Measurement of kappa number variability on the fiber level

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ABSTRACT: A method recently developed to measure the kappa numbers of single fibers by staining with a fluorescent dye, acridine orange (AO), has now been used to develop an automated flow-through instrument that permits routine analysis of kappa number on thousands of fibers in a pulp sample. The instrument can reliably collect and process fluorescent images of AO-stained fibers to give the fiber kappa number distribution of a pulp sample in a few minutes. Fluorescence measurements in the flow-through instrument are found to be consistent with those made with a fluorescence microscope, provided the signal processing in the flow-through instrument is handled properly. The kappa number distributions of pulps analyzed with a density gradient column compare favorably to those measured with the flow-through instrument.

Application: A new tool is available for measuring kappa number distributions and can be used to improve the uniformity of pulp.

Uniform pulp has many benefits for the economic and environmental performance of the pulping industry. Process improvements that promoted uniformity made extended delignification possible, lowering bleaching costs and enhancing environmental performance [1]. A more uniform pulp has superior strength [2], although this improvement may not be observed in some bleached pulps [3]. In high-yield pulping, greater uniformity leads to fewer knotter rejects at a given kappa number [4], and lower reject levels allow an increase in the target kappa number, shortening cook times and improving digester throughput.

The measurement of pulp uniformity at the fiber level began in the 1970s. Paulson used a density gradient column to measure the lignin content distributions of thin and thick chips as well as chips from compression wood [5]. Chemical separation in the density gradient column takes advantage of the fact that lignin and cellulose have different densities. Fibers will migrate to those sections of the column that match their densities. Recently, Rudie and Boyer used a density gradient column to compare mill and laboratory pulps and found that mill pulps tend to be less uniform than the pulps produced in a lab [6]. They also used Fourier transform infrared spectroscopy to validate the density gradient method by showing that both methods produce similar distributions for fiber kappa number.

A new method to measure pulp uniformity has been developed at the University of Washington [7]. This method uses the fluorescence of fibers stained with acridine orange to measure the kappa number. After a large number of fluorescent stains were screened as lignin indicators, acridine orange (AO) showed a noticeable color shift in the presence of lignin. The ratio of the spectral peak height of the dimer form of AO (red) to the peak height of the monomer form of AO (green) was shown to correlate linearly with lignin content. On the basis of this ratio of red to green, measurements of lignin content distributions were made under a fluorescence microscope.

Using the AO fluorescence microscope method, researchers have measured the kappa number distributions for numerous pulps. Nonuniformity has been found even in pulps carefully prepared with thin chips under mild pulping conditions [8].

While the acridine orange fluorescence method is useful for measuring fiber kappa numbers, it has some limitations. First, the method is slow to run with a fluorescence microscope. Only one fiber at a time can be scanned, which means only 20 or 30 fibers may be analyzed in an hour—hardly sufficient to construct a histogram of fiber kappa numbers. In addition, the calibration curve relating fiber kappa number to the red-green ratio is not universal. The species of wood and the presence of significant quantities of repolymerized lignin may affect the calibration between the kappa number and the ratio of red fluorescence to green fluorescence.

To be used for routine analysis, the AO fluorescence method must be modified for use in a flow-through analysis apparatus. Fluorescence is the ideal spectroscopic method to use in flow-through analysis systems because of its large signal-to-noise ratio. The objective of this research, then, was to develop and apply a flow-through fluorescence image analyzer that can use the fluorescence of AO-stained fibers to measure single fiber kappa numbers.

This instrument could be applied in investigating the effects of chip properties and digester configurations on pulp uniformity. The instrument could also be used to improve the calibration of the AO fluorescence method by allowing many pulps to be thoroughly analyzed in a reasonably short period of time. Here, we describe the development and evaluation of the instrument and present some preliminary analyses of laboratory and commercial pulps.

APPARATUS

The flow-through fluorescence image analyzer, or fiber kappa analyzer (FKA), consists of a hydraulic section, an optical section, and a data processing section. These components function together to deliver fibers to a sensing zone, to capture images of their fluorescence, and to quantify red and green fluorescence from the captured images.

Figure 1 shows a flow diagram for the FKAs hydraulic section. The AO-stained fiber sample slurry is mixed with dilute
sodium hypochlorite from Gear Pump 1 just before it reaches the flow cell. Hypochlorite reacts with the acridine orange in solution and reduces background fluorescence in the image, which would otherwise interfere with a quantitative measurement of the intensity of fiber fluorescence. The flow cell is made from a 500 µm, soft polyethylene gasket sandwiched between a plexiglass back and a glass window on the front of the cell. The fibers are filtered out of the stream after the flow cell, and the total flow is pumped out with Gear Pump 2 at approximately 40 mL/min. A tank after Gear Pump 2 ensures that air will not back up into the pump and cause it to lose its prime.

The optical section of the instrument is shown in Fig. 2. It resembles a modern epi-illumination fluorescence microscope. Blue light from a 5 Joule xenon strobe passes to a dichroic mirror, where it reflects onto the AO-stained fibers. The stimulated fluorescence ranging from green to red wavelengths is collimated by the objective lens and is transmitted through the first dichroic. A second dichroic mirror splits green and red light. Red light passes through a 590 nm long pass filter to a CCD (charge-coupled device) camera, and green light passes through a 510-570 nm bandpass filter to a second CCD camera. Both cameras are fitted with video lenses to focus the collimated light into a fluorescence image on the CCD sensor.

A personal computer fitted with frame-grabber circuit boards and a data acquisition card initiates the capture process, and a custom-made timing box synchronizes the cameras with the flash lamp and frame-grabbers. Once the images are transferred to the PC, National Instruments LabView software handles data processing. The raw fluorescence images are flattened to correct for vignetting, and the fluorescent background is removed. A binary threshold locates objects in the field, and morphological processing identifies fiber clumps and single fibers. The red and green fluorescence ratio is calculated for each fiber, and the data are cataloged into an array.

**ANALYSIS PROCEDURE**

Analysis of wood fibers with the flow-through instrument first requires that the instrument be aligned and calibrated. Using a slide with an image of a grid, backed with fluorescent paper, the technician aligns the red and green images to within a pixel and then calibrates the image analyzer using a fluorescence standard. The calibration corrects for uneven illumination of the field, vignetting in the images, and fluctuations in camera gains. The calibrated images are flattened, and they have reproducible responses to red and green fluorescence.

The pulp sample is prepared in a liter of 0.00005 M acridine orange at a consistency of 0.01%. The slurry is blended for 5 s with a commercial Waring blender to separate fiber clumps. The pulp is allowed to react for at least 10 min with the acridine orange before it is analyzed in the FKA.

**Instrument validation**

To assess the performance of the FKA, we used uniform fluorescent polystyrene beads manufactured as standards for flow cytometry. Uniform fibers would be preferable, but no fiber source has been identified that is uniform enough in the fluorescence spectrum to evaluate the instrument’s performance. The measurement of the signal-to-noise ratio from the uniform standards can be used to estimate the FKA’s precision in the red/green measurement of a wood fiber. Figure 3 shows the
measured red/green distribution of uniform 25 µm beads flowing through the FKA.

The mean red and green fluorescence intensities of these beads are approximately the same as those of an average stained fiber. The coefficient of variation of the R/G ratio for the flowing beads is 6.5%, whereas that of a single bead repeatedly measured in one position is 3.2%. For a larger particle, such as a fiber, the random errors decrease as a result of an increased number of pixel samples. The coefficient of variation of the R/G ratio for a single fiber repeatedly measured in one position is 0.49%. Applying the assumption that variance is additive, a coefficient of variation of 5.5% can be estimated for a uniform fiber source, which corresponds to an uncertainty of ±2 kappa number units for a fiber of kappa number 30. This low uncertainty guarantees that the variance in the instrument contributes negligibly to the variance measurements of the pulp samples.

**Comparison with microscope method**

We used uniform laboratory pulps that had been prepared previously for development of the AO fluorescence method [8]. These samples were analyzed with the fiber kappa analyzer to verify that earlier results could be reproduced with the new instrument. **Figure 4** compares the distributions of two representative pulps measured on the FKA with the corresponding distributions measured by the fluorescence microscope method. The microscope distribution is noisy (with roughly 50 fibers measured per sample), but the resolution is sufficient to illustrate that the distributions match fairly well.

**Validation with independent samples**

The FKA was used to analyze pulp samples prepared and analyzed on a density gradient column at the Institute of Paper Science and Technology (IPST). These IPST pulps were produced in cooks with a liquor-to-wood ratio of 6:1, a sulfidity of 30%, and a 24% effective alkali charge. Shown in Figs. 5–8 are the kappa number distributions of some of the IPST pulps measured with the FKA and with the density gradient column.

The pulps in Figs. 5 and 6 were prepared from 2.5 mm-thick southern pine chips. Cook 4 (Fig. 5) was pulped at 165°C to an H-factor of 1892. Cook 9 (Fig. 6) was pulped at 154°C to an H-factor of 786 [9]. Error estimates for the FKA sample in Fig. 6 reflect Poisson counting statistics. Both Figs. 5 and 6 show that analyses performed with the FKA produce results similar to results of analyses conducted with a density gradient column.

The pulps in Figs. 7 and 8 were prepared at IPST from chips that were 10 mm thick. Cook 3 (Fig. 7) was pulped at 170°C to an H-factor of 2803, and Cook 7 (Fig. 8) was pulped at 160°C to an H-factor of 1274 [9]. These thick-chip pulps have wider distributions in kappa number than the thin chip pulps of Cooks 4.
The favorable comparison of the kappa number distributions as measured by the FKA and by the density gradient column validates the accuracy of the flow-through analyzer. The instrument has since been applied to measuring the kappa uniformity of various laboratory and commercial pulps. Some cases of interest are presented here.

The first set of pulps (provided by a corporate research facility) included softwood chips segregated by size and pulped separately under identical pulping conditions. The samples were pulped at a temperature of 165°C with an effective alkali charge of 14.5%. The liquor-to-wood ratio was 3.5, and the sulfidity was 27.5%. A control sample with the original chip size distribution was also pulped.

Based on a diffusion-limited pulping model, all the pulps should look similar at the low end of the distribution. However, the thick chips should have more high-kappa-number fibers, which come from the chip center. Figure 9 shows the fiber kappa number histograms for the thickness study. The kappa number distributions in Fig. 9 behave as expected. The low target kappa number for these pulps explains why the differences between chip classes are not larger. At the final average kappa number of 19, many of the fibers on the low side of the distri-
butions are in a residual delignification stage, causing the distributions to narrow. **Figure 10** shows that the fiber kappa number distribution of the control pulp can be predicted from the weighted sum of the different chip classes, adding credibility to the distributions shown in Fig. 9.

Another set of pulps analyzed by the FKA was also provided by a corporate research facility. Softwood pulps were prepared by a laboratory batch digester configured to simulate EMCC, EMCC–AQ, and conventional kraft cooking with typical commercial pulping conditions. **Figure 11** shows the distributions of representative pulps of kappa no. 22 from each digester configuration. Surprisingly, no significant differences in uniformity were observed between these pulps.

If we study pulps of lower kappa number, however, some differences in the uniformity that result from these different pulping technologies may be seen. **Figure 12** shows the relationship between the coefficient of variation of the single fiber kappa number distribution and average kappa number for the three cooking configurations. In the region between kappa no. 22 and kappa no. 28, the coefficient of variation is about the same for all three pulp types—hence the similarities between the distributions at kappa number 22. Below this region, the coefficient of variation increases for EMCC–AQ pulping, while it stays fairly constant for conventional and EMCC pulps.

At this late stage in pulping, a constant coefficient of variation results from slow delignification in fibers of low kappa number, whereas an increasing coefficient of variation suggests that these fibers are still experiencing fairly rapid delignification. The presence of anthraquinone in the EMCC–AQ cook may result in more reactive lignin at the end of the cook. McDonough and Herro previously found a similar result in studying the effect of AQ on bleachability. They hypothesized that anthraquinone inhibits lignin condensation and bond formation between lignin and carbohydrates during the cook, thus improving the reactivity of lignin remaining in a low-kappa-number pulp [10].

Comparison of kappa number distributions between laboratory pulps and commercial pulps indicates that pulp uniformity can be improved through the manipulation of cooking parameters and chip quality. **Figure 13** compares the kappa number distribution of a laboratory pulp with that of a commercial pulp and shows the extent of the improvement that may be achieved under ideal pulping conditions. The nonuniformity in the lab pulp, which was prepared from thin chips pulped at a low temperature with high chemical charges and a high liquor-to-wood ratio, suggests that there is a limitation on the uniformity achievable in a kraft cook. However, there is an opportunity for improving uniformity in commercial pulps because the commercial pulp is considerably less uniform than the laboratory pulp, despite having a lower average kappa number.

**CONCLUSIONS**

The FKA can rapidly measure the red to green fluorescence ratio of many fibers, reproducing the results of the acridine orange fluorescence microscope method for determining fiber kappa number distributions. The instrument’s signal-to-noise ratio is sufficient for resolving the important features of the distributions. The acridine orange fluorescence method produces results similar to those of a density gradient column, which has been the commonly accepted method for measuring kappa number distributions.

Using the FKA, pulps from different chip sizes were shown to exhibit nonuniformity, which would be expected for diffusion-limited pulping. The instrument also measured the uniformity of pulps from different digester configurations and found only small differences in the kappa number distributions. The presence of anthraquinone in a cook, however, was found to affect the behavior of the kappa number distributions, probably by improving lignin reactivity at the end of the cook. Both commercial and laboratory pulps have been measured with the FKA. Commercial pulps are more nonuniform, but laboratory pulps also exhibit nonuniformity.

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**LITERATURE CITED**


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The authors of this paper received the 2000 David Wetterborn Award at the 2001 TAPPI Pulping Conference for this work.

This paper is also published on TAPPI’s web site <www.tappi.org> and summarized in the December Solutions! for People, Processes and Paper magazine (Vol. 85 No. 12).
INSIGHTS FROM THE AUTHORS

New technology to rapidly measure the kappa number distribution of a pulp sample has been developed. Lower variability in the kappa distribution may allow for lower average kappa numbers in the digester, reducing the charge of bleaching chemicals required to produce a particular product.

Methods of measuring the distribution of fiber kappa number have been developed in the past. These methods include a density gradient column, Fourier transform infrared microscopy, and fluorescence microscopy. The hurdle all these methods have failed to clear is an economic one. In short, they require a substantial investment of time to produce a small quantity of data. The idea in developing the flow-through instrument was to take an existing fluorescence microscopy method and adapt it to be applied rapidly in an automated instrument.

The development of the instrument required a wide range of resources, including wood chemistry, optics, electronics, and computer programming. To contend with the diverse skill requirements, researchers from paper science teamed up with researchers from analytical chemistry.

One of the most personally rewarding experiences I had during this research was realizing that unexpected results, which may be difficult to interpret at first, often yield the most interesting findings. We were surprised when we first found results suggesting that AQ pulps may be less uniform at low kappa numbers than pulps of conventional cooks. After a while, we realized that this finding suggests that AQ improves delignification rates for low-kappa-number fibers. Although others have previously noted this possibility in studies that were probably better suited for verifying the hypothesis, it was a new discovery for me at the time. That experience will always remind me that effective research often comes from understanding the data that disproved your hypothesis rather than from creating a hypothesis and finding data to support it.

Richard Gustafson’s research group at the University of Washington continues to use the instrument to make measurements on pulp samples and assess the effects of pulp uniformity on downstream processing and pulp properties. The fluorescence imaging technique is also being applied to measuring single fiber properties other than kappa number.

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RESEARCH NEWS BRIEFS

Metso and Dow partner to develop new paper coating process -- Metso Paper and Dow Chemical Company’s Emulsion Polymers unit have signed a cooperative agreement to develop and bring to market a new paper and board coating process based on multi-layer curtain coating. The plan calls for Dow to develop the coating chemicals and colors, with Metso developing the coating station technology.

New owners for Beloit’s Rockton R&D facility -- The former Beloit Corporation Research and Development facility in Rockton, Illinois, USA, has been purchased by Paperchine, Inc., a company established in 2000 by a group of former Beloit executives. The deal was expected to close at the end of October. Paperchine offers technical and engineering services, and provides parts to the paper industry.

P&G acts to protect trade secrets -- The Procter & Gamble Company has filed suit against Potlatch Corporation to protect trade secrets in the manufacturing technology used to make “Bounty” towels and “Charmin” bath tissue after Potlatch hired two key technical experts from P&G. The complaint alleges the former P&G employees have substantial knowledge of critical company trade secrets and confidential information relating to P&G’s through-air-drying paper-making technology and processes.