

THE RELATION BETWEEN CARBOHYDRATE COMPOSITION AND SOFTWOOD KRAFT PULP YIELD

David Vaaler¹, Øyvind Eriksen¹, Espen Ribe² and Størker Moe¹

¹*Department of Chemical Engineering, Norwegian University of Science
and Technology, NTNU, NO-7491 Trondheim, Norway*

²*Södra Cell FoU, Södra Cell Tofte, NO-3481 Tofte, Norway*

ABSTRACT

A large number of kraft pulps has been manufactured with or without additives like anthraquinone, polysulfide or H₂S impregnation. Carbohydrate analysis of the pulps showed that the main mechanism for yield increase by additives is increased retention of glucomannan. On the other hand, the retention of cellulose was somewhat affected by the use of anthraquinone and higher kappa number. Xylan yield was constant within experimental error for all the investigated pulps. In the region between 43% and 53% bleached yield, kraft pulp yield can be predicted using a simple analysis of the glucomannan content of the pulp and knowledge of the raw material composition. The prediction error for bleached pulp yield was about ±1.5% on o.d. wood for spruce pulp and ±0.7% on o.d. wood for pine pulp. In a comparison with mass balance data from an actual mill, the prediction error was about ±0.5% on o.d. wood.

I. INTRODUCTION

The determination of pulping yield is not a straightforward task. For batch digesters, it is possible to install a basket with chips in the digester and measure the amount of pulp produced from the known quantity of chips (1). For continuous digesters, however, this is not possible. Normally, the mass balance for the mill is the basis for the yield determination. Since it is hard to estimate accurately the amount of wood consumed and the amount of pulp produced in a period of time, the pulp yield is today usually determined based on three to six months of production. Consequently, the long retention time for accurate determination of pulp yield makes it difficult for mills to optimise their process with respect to pulp yield.

It would be desirable to estimate the yield without dealing with the pulp mill mass balance. Several models for measuring pulp yield based on pulp properties are already published (2, 3, 4, 5, 6). It is well known that the total pulp yield is related to the kappa number for conventional kraft cooking at constant sulphidity and effective alkali charge (2). The following relation was shown:

$$Y_{\text{tot}} = 0.14 \cdot \text{Kappa number} + \text{Const.}$$

Juvekar et al. (3) published an empirical method for determination of total pulp yield based on process parameters such as effective alkali (EA) and H-factor. Marcoccia et al. (4) found a semi-empirical method for estimating the yield in kraft pulping of Northern hardwoods on the basis of carbohydrate composition and pulp viscosity. Easty and Malcolm (5) published the "carbohydrate-lignin method", which estimates the pulp yield based on the assumption of constant cellulose yield:

$$Y_{\text{tot}} = Y_{\text{Cell}} \cdot (\text{Cell} + \text{Hemi}) / \text{Cell} + Y_{\text{Cell}} \cdot (\text{Lign} / \text{Cell})$$

where Y_{Cell} is the cellulose yield (based on o.d. wood) and Cell, Hemi and Lign are weight fractions of respectively cellulose, hemicellulose and lignin.

All these methods are quite complex and therefore not so easily put in to practice. In the 1970s Kleppe (6) used plots of pulp yield versus the content of mannan to estimate the effect of a mill trial at Peterson Linerboard, Moss. However, the analytical technique for determination of mannan in the pulp was not as accurate as today and it was reported that the yield-mannan correlation was not valid for conventional kraft cooks.

The purpose of this paper was to investigate whether the carbohydrate composition can be used to estimate the pulp yield. A large number of laboratory unbleached and bleached kraft pulps have been produced and accurate pulp yields are measured. The carbohydrate composition has been determined by an accurate and easy method based on enzymatic hydrolysis (7, 8).

II. EXPERIMENTAL

Cooking. Air-dried roundwood chips and sawmill chips of Scots Pine and Norway Spruce were laboratory screened according to SCAN CM 40:94. The cooks were carried out in either a circulation digester or in autoclaves. Autoclave cooks were performed with a liquor-to-wood ratio of 3.5 and a maximum temperature of

163°C, whereas the cooks in the circulation digester had a liquor-to-wood ratio of 4.0 and a maximum temperature of 167°C. The alkali charge was adjusted to achieve an effective alkali residual of 7-14 g NaOH/l. The cooks were manufactured according to Vaaler *et al* (9). The H₂S impregnated pulps were carried out as described by Vaaler and Moe (10). 37 spruce and 13 pine unbleached pulps were produced. The pulp yield was measured gravimetrically using the weight of the whole autoclave and the dryness content (SCAN C 3:78). The pulp was washed and screened with a 0.15 mm slots screen.

Bleaching. 13 spruce and 8 pine pulps were oxygen delignified and bleached using a standard ECF bleaching sequence OD₀(EO)D₁ED₂. The conditions were chosen in order to achieve a kappa number 13-15 after O-stage and final brightness of 90% ISO. The pulp yield was determined gravimetrically after O-stage and for fully bleached pulp. 4 spruce pulps were bleached using a D₀ED₁ED₂ without O-stage to a brightness of 86 % ISO.

Carbohydrate composition. The pulp were characterised for kappa number according to SCAN C 1:00 and amount of lignin was determined as (4):

$$\% \text{ Lignin} = 0.147 \cdot \text{Kappa number}$$

The carbohydrate composition was determined by enzymatic hydrolysis with cellulase, xylanase and mannanase from Röhms Enzymes, Finland at 55°C for 48 hours with mannitol as an internal standard according to Vaaler *et al.* (7, 8). The enzymes decompose the carbohydrates to their monomers and the mixture of monomers was analysed on an HPLC. The detected monomers are usually reported as glucan, mannan and xylan, which are polymers of respectively glucose, mannose and xylose. However, it is more relevant to estimate the content of cellulose and glucomannan. This was done by:

$$\text{Cellulose} = \text{Glucan} - 1/3 \cdot \text{Mannan}$$

$$\text{Glucomannan} = 4/3 \cdot \text{Mannan}$$

The contents of arabinan and galactan are ignored.

III. RESULTS AND DISCUSSION

Carbohydrate yields. Increasing the content of lignin, cellulose, glucomannan and/or xylan increases the total pulp yield. Only 10% of the cellulose dissolves during cooking and the yield of cellulose is usually considered as constant (4). This indicates that an increase in pulp yield is mainly due to an increase in the hemicellulose content and mainly due to the higher retention of glucomannan. In fig. 1 the yield of each carbohydrate component is plotted versus the lignin free pulp yield. The retention of cellulose does not seem to be constant and the assumption of constant cellulose retention during kraft cooking made by Easty and Malcome (4) in the “carbohydrate-lignin method” does not seem to be valid in this case.

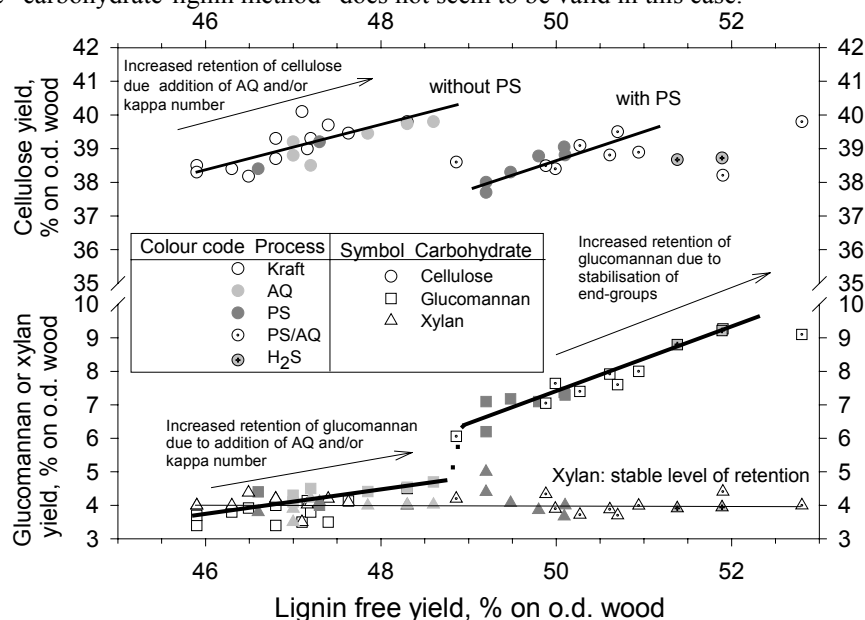


Fig. 1. Retention of the carbohydrates as a function of lignin free pulp yield. The retention of glucomannan increases with pulp yield, especially when PS and H₂S are used. The cellulose retention increases with addition of anthraquinone or increased kappa number, and not when polysulfide or H₂S is used.

Cellulose. Apparently, there are two ways to increase the retention of cellulose in the pulp. First, the kappa number of unbleached pulp could be increased and secondly anthraquinone (AQ) could be added. AQ is known to increase the delignification rate considerably (6) similar to cooks aiming for high kappa numbers. The yield

increase can be explained by a shorter exposure to hot alkaline liquor, the carbohydrates undergo less oxidative cleavage reactions and thus less peeling reactions. In contrast to AQ, the uses of polysulfide or H₂S do not increase the retention of cellulose. This is expected since polysulfide does not reduce the needed cooking time unless the decomposition of polysulfide causes a high sulfidity. When AQ is applied (not in combination with PS) the increase in pulping yield is due to about equal amounts of cellulose and glucomannan (10).

Hemicelluloses. Irrespective of cooking processes, the retention of glucomannan seems to increase when the lignin free pulp yield increases, especially for PS and H₂S pulps. Only a small part of the increase in pulp yield seems to correspond to increased retention of cellulose. Both polysulfide and hydrogen sulfide gas impregnation are known to stabilise the reducing end-groups in the polysaccharide chains (11) and thus reducing the extent of peeling reactions. Xylan behaves differently from cellulose and glucomannan and the retention of xylan is approximately constant (at 4% on o.d. wood irrespective on cooking process applied). All the pulps used in this study were cooked in a conventional batch process in which all white liquor is added in the beginning of the cook. If modified extended cooks with more even alkali profile had been applied the retention of xylan may have been lower (12).

Yield-vs.-glucomannan plot.

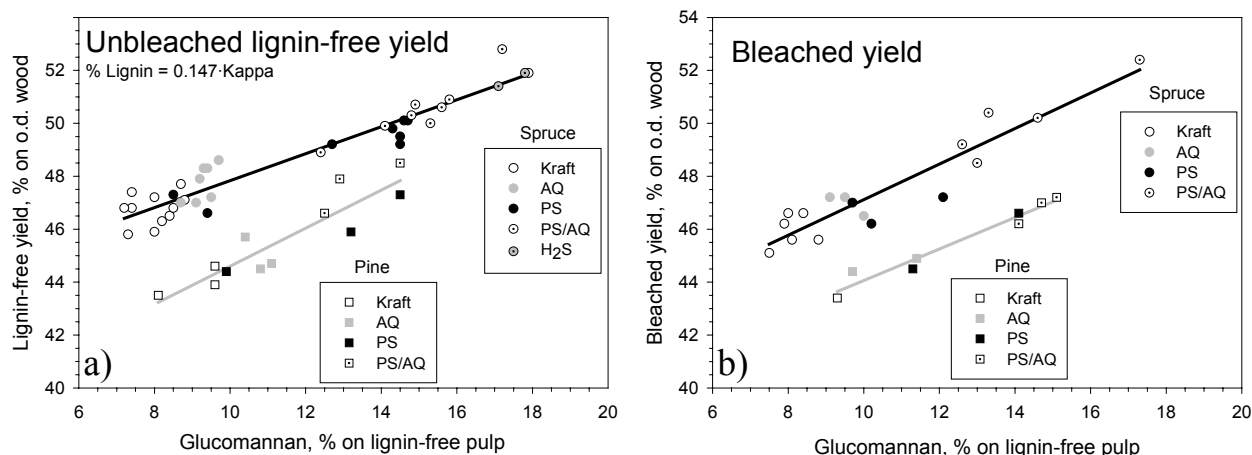


Fig. 2. Unbleached (a) and bleached (b) pulp yield as a function of glucomannan. The error in predicting a pulp yield with 95% confidence interval is for; unbleached spruce (a): ± 1.0 , unbleached pine (a): ± 1.5 , bleached spruce (b): 1.5, bleached pine (b): 0.7, all as % on o.d. wood.

The linear relation between glucomannan and pulp yield in fig. 1 indicates that glucomannan can be used to estimate the yield of a softwood kraft process. However, for a conventional kraft or an AQ process, the pulp yield may be underestimated. As mentioned earlier, the pulp yield in such processes increases due to higher retention of cellulose and glucomannan. In the other processes, glucomannan is the main polysaccharide attributing to the increase of pulp yield. Consequently, it is expected that the slope for the yield-vs.-glucomannan plot for conventional kraft and AQ cooks should be approximately twice the slope for polysulfide and H₂S cooks. However, the data in fig. 2 is ambiguous and does not seem statistically correct to separate the kraft and AQ pulps from the polysulfide and H₂S pulps.

The error in pulp yield in the glucomannan model was at maximum 1.5 % on o.d. wood. Apparently it seems that the error of this model makes it almost useless for standard kraft processes. However, the model could be useful if major cooking or bleaching modifications like addition of AQ and/or PS in cooking, new bleaching sequences etc are implemented in the mill. Another application could be daily control of the pulp to check that the estimated pulp yield and the carbohydrate composition are according to the target.

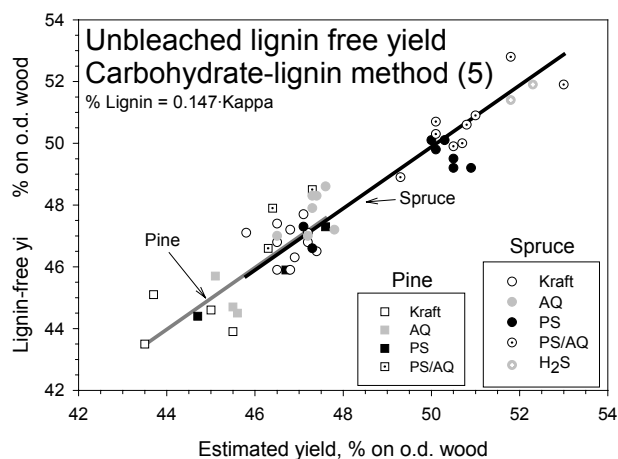


Fig. 3. Calibration curves for the carbohydrate-lignin method (5). The error in prediction a pulp yield with 95% confidence interval are for; unbleached spruce: ± 1.5 , unbleached pine: ± 2.0 , all as % on o.d. wood

In order to find a better model with higher accuracy, statistical analysis of the data were tried out, but all models failed due to their complexity and lack of physical explanations (e.g. $Y_{\text{lign free}} = a \cdot \log[\text{SCAN viscosity}/(\text{Cell-GlcMan})^2] + b$). The “carbohydrate-lignin method” was tried out for the unbleached pulps (see fig. 3) and the result seemed to be poorer compared to the yield-vs.-glucomannan plot. The main reason for the inaccuracy is the incorrect assumption of constant retention of cellulose.

The bleached yield plots show the same trends compared to the unbleached pulps. During bleaching the carbohydrate composition is not changed (not shown here) and the estimated unbleached lignin free yield is approximately 0.5 % on o.d. wood higher than the bleached.

To verify the model, four industrially produced kraft pulps from Peterson Linerboard, Moss were analysed. The Moss mill applies polysulfide and anthraquinone in the cooking process and utilises both spruce and pine in the process. The two spruce and pine models (see fig. 2) were interpolated for a known spruce-to-pine ratio. These results were compared to the yield obtained by the mass balance for one-year production of the mill and the estimated yields were ± 0.5 % on o.d. wood at normal production conditions. When the strength of polysulfide liquor decreases, the yield decreases with approximately 2 % on o.d. wood. These values were to be expected and the results indicate that the model can be used to estimate short-term problems in the digester.

If modified cooking processes such as EMCC or other processes are applied, new calibration lines should be applied. Extended cooks have different level of xylan compared to conventional cooks and yield-vs.-hemicellulose plots may be more correct to use.

IV. CONCLUSIONS

Yield increase in kraft pulping is mainly due to increased retention of glucomannan. In the region between 43% and 53% bleached yield, kraft pulp yield can be predicted using a simple analysis of the glucomannan content of the pulp. However, the use of AQ or increasing the kappa number resulted in higher cellulose retention. The prediction error for bleached pulp yield was about $\pm 1.5\%$ on o.d. wood for spruce pulp and $\pm 0.7\%$ on o.d. wood for pine pulp. In a comparison with mass balance data from an actual mill, the prediction error was low.

V. ACKNOWLEDGEMENTS

One of the authors (DV) gratefully acknowledges financial support from Södra Cell, Peterson Linerboard, the Research Council of Norway and The Norwegian University of Science and Technology. Thanks to Solveig Kongsjorden, Björn Dillner and Arne Antonsen at Södra Cell Tofte and Berit Seem at Peterson Linerboard Moss for their expert and helpful discussions. We also thank Kai Toven (PFI) and Sigrid Ljones (NTNU) for reviewing the manuscript and providing useful comments.

VI. REFERENCES

1. Gullichsen, J., Kolemäinen, H. and Sundqvist, H., On the nonuniformity of the kraft cook, *Paperi ja Puu*, 74(6):486-490 (1992)
2. Kleppe, P.J. Kraft pulping, *Tappi*, 53(1):35-47 (1970)
3. Juvekar, P., Ransdell, J., Cole, B. and Genco, J., Kraft pulping kinetics of Eastern White Cedar, *Proc. AIChE Symposium, Advances in Pulping and Papermaking*, 91(307):1-18 (1995)
4. Marcoccia, B.S., Stromberg, B. and Prough, J.R., Achieving major increases in hardwood yield with L-solids cooking, *TAPPI Proc. Breaking the pulp yield barrier symposium, Atlanta*, 79-89 (1998).
5. Easty, D.B. and Malcolm, E.W., Estimation of pulping yield in continuous digesters from carbohydrate and lignin determinations, *Tappi J.*, 65(12):78-80 (1982)
6. Kleppe, P.J., Polysulfide pulping in a dual-vessel Kamyrdigester, *Tappi*, 58(8): 172-176 (1975)
7. Vaaler, D., Syverud, K. and Moe, S.T., Characterisation of pulp carbohydrates by enzymatic hydrolysis and determination of pulping yield with carbohydrate profiles, 3rd Biennial Johan Gullichsen Colloquium, Helsinki, 87-93 (2001).
8. Vaaler, D., Syverud, K. and Moe, S.T., An easily available method for determination of carbohydrate composition of chemical pulps using enzymatic hydrolysis, submitted to *Nordic Pulp and Paper Research Journal*
9. Vaaler, D., Ljones, S., Ribe, E. and Moe, S.T., effects of hemicellulose stabilisation and raw material on the beatibility of softwood kraft pulps, *Proc. 7th EWLP, Aug. 2002, Åbo*.
10. Vaaler, D. and Moe, S.T., Carbohydrate profiles of kraft pulps manufactured with white liquor additives, *Proc. 11th ISWPC, vol 2:287-281, Nice, (2001)*
11. Kleppe, P.J. and Kringstad, K., Sulphate pulping by polysulphide process, *Norsk Skogind.*, 17(11):428-440 (1963)
12. Sjöström, E., *Wood chemistry. Fundamentals and applications*, Academic press, San Diego, USA, 51 (1993)