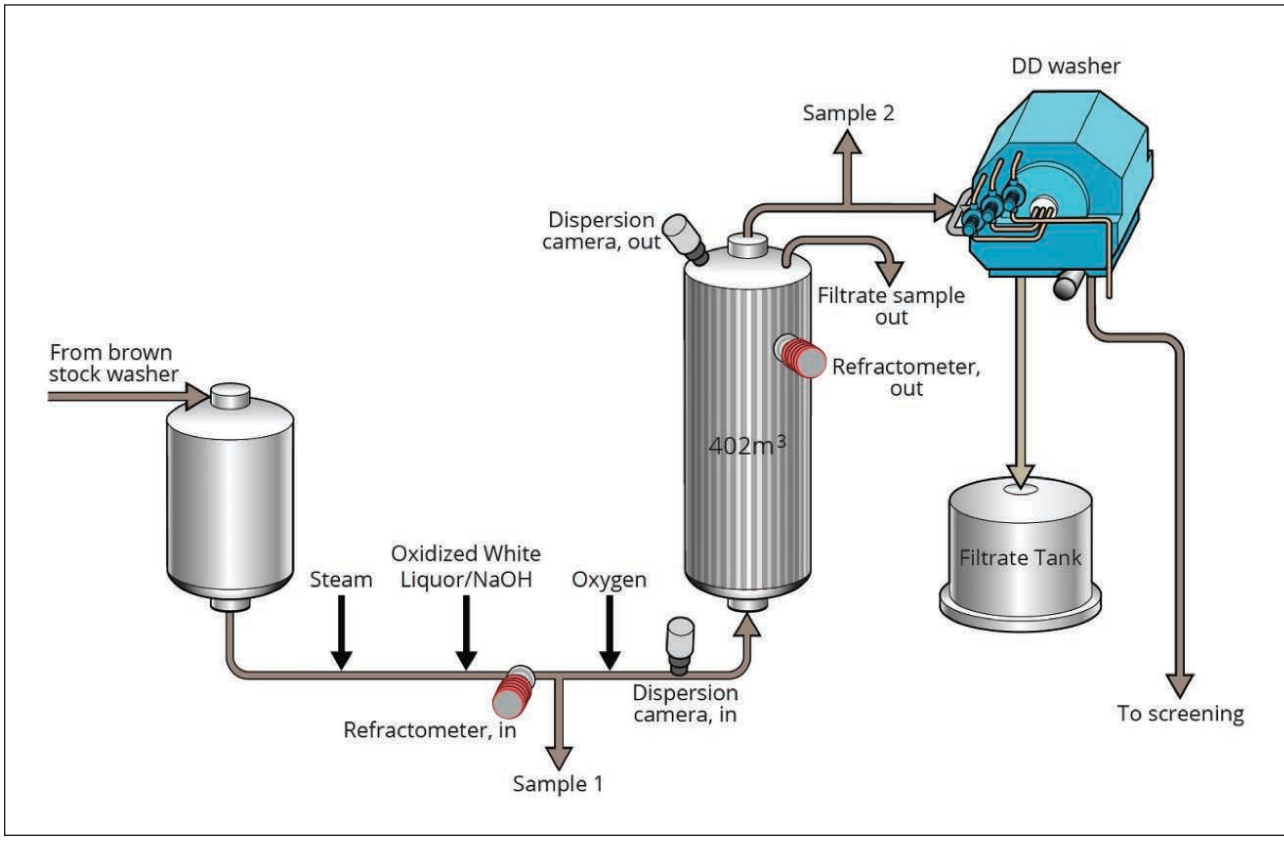
The effectiveness and potential of a powerful oxygen stage is obvious when comparing it with cooking and bleaching using a yield vs. kappa number curve, as can be seen from **Fig. 1** [4]. According to Gullichsen et al. 1992 [5], removing 1 kappa unit in cooking, decreases the yield by 0.16%, whereas removing 1 kappa unit in oxygen delignification decreases the yield by 0.12%.

The purpose of this work was to study the effects of process conditions on the dissolved solids, kappa, and pulp quality, and to quantify the state of gas dispersion in the process and the effects of oxygen bubble size on different factors.

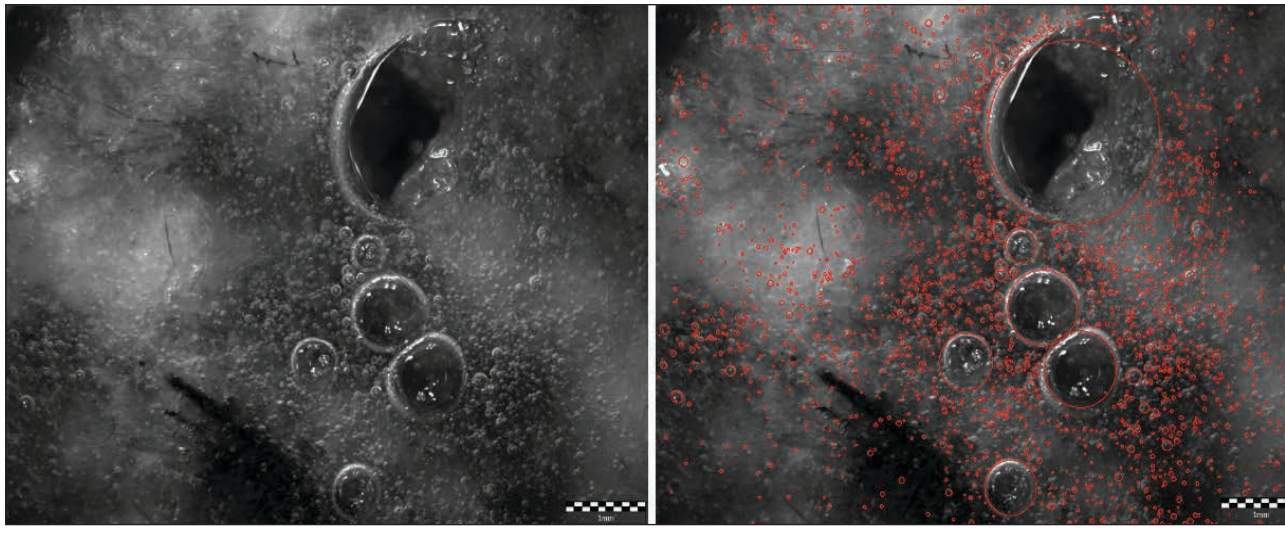
MATERIALS AND METHODS

The study was carried out by installing two continuous refractometers that measured the concentration levels (i.e., total dissolved solids [TDS]) of filtrates in the oxygen stage feed and at the top of the reactor in a Finnish hardwood kraft pulp mill (**Fig. 2**). Data from these two measurements allow us to calculate the reactor's residence time and oxygen stage's pulp yield. Simultaneously, gas dispersion was monitored in real time using a continuous Pixact Bubble Monitoring (PBM) system (Pixact Ltd.; Tampere, Finland). PBM was used to evaluate the oxygen gas dispersion, which is connected to the mixing efficiency of used oxygen charge into pulp suspension. The principle behind the PBM system was presented in detail in an earlier study [6].

A complete 2-week mill trial was performed. The alkali



2. Installation sites of the refractometers and Pixact Bubble Monitoring (PBM) systems in the pulp mill's oxygen delignification (NaOH = sodium hydroxide; DD = drum displacer).



3. a) Original image of bubble flow illuminated with ring light, and b) the detected bubbles are circled with red outlines on top of the image [6].

used in the first test week was oxidized white liquor. During the second week of testing, fresh caustic (14% sodium hydroxide) was used. Three oxygen dosages were used (5 kg/a.d. metric ton, 6.5 kg/a.d. metric ton, and 8 kg/a.d. metric ton) at three different mixer rotation speeds (1000 rpm, 1088 rpm, and 1175 rpm), three operating pressures (280 kPa, 330 kPa, and 380 kPa), and three reactor temperatures (90°C, 92.5°C, and 95°C). Consistency was quite stable, at about 11%, and the alkali dosages were controlled so that the pH was about 10.5 in the discharge of the reactor. In test week 1, we had 10 test points and in week 2, we had 15 points.

Pulp samples were taken from the oxygen stage feed pulp (sample 1) and after the oxygen reactor (sample 2), as denoted in Fig 1. The kappa number was measured from the pulp samples. The filtrate sample was also extruded from the pulp through wire gauze after sampling. The pH, conductivity, and chemical oxygen demand (COD) were measured from the filtrates. The samples were analyzed using the following methods:

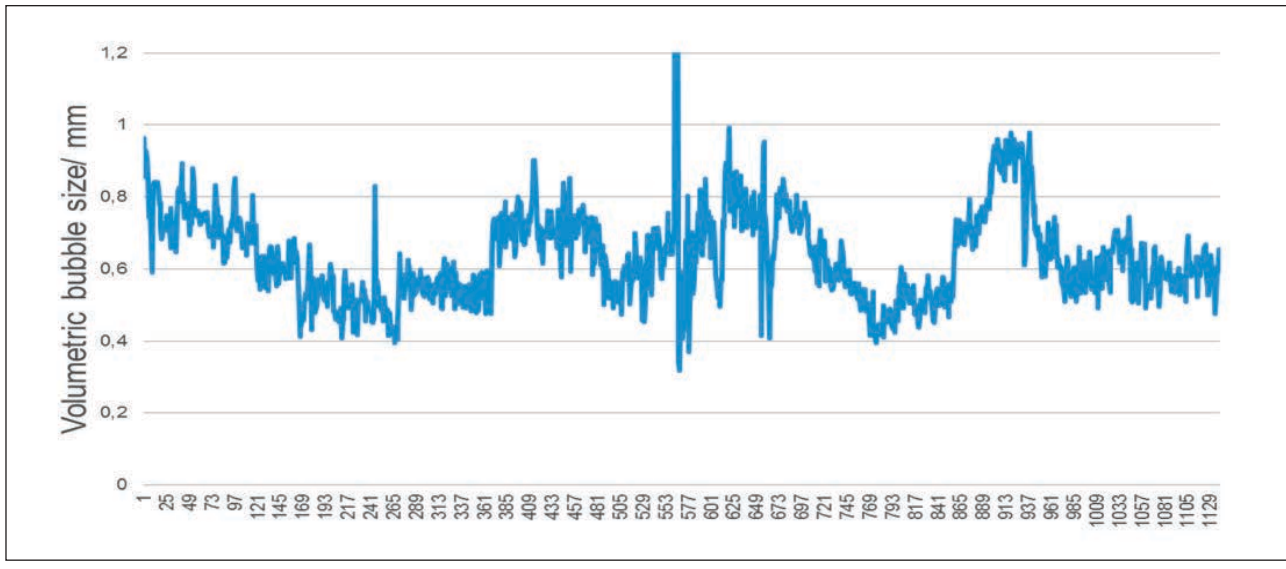
- Determination of dry matter content (analytical) (ISO 638 "Paper, board and pulps — Determination of dry matter content — Oven-drying method")
- Determination of dry matter content (on-site), refractometer
- Conductivity (on-site), Mettler Toledo conductivity meter (Columbus, OH, USA)
- pH (on-site), Mettler Toledo conductivity meter
- COD liquor, samples filtrated using 1.6 μm grade GF/A paper and then analyzed in a COD analyzer (ISO 15705 " Water quality — Determination of the chemical oxygen demand index [ST-COD] — Small-scale sealed-tube method")
- Pulps, determination of kappa number (ISO 302 "Pulps — Determination of Kappa number")

RESULTS AND DISCUSSION

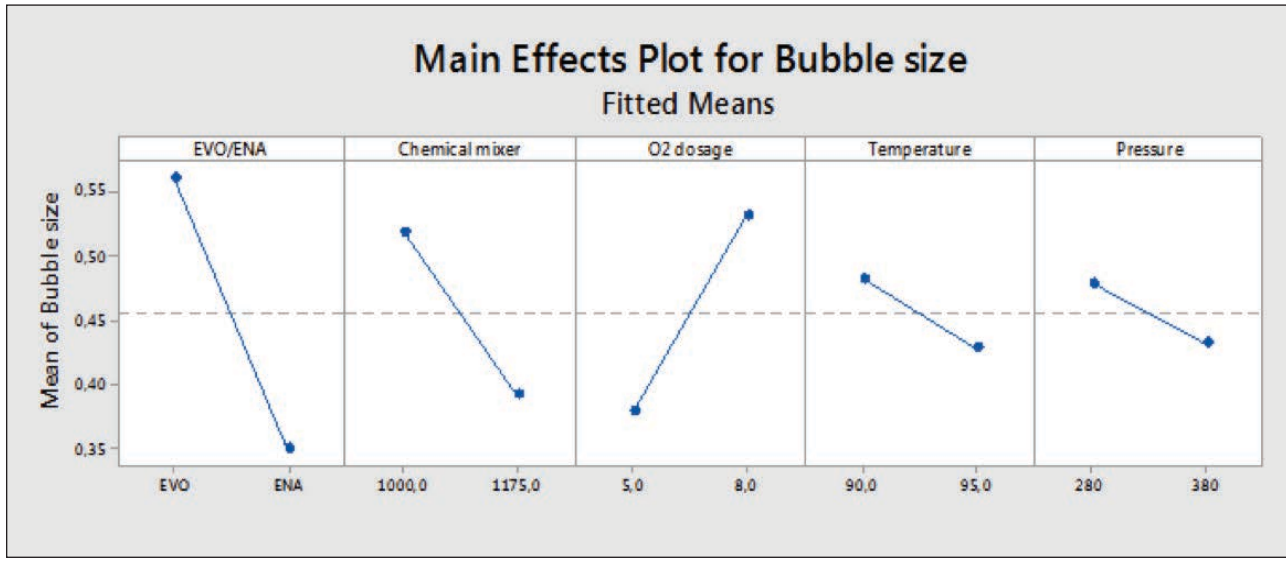
Continuous PBM system

We used an image analysis algorithm developed by Pixact Ltd. to detect gas bubbles and measure their diameters. **Figure 3a** shows an original image of the bubble flow [6]. Figure 3b shows the detected bubbles. The bubble size data produced by PBM are averaged over 60 s and reported every 30 s to the mill's data collection and as a row in an Excel file. The data include numerical, Sauter diameter, and volumetric distributions of bubble size and other relevant statistical values, such as mean and standard deviation values; percentiles of D10, D50, and D90 of the distributions; and number of bubbles per image. This makes it possible to calculate and monitor different bubble size fractions under different process conditions.

Figure 4 [6] shows the volumetric bubble size measured over the 1.5-month period. The measurements and pictures obtained (Fig. 3) indicate that gas distribution in this hardwood pulp suspension was not as homogeneous as in the softwood pulp suspension observed earlier [7]. There happened to be several very large bubbles, which were also irregularly shaped and could not be measured accurately. However, the average arithmetic bubble diameter was 48 μm under typical process conditions and the average volumetric bubble diameter was around 500 μm. The arithmetic bubble diameter is approximately equal, but the volumetric average diameter is 10 times higher than the measurements made on the softwood pulp line [7]. Figure 4 also displays the short-term and long-term variation in the average volumetric bubble size, ranging from 0.4 mm to 1 mm. This means that the surface area of the bubbles enabling the dissolution of oxygen changes in the same ratio. The existence of large bubbles also might promote the coalescence and uneven distribution of oxygen in the pulp. The mill has been in a normal production state, including typical process variations: production, chemical dosage, pulp consistency, etc.



4. Volumetric bubble size after the oxygen mixer on a Finnish hardwood pulp fiber line during a measuring period of 1.5 months [6].



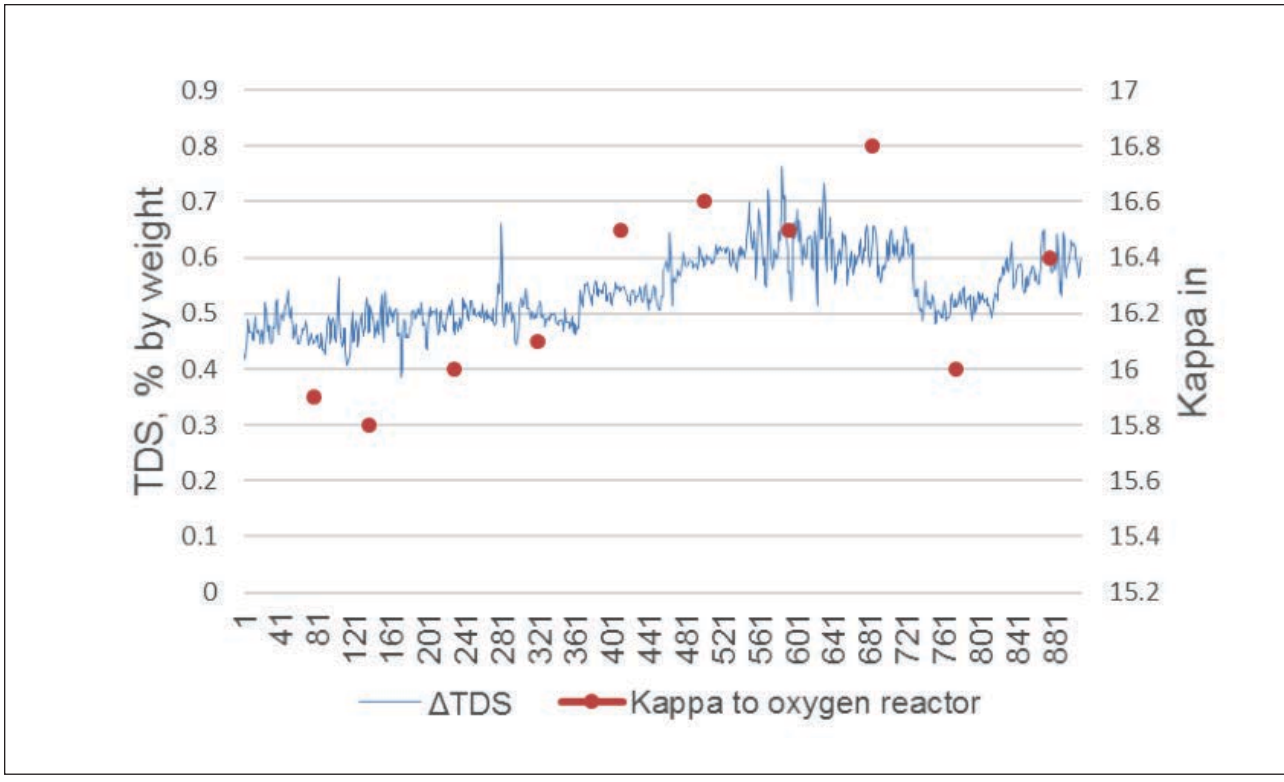
5. Results from the factorial analysis, main effects plot for bubble size (EVO = oxidized white liquor; ENA = sodium hydroxide) [6].

The results from the factorial analysis (**Fig. 5**) [6] confirmed that all the trial factors had a statistically significant effect on the bubble size. The effect of the alkali form (EVO = oxidized white liquor and ENA = sodium hydroxide) was the most significant, but the rotor speed of the chemical mixer also had a remarkable effect, even with a small increase from 1000 rpm to 1175 rpm. The results from the factorial analysis also confirm the assumption that the measuring method is able to measure the effect of mixing efficiency and other process parameters on the state of dispersion.

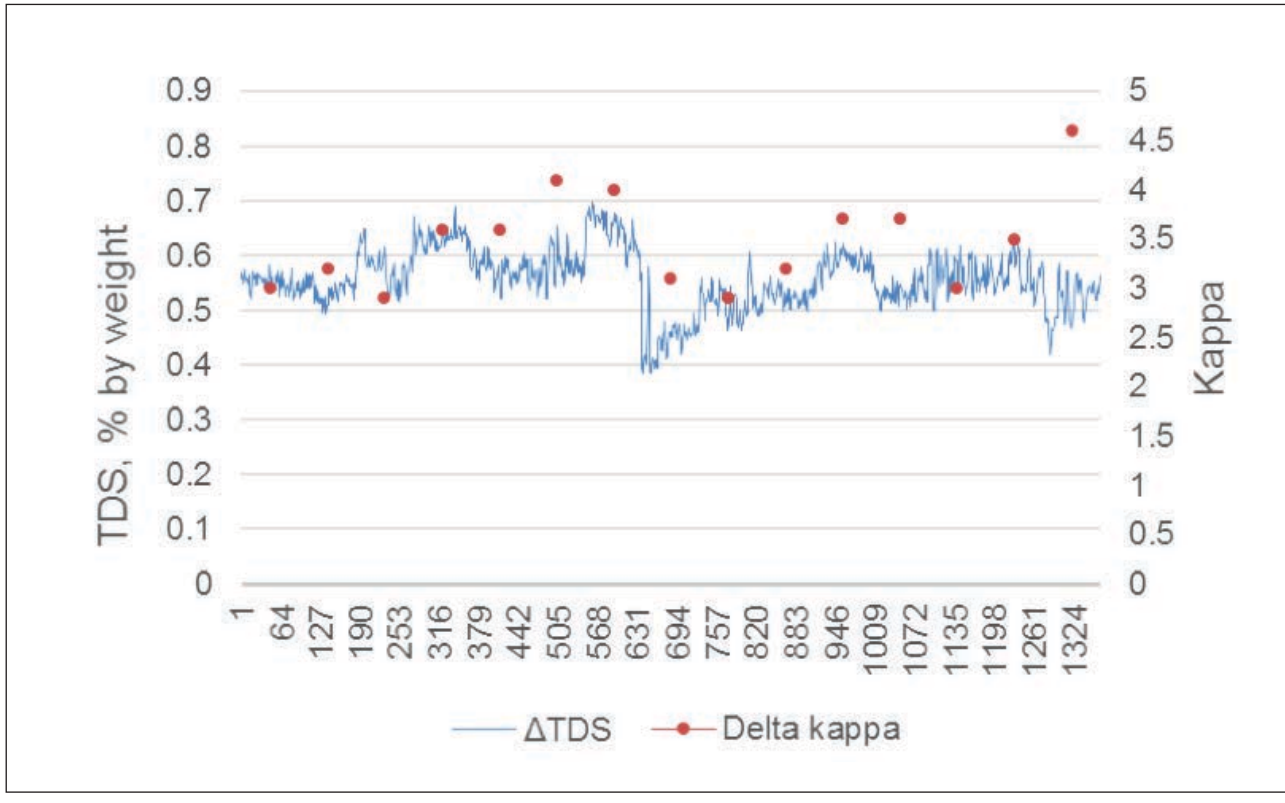
Total dissolved solids (TDS) measurement by process refractometer

The refractometer measurements allowed us to calculate the change in the dissolved solids within the oxygen reactor. As the figures illustrate, this correlated clearly with the oxygen delignification feed kappa (**Fig. 6**) [8] and changes in kappa (**Fig. 7**) [8]. Changes in temperature also clearly affected the behavior of dissolved solids (**Fig. 8**) [8].

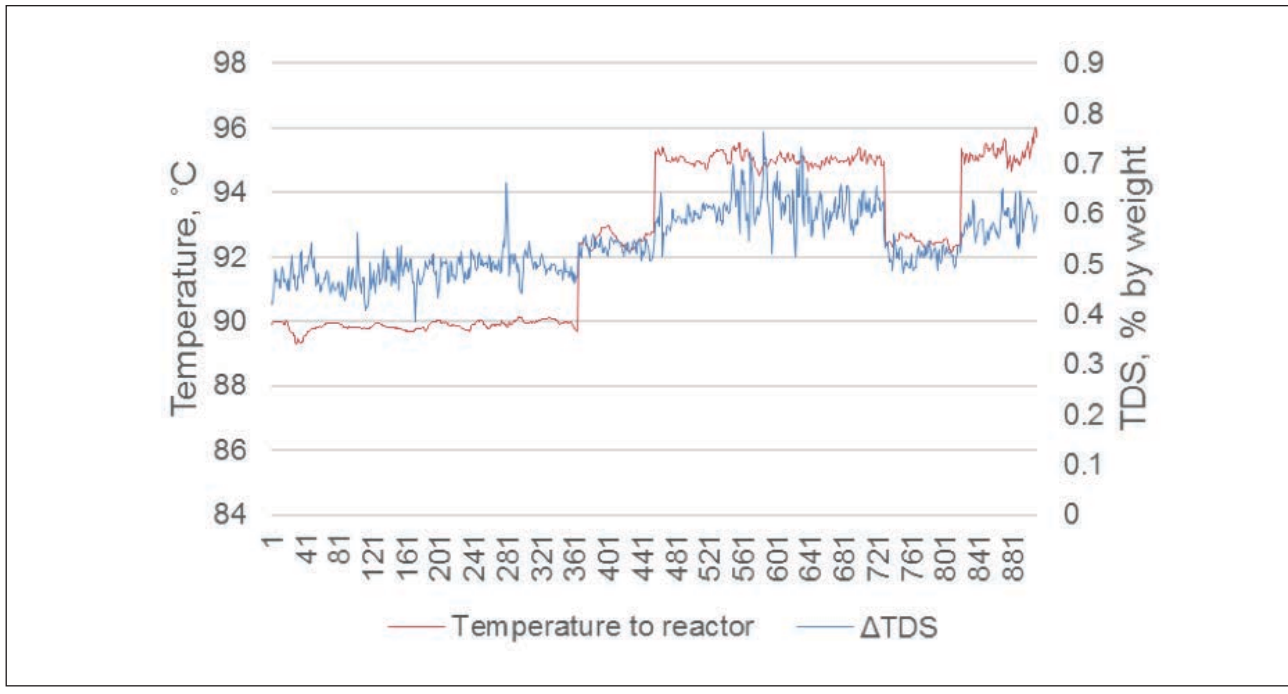
As expected, the medium consistency (MC) mass flows were plug flow in the oxygen reactor. Gas flows, however, might find an easier passage for themselves, which leads to their channeling. Dissolved solids in the liquid phase will also be seen to pass in a plug-flow like way. Measuring the TDS before and after the oxygen stage and aligning these two measurements allows us to calculate the reactor's residence time. **Figure 9** [8] shows how the residence time calculation was carried out using TDS measurements. The average residence time, when pulp goes from measurement point 1 to point 2, was 36 min. The larger differences in the graphs



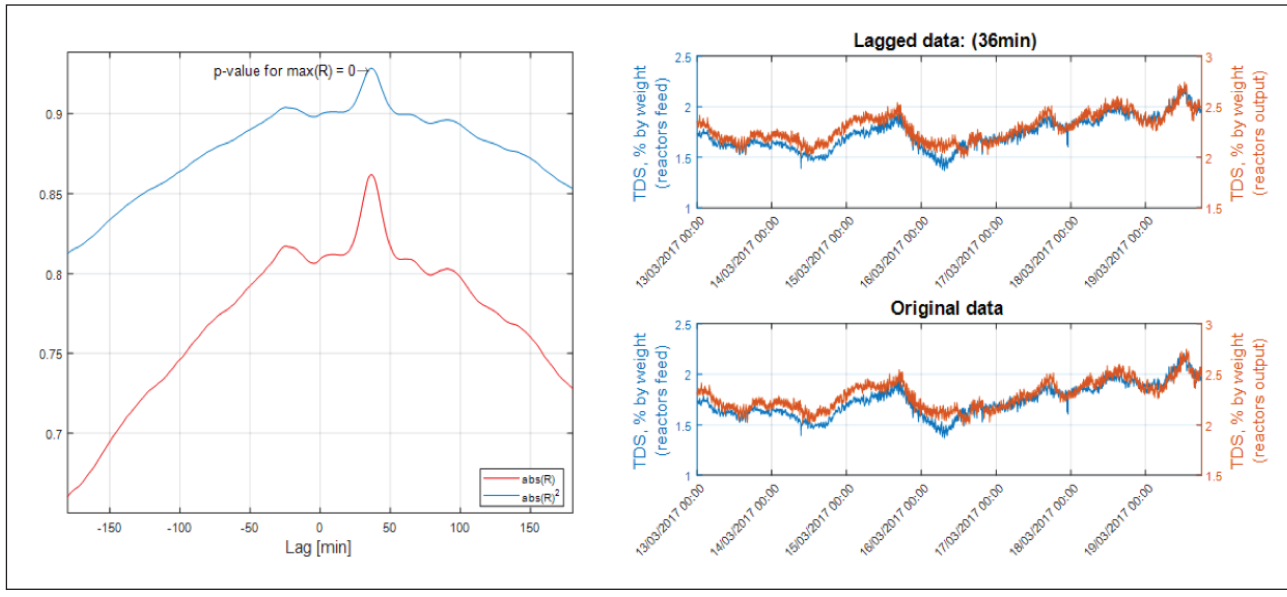
6. ΔTDS (total dissolved solids) and kappa$_{in}$ to oxygen reactor (test week 1) [8].



7. ΔTDS (total dissolved solids) and Δkappa$_{in}$ to oxygen reactor (test week 2) [8].



8. Temperature and ΔTDS to oxygen reactor (test week 1) [8].



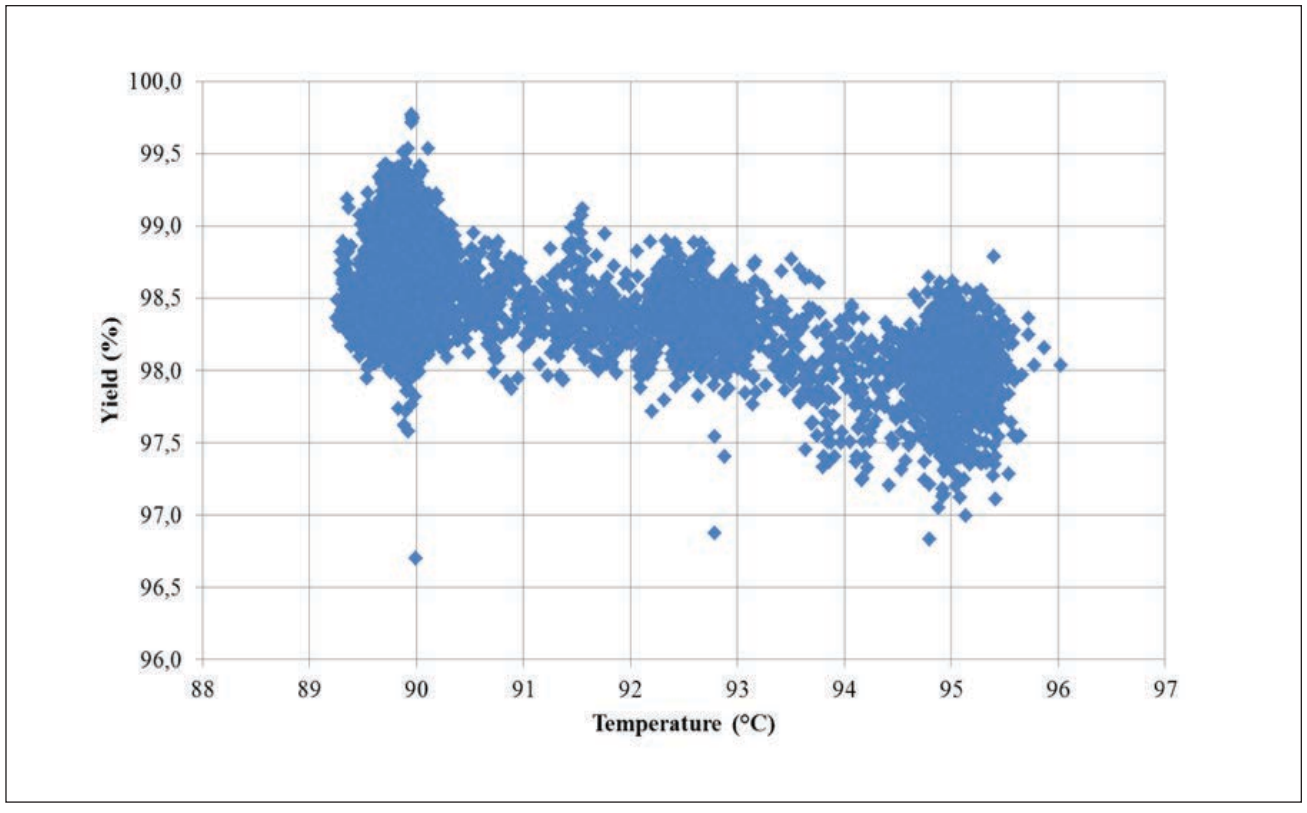
9. Calculation of the oxygen stage time delay [8].

represent changes in production levels and times when the delay deviated from the average delay of 36 min. The results were consistent with the delays calculated from the oxygen stage feed.

The measurements, alongside additional measurements and calculation, allow us to calculate the oxygen stage pulp yield. **Figure 10** [8] shows the yield as a function of reactor temperature. The pulp yield seems to decrease when the reactor temperature increases. We did not observe an increased kappa drop as a function of temperature. A lower temperature leads to an increased pulp yield in oxygen delignification, which leads to lower wood consumption. The level of the pulp yield is lower, which would be expected based on the literature [5].

CONCLUSIONS

The PBM system can be used for continuous monitoring of gas dispersion in oxygen delignification. In addition to the improvement of general knowledge related to the process, this method could form the basis for adjusting the oxygen



10. Oxygen stage pulp yield calculation as a function of temperature [8].

charge and gas dispersion in delignification processes.

TDS measurements at the oxygen stage feed and at the oxygen reactor outlet allow us to calculate the changes in dissolved solids within the oxygen reactor (delta concentration) and provide a new way of calculating the residence time in the oxygen reactor, as well as pulp yield. Measurements at the oxygen stage feed also indicate the amount of washable dissolved material coming through to the oxygen stage. These TDS measurements, together with other measurements, allow for future monitoring and controlling of the oxygen process. **TJ**

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LITERATURE CITED

1. McDonough, T.J., in *Pulp Bleaching: Principles and Practice* (C.W. Dence and D.W. Reeve, Eds.), TAPPI Press, Atlanta, GA, USA, 1996, pp. 213-239.
2. Agarwal, S., *J. Pulp Pap. Sci.* 25(10): 361(1999).
3. Elton, E., Magnotta, V., Markham, L., et al., *Tappi* 63(11): 79(1980).
4. Pikka, O., Vesala R., Vilpponen, A., et al., in *Chemical Pulping*, Finnish Paper Engineers' Association, Jyväskylä, Finland, 2000, pp. 616-664.
5. Gullichsen, J., Kolehmainen, H., and Sundqvist, H., *Pap. Puu* 74(6): 486(1992).
6. Mutikainen, H., Kopra, R., Pesonen, A., et al., "Measurement, state, and effect of the gas dispersion on the oxygen delignification," *Int. Pulp Bleaching Conf.*, ABTCP, São Paulo, SP, Brazil, 2017.
7. Mutikainen, H., Peltonen, K., Pikka, O., et al., "Characterization of oxygen dispersion in delignification process," *Int. Pulp Bleaching Conf.*, INP Pagora, Grenoble, France, 2014.
8. Kopra, R., Mutikainen, H., Pesonen, A., et al., "Using online total dissolved solids (TDS) measurements for investigating the performance of oxygen delignification," *Int. Pulp Bleaching Conf.*, ABTCP, São Paulo, SP, Brazil, 2017.

ABOUT THE AUTHORS

Oxygen delignification continues the delignification that starts in the cooking process in a more selective manner than occurs in the digester. It can achieve economic savings by optimizing the oxygen stage. It affects the quality and yield of the pulp and also the consumption of energy and chemicals.

We have been the pioneers of oxygen dispersion research and have been studying the behavior of dissolved solids during brownstock washing and oxygen stages for approximately 10 years. We have also published our findings in several journals and presented our results at various conferences.

The most challenging aspect for us has been to ensure that our measurement technology is reliable enough to allow us to obtain accurate data on the dispersion in challenging processing conditions. We have cooperated in this field for several years now with bubble imaging device manufacturers. The durability and accuracy of imaging is finally at a level where it can be used in the process for months without maintenance. The total dissolved solids (TDS) measurements have succeeded very well because of our extensive experience.

The most important finding of this study is most likely that we have managed to prove that it is natural for the bubble size to vary widely and that we can also affect this by changing the process conditions. The TDS measurement, on the other hand, has provided a new point of view from which to measure the change in dissolved solids during the oxygen stage. This change correlates on some level with kappa reduction.

Previously, we studied the performance and bubble size of a softwood line's oxygen stage. To our surprise, the dispersion of the bubble size was very different on the hardwood line in comparison with the softwood line. The TDS measurements enabled us to calculate the reactor's residence time and pulp yield. The results seem to indicate that temperature changes have a rather significant effect on the yield in the oxygen stage.



Kopra



Mutikainen



Dahl

The measurements provide mills with an opportunity to monitor the oxygen stage in a completely new way. This information will also provide tools to optimize the process parameters.

The next objective is to get references from other mills, especially from those that produce eucalyptus pulp. Our long-term goal is to start using these measurements when making adjustments to the oxygen stage.

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