Estimating the pulping yield by carbohydrate analysis

DAVID VAALER, KRISTIN SYVERUD, BERIT SEEM, AND STØRKER T. MOE

ABSTRACT: A method has been developed for estimating the pulping yield from the composition of the carbohydrate content of the pulp. When yield-increasing additives such as anthraquinone and polysulfide are used, the increase in yield can be estimated from the content of glucomannan. The utility of this method has been confirmed in both laboratory experiments and full-scale mill experiments. The carbohydrate composition was determined with enzymatic hydrolysis followed by high-performance liquid chromatography (HPLC).

Application: Kraft mills with continuous digesters can use this method to estimate the yield gain when additives are introduced or to control the yield when process parameters are changed.

Determining the pulping yield in a mill is not a straightforward task. In a batch digester, we can install a basket with a known quantity of chips and measure the amount of pulp produced in the basket [1]. For continuous digesters, however, this approach is not possible. Normally, the estimation of pulping yield is based on mass balances determined over a period of 3–12 months of production.

A simple and precise method for quantifying carbohydrates in pulps should therefore prove useful. Such a method has now been developed based on using high-performance liquid chromatography (HPLC) to quantify the content of carbohydrates. This analysis technique can be used to estimate yields in continuous digesters when yield-increasing additives are introduced or to determine the hemicellulose content of the pulp. The method is easy to use and is fairly inexpensive.

BACKGROUND

In conventional kraft cooking at constant sulfidity and effective alkali, the total pulping yield is related to the kappa number [2]. The following relationship has been shown to be valid for the kraft pulping of Scandinavian softwood:

$$Y = 0.14\ \mathrm{k} + \mathrm{C} \qquad (1)$$

where Y is the total yield, k is the kappa number, and C is a constant. However, the constant C changes if major pulping variables are changed, which is a disadvantage for this model.

Juvekar *et al.* have published an empirical method for determining the total pulping yield based on process parameters such as effective alkali (EA) and H-factor [3]. Several models have been published for estimating the pulping yield based on pulp properties [4–7]. In the 1970s, Kleppe estimated the yield increase during mill trials at Peterson Linerboard, Moss, Norway, by determining the percentage of mannan in the pulp [4]. However, the analytical technique for determining the mannan content was not as accurate as it is today, and no graphs were published in which the yield was plotted against glucomannan content.

Marcoccia *et al.* found a semi-empirical method for estimating the yield in the kraft pulping of Northern hardwoods on the basis on carbohydrate composition and pulp viscosity [5]. Easty and Malcolm published the "carbohydrate–lignin method" [6], which estimates the pulping yield based on the assumption that the cellulose yield is constant:

$$Y_{tot} = Y_{Cell}\frac{(C+H)}{C} + Y_{Cell}\frac{L}{C} \qquad (2)$$

where Y_{tot} and Y_{Cell} are the total pulping yield and the cellulose yield (based on o.d. wood), and C, H, and L are the weight fractions of cellulose, hemicellulose, and lignin. More recently, van Heiningen *et al.* published an improvement on the carbohydrate–lignin method in which the cellulose yield is not assumed to be constant [7]. In their method, the yield is calculated by the analysis of carbohydrate content and the measurement of viscosity.

If the pulp's carbohydrate content is to be used for determining the yield, the carbohydrate analysis has to be accurate and not too labor-intensive. In this work, we chose a method [8] in which the pulp is hydrolyzed first by commercially available enzymes [9–13]. A second hydrolysis is carried out with trifluoroacetic acid (TFA) [14–17]. Finally, the monosaccharides are detected by aqueous HPLC.

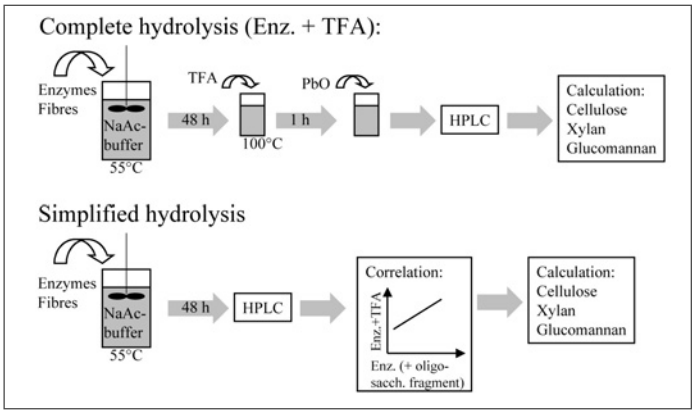
This approach eliminates the two-stage acidic hydrolysis [18] prescribed in TAPPI T 249 cm-85 and circumvents the need for specialized, extremely selective enzymes [9]. We chose HPLC instead of gas chromatography (GC) because HPLC does not entail chemical derivatization, which is necessary in GC detection of monosaccharides [19, 20]. Also, HPLC does not demand such highly specialized equipment as that required by detection methods like Capillary Zone Electrophoresis [21].

EXPERIMENTAL PROCEDURES

Enzymatic and acidic hydrolysis

A pulp sample of 2.30 g in 12.5 mL of acetic acid buffer (pH 5, 1*M* solution) and 0.5000 g of mannitol (internal standard) was diluted with water to a total weight of 125 g. The fibrous suspension was stirred at 55°C for 48 h, and 1.0 mL of enzymes was added six times at regular intervals. The enzyme mixture consisted of equal parts of ECOPULP^{CR} TX-200 C (xylanase), ECOPULP^{CR} C15 (cellulase), and Mannanase AMB (with all of these enzymes supplied by Röhm Enzymes Finland Oy).

Since primary hydrolysis with commercial enzymes normally gives a mixture of mono- and oligosaccharides, we carried out a second hydrolysis using trifluoroacetic acid (TFA) to get a complete degradation to monosaccharides. We optimized the acidic hydrolysis for each pulp



1. Schemes for the complete hydrolysis (above) and the simplified hydrolysis (below).

	CARBOHYDRATES, %			
Kraft	Total yield	Cellulose	Glucco-mannan	Xylan
Enzyme only	83.9±1.6	73.3±1.1	3.6±0.7	7.5±0.2
Enzyme + TFA	90.3±1.9	73.7±1.1	8.5±0.6	8.1±0.2
Simplified	88.9±1.6	73.0±1.2	7.6±0.3	8.3±0.2
PS/AQ				
Enzyme only	87.5±1.1	73.3±1.5	7.2±0.9	6.5±0.4
Enzyme + TFA	93.4±2.1	71.6±1.5	14.9±0.3	6.9±0.4
Simplified	93.7±2.9	71.3±2.4	15.2±0.5	7.1±0.6

Values are given with 95% confidence intervals.

I. Comparison of methods for analyzing carbohydrates.

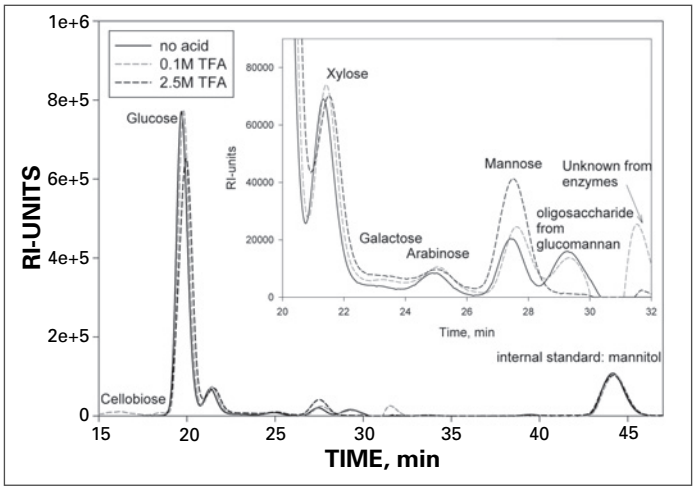
carbohydrate (cellulose, xylan, and glucomannan) by running samples at different degrees of hydrolysis using various concentrations of TFA.

The pulp was hydrolyzed with TFA in heat-resistant, sealed bottles bathed in boiling water for 1 h. The solution was neutralized with lead-(II)-oxide (PbO) and was filtered twice through a 0.22 μm filter before being injected into the HPLC. In normal lab procedure, TFA is evaporated because of its low boiling point (72°C), but we considered it too time-consuming to include this evaporation in the method. All hydrolysates were stored at 4°C.

HPLC analysis

Chromatographic separation of the hydrolysate was performed on a Chrompack Carbohydrates Pb column with deionized (18.2 MΩ), filtered, and degassed water as the mobile phase. The column temperature was 80°C. The HPLC system was a Shimadzu system consisting of a LC-6A pump, a manual injector, a CTO-10A column oven, and a RID-6A refractive index detector. The chromatogram was acquired using Shimadzu's CLASS-VP chromatography software.

Chromatogram processing. For each chromatogram, the chromatography software generated an ASCII file containing data. Data from a blind sample without pulp or mannitol was subtracted, and a new chromatogram was generated. This procedure adjusts for the monosaccharide contribution of the enzyme mixture.



2. Chromatogram illustrating the separation of monosaccharides by aqueous HPLC. The curves show the influence of acidic hydrolysis.

The ASCII file was imported into a commercial PC software program (PeakFit™ from SPSS Science) for further processing. A baseline correction was performed inside the software, and the chromatogram was fitted to the required number of individual peaks.

Calculations. The pulp kappa numbers were measured according to SCAN C 1:00, and the amount of lignin was determined according to Eq. 3 [4]:

$$\text{lignin, \%} = 0.147 \times \text{kappa no.} \quad (3)$$

Cellulose, xylan, and glucomannan were calculated as follows:

$$\text{cellulose} = \text{glucan} - 1/3\ \text{mannan} \quad (4)$$

$$\text{xylan} = \text{xylan (from xylose)} \quad (5)$$

$$\text{glucomannan} = 4/3\ \text{mannan} \quad (6)$$

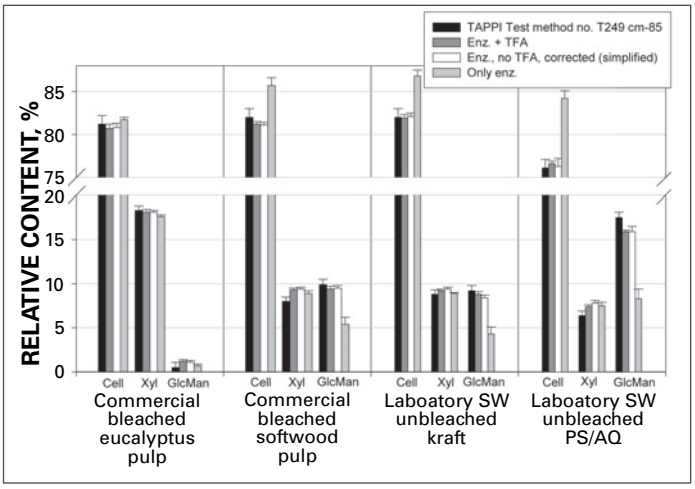
where glucan, xylan, and mannan are the anhydrosaccharides of glucose, xylose, and mannose.

Calibration. Standard solutions were prepared consisting of D-glucose, D-xylose, D-galactose, L-arabinose, and D-mannose in different ratios. Mannitol was used as an internal standard. The chromatograms were analyzed as described earlier.

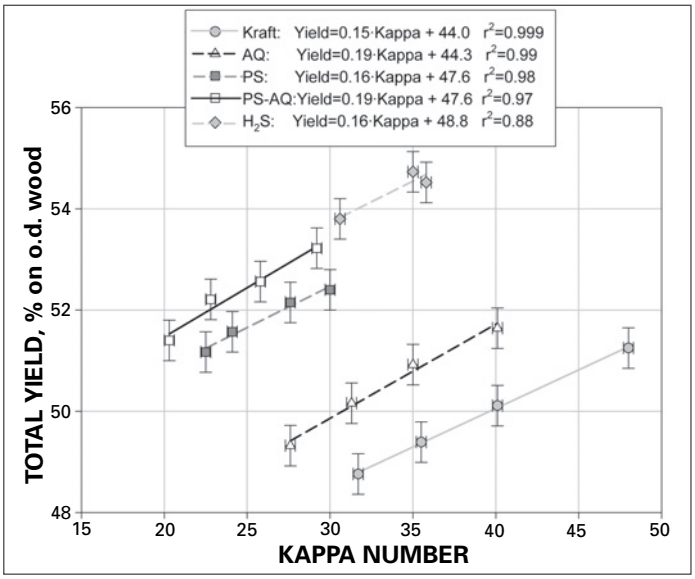
Simplified analysis procedure. To simplify the procedure, we avoided the TFA hydrolysis (and thus the use of the somewhat hazardous TFA and PbO) by correlating the amount of carbohydrates detected in the enzymatic hydrolysis with the amount found at optimum TFA hydrolysis (defined as the maximum amount of carbohydrates detected). The schemes for the complete and the simplified procedure for softwood are given in **Fig. 1**.

Yield measurement

A mixed sample of air-dried roundwood chips (50%) and sawmill chips (50%) of Scots pine and Norway spruce was laboratory screened according to SCAN CM 40:94. The accept fraction was divided between the autoclaves. Autoclave cooks were performed with a liquor-to-wood ratio of 3.5 and a maximum



3. Comparison between carbohydrate analyses of pulps by TAPPI T 249 cm-85, by enzymatic hydrolysis with TFA, by the simplified method, and by enzymatic hydrolysis only. (Error bars indicate 95% confidence intervals.)



4. Yields of different cooks. Five linear regressions were estimated, one for each cooking process. (From data published elsewhere [8].)

temperature of 163°C.

Orange liquor from Peterson Linerboard was used as the source of polysulfide. Different levels of anthraquinone (AQ) were added in the cook to increase the pulping yield. The alkali charge was 18% EA (as NaOH) on o.d. wood, and the H-factor was 950 ±50 (kappa no. 50–70). The cooks were performed as detailed elsewhere [8], and the pulping yield was measured gravimetrically.

We analyzed five mill pulps from polysulfide cooks with different AQ contents (varying from 0% to 0.06% on o.d. wood). The samples were washed, and any large knots were removed by hand because knots hydrolyze poorly. The number of removed knots was always small. The kappa number of the selected pulps did not exceed 75.

RESULTS AND DISCUSSION

Enzymatic and acidic hydrolysis

As **Table I** shows, the yield after enzymatic hydrolysis is approximately 85%. To further increase the hydrolysis yield, we performed a relatively mild TFA hydrolysis. **Figure 2** shows a typical chromatogram for a sample at different TFA concentrations in the secondary hydrolysis. As Table I and Fig. 2 show, the acid hydrolysis step is needed to completely degrade oligosaccharides, especially for xylan and glucomannan.

Most of the increase in the hydrolysis yield is attributable to the higher yield of glucomannan, although a slightly higher yield in xylan contributes to some extent. The cellulose fraction of the hydrolyzed pulp also decreases somewhat as a result of the degradation of glucose.

Simplified procedure

To save time and labor in the method, we used only one HPLC run for each pulp analysis. If we assume that the peak at 28.5–30 min is mainly caused by unhydrolyzed fragments of glucomannan (*i.e.*, a glucomannan oligosaccharide), it is possible to simplify the procedure. First, we find the sum of the relative areas of the mannose peak and the peak assigned to the glucomannan oligosaccharide at no acid hydrolysis. This sum correlates well with the relative area for mannan obtained at optimum hydrolysis.

The correlation factor for these areas is defined as w_{tot}/w_{enz}. The variable w_{tot} is the maximum amount of anhydrosaccharide detected. The variable w_{enz} represents the amount of hydrolyzed anhydrosaccharide and the corresponding oligosaccharide fragment after enzymatic hydrolysis.

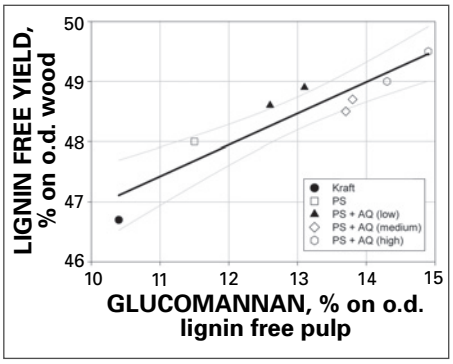
The correlation factors for glucan (cellulose), xylan, and mannan (glucomannan) were found to be 1.010±0.004, 1.11±0.04, and 1.07±0.03, respectively, at 95% confidence (with 22 pulps analyzed). When the simplified method and the method using enzyme and TFA hydrolysis were compared, no significant differences were found.

Comparison with the TAPPI method

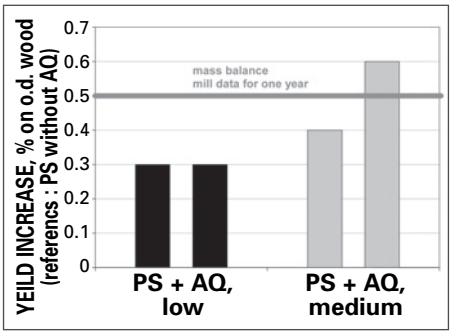
We analyzed four different pulps using pure enzymatic hydrolysis, complete hydrolysis with TFA, the simplified method, and the TAPPI method. The hydrolysis yield for enzymatic hydrolysis is very high (90–96%), which corresponds to results in a study performed by Dahlman *et al.* [13]. **Figure 3** shows that both the TAPPI method and the complete hydrolysis with enzyme and TFA gave comparable results.

Even though TFA is considered more suitable than strong mineral acids for the second hydrolysis, it decomposes the monomers to some extent. Xylose (or xylan) and glucan (or cellulose) are degraded more with increasing TFA concentration than is mannan (or glucomannan) [16]. Albersheim *et al.* have found similar results [17]. These conditions are probably more pronounced with the use of sulfuric acid, indicating that the TAPPI method may underestimate the xylan content in softwood.

Figure 3 shows that the values for xylan content of softwood pulp hydrolyzed according to the TAPPI method are underestimated by 12±7% compared to the enzymatic hydrolysis method. Recalculated data from Dahlman *et al.* [13] show that



5. Lignin-free yield of laboratory cooked, high-kappa pulps as a function of glucomannan. (The 95% confidence interval for the regression line is 0.3% on o.d. wood.)



6. Estimated increase in mill pulp yield at kappa no. 70.

the TAPPI method underestimated xylan by 12±4%.

Hardwood pulps may respond differently to acidic hydrolysis, partly because the hemicelluloses in hardwood and softwood are different [22] and partly because the content of xylan in hardwoods is about twice the content of xylan in softwoods. Nevertheless, Fig. 3 shows no significant difference between the traditional TAPPI analysis and the methods presented here (the complete and the simplified procedures) when eucalyptus pulps are analyzed.

Pulping yield measurements

Without considering pulping conditions, we used the carbohydrate composition method to estimate the kraft pulp yield in both laboratory and mill experiments.

Laboratory experiments. Plots of yield vs. kappa no. are often used to evaluate the yield gain [23]. However, a single plot is not sufficient if yield-increasing additives like polysulfide are used in the pulping process.

Figure 4 shows how the use of various additives affects the pulping yield. If the addition of anthraquinone or polysulfide varies, the linear regression curve shifts. Consequently, the relationships between the yield and the kappa number are only valid if the pulping liquor composition is identical to the conditions used when the calibration curve was obtained.

As a result, it could be useful to find a method for estimating yield that does not need process conditions as input variables. When yield-increasing additives are used, glucomannan is the main polysaccharide contributing to the increase in pulping yield in softwood [24], as **Fig. 5** shows. The prediction error in the pulping yield in the glucomannan model was at maximum of 0.3% on o.d. wood.

Mill experiments. To see if the glucomannan model can be used in continuous digesters, we analyzed five industrial kraft pulps from Peterson Linerboard. This mill applies polysulfide and anthraquinone in the cooking process and utilizes both spruce and pine. The pulping conditions were approximately constant during the testing period. The only variable that was changed in the trial period was the anthraquinone addition. In the laboratory, each 0.01% addition of AQ on o.d. wood increased the pulping yield by 0.1% on o.d. wood [25].

Figure 6 shows that the yield increase was determined to be between 0.3% and 0.6%, as expected. In the figure, these results are compared to the yield obtained by the mass balance determined over one year of production. As a reference, we use a pulp made with polysulfide and without anthraquinone. The estimated increase in the mill yield obtained by mass balances was 0.5% on o.d. wood at normal production conditions.

The mill conditions denoted as "PS + AQ (low)" represent a typical condition for the mill. The calculated mill yield obtained by mass balances is close to the estimated yield obtained by carbohydrate composition. These results indicate that the model can be used to estimate short-term variations in yield in the mill.

CONCLUSIONS

A linear correlation was found between lignin-free pulping yield and the content of glucomannan in the pulp. This model can be used to estimate the yield gain in continuous digesters. Usually, the yield gain has to be calculated from the mass balances determined for the pulp mill over a period of at least three months.

A simple and precise method for quantifying carbohydrates in pulps has been developed. Enzymatic hydrolysis of the pulp is followed by a controlled second hydrolysis with TFA, and HPLC is used for quantification. There is no need for any pulp pretreatment or monosaccharide derivatization. The carbohydrate analysis can be implemented to estimate the yield in continuous digesters or to determine the hemicellulose content of the pulp. **TJ**

ACKNOWLEDGEMENTS

Thanks to Pasi Taipalus at Röhm Enzyme Finland Oy for supplying the enzymes. The authors gratefully acknowledge financial support from the Norwegian University of Science and Technology (NTNU), the Research Council of Norway, Södra Cell, Peterson Linerboard, and Borregaard Chemcell. The authors thank Anne Marie Reitan for excellent pulp analysis using the traditional TAPPI method and Merete Wiig for laboratory cooperation. Øyvind Gregersen and Peder Kleppe are acknowledged for valuable discussions.

LITERATURE CITED

1. Gullichsen, J., Kolemainen, H., and Sundqvist, H., *Paperi Puu* 74(6): 486(1992)
2. Kleppe, P.J., *Tappi* 53(1): 35(1970).
3. Juvekar, P., Ransdell, J., Cole, B., and Genco, J., *Proc. 1995 AIChE Symposium*, Advances in Pulping and Papermaking, AIChE, New York, p. 307.
4. Kleppe, P.J., *Tappi* 58(8): 172(1975).
5. Marcoccia, B.S., Stromberg, B., and Prough, J.R, *Breaking the Pulp Yield Barrier Symposium Proceedings*, TAPPI PRESS, Atlanta 1998, p. 79.
6. Easty, D.B., and Malcolm, E.W., *Tappi J.* 65(12): 78(1982).
7. Van Heiningen, A.R.P., Gao, Y. and Da Silva Perez, D., proceedings of the *7th European Workshop on Lignocellulosics and Pulp*, Åbo Akademi University, Turku/Åbo, Finland, 2002, p. 63.
8. Vaaler, D., and Moe, S.T., *Proc.*

11th ISWPC, Vol. 2, Ecole Francaise de Papeterie et des industries Graphique (EFPG), Grenoble, France, 2001, p. 287.
9. Buchert, J., Siika-aho, M., Bailey, M., *et al.*, *Biotechn. Techniques* 7(11): 785(1993).
10. Konno, M., Sakamoto, R., and Kamaya, Y., *J. Ferment. Bioeng.* 82(6): 607(1996).
11. Tenkanen, M., Hausalo, T., Siika-aho, M., *et al.*, *Proc. 8th ISWPC*, Vol. 3, APPITA, Australia, 1995, p. 189.
12. Syverud, K., Moe, S.T., and Minja, R.J.A., *Proc. 10th ISWPC*, Vol. 2, APPITA, Australia, 1999, p. 232.
13. Dahlman, O., Jacobs, A., Liljenberg, A., and Olsson, A.I., *J. Chromatography A* 891: 157(2000).
14. De Ruiter, G.A., Scholes, H.A., Voragen, A.G.J., and Rombouts, F.M., *Anal. Biochem.* 207: 176(1992).
15. Minja, R. J.A., Ph.D. thesis No. 1998:58, Norwegian University of Science and Technology, 1998.
16. Vaaler, D., Syverud, K., and Moe, S.T., 3rd Biennial Johan Gullichsen Colloquium, The Finnish Paper Engineers' Association, Helsinki, Finland, 2001, p. 87.
17. Albersheim, P., Nevins, D.J., English, P.D., and Karr, A., *Carbohydr. Res.* 5: 340(1967).
18. Saeman, J.F., Moore, W.E., Mitchell, R.L., and Millett, M.A., *Tappi* 37(8): 336(1954).
19. Crowell, E.P., and Burnett, B.B., *Analytica Chem.* 39(1): 121(1967).
20. Borchardt, L.G., and Piper, C.V., *Tappi* 53(2): 257(1970).
21. Ristolainen, M., *J. Chromatogr. A* 832: 203(1998).
22. Sjöström, E., *Wood chemistry: Fundamentals and Applications*, Academic Press, San Diego, 1993, p. 51.
23. MacLeod, M., Radiotis, T., Uloth, V., and Tench, L., *TAPPI J.* 1(10): 3(2002).
24. Kleppe, P.J., and Kringstad, K., *Norsk Skogindustri* 17(11): 428(1963).
25. Vaaler, D., unpublished data.

Received: June 5, 2003
Revised: November 11, 2004
Accepted: December 1, 2004

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the April *Solutions! for People, Processes and Paper* magazine (Vol. 88 No. 4).

INSIGHTS FROM THE AUTHORS

One problem that has interested the pulp industry is estimating the pulping yield in continuous digesters. Considering Peder Kleppe's findings in the 1970s, it felt natural to investigate whether a more precise and accessible method for carbohydrate determination could improve on his simple mannan model.

The question of how to determine pulping yield in continuous digesters has been addressed for a long time, by several research groups. We hope that the simplicity of the method we have applied can make it more useful for mill applications. Also, to our knowledge, other research groups have not studied kraft pulps manufactured using industrially relevant mill-enhancing additives like polysulfide.

In this work, the analytical challenge proved to be the most difficult aspect. Our first goal was to develop an alternative method for determining the carbohydrate composition of kraft pulps, using alternative analytical equipment. A lot of work was put into making the analysis procedure both accurate and repeatable.

The most interesting discovery was the low importance of the cellulose yield on total pulping yield. Considering that about 90% of the cellulose is retained during the kraft cook, this should not be very surprising, but very often the importance of the hemicelluloses is overlooked, since they usually make up only 15-20% of the total pulp carbohydrates.

With the work we developed here, kraft mills using continuous digesters can estimate the yield gain when yield-increasing additives are introduced in the cooking process. Our method can also be used to estimate the yield change when one or a number of process parameters are changed.

The next step in this research is to improve the yield determination method. This means that we want to test several wood species and pulping conditions (e.g. modified cooking, residual alkali). In addition, the precision of the method should be improved by adding another pulp property to the model, such as viscosity.

Vaaler is a Ph.D. student and Moe is an associate professor at the Dept. of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Syverud is a senior research scientist at the Paper and Fibre Research Institute (PFI), Trondheim, Norway. Seem is a process engineer at Peterson Linerboard, Moss, Norway. Email Moe at storker.moe@chemeng.ntnu.no.


Vaaler


Syverud


Seem


Moe