INFLUENCE OF COOKING CONDITIONS ON THE PROPERTIES OF FIRST-THINNING SCOTS PINE (*Pinus sylvestris*) KRAFT PULP

RIIKA RAUTIAINEN and RAIMO ALÉN

University of Jyväskylä, Department of Chemistry, Laboratory of Applied Chemistry, P.O. Box 35, FI-40014 Finland

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Kraft pulping of first-thinning Scots pine (*Pinus sylvestris*) was investigated under varying conditions to clarify the simple relationships between the principal cooking parameters (active alkali, sulfidity and cooking time) and the basic pulp properties (yield and kappa number). It was found out that, regardless of sulfidity (25 or 40%), an increase in the active alkali ($25 \rightarrow 30\%$ on wood as NaOH) resulted – for the same cooking time – in a more effective removal of lignin (of about 10%), but also in a pronounced yield loss (4-6%). On the other hand, when aiming at the same target kappa number (of about 25), the cooking time at the maximum temperature (170 °C) could be decreased by about 35%, at the same active alkali increase.

Keywords: kraft pulping, delignification, first-thinning, pulp properties, Scots pine

INTRODUCTION

Although, at present, wood materials from first-thinning are mostly burned to produce energy,^{1,2} the idea of using at least a part of these tree resources for non-fuel purposes is attractive. Compared to the industrial uses of mature wood, it is obvious that a more versatile application of such wood raw materials involves several difficulties, including their inferior wood properties, low recovery and high harvesting costs, as well as "ineffective" behavior during pulping.³⁻⁸ Rather scarce relevant information on the tailored manufacture of chemical pulps from first-thinning wood materials is available. It is known however that, for example, cost savings in thinning harvesting can be achieved by an efficient integration into industrial roundwood harvesting,^{9,10} and also by streamlining the harvesting operations.^{7,11,12} It has been shown that the wood properties typically change within the first-thinning pine stem.^{13,14} Consequently, in the case of kraft pulping, it is possible to screen this mainly

juvenile wood-containing material to meet the final product requirements.¹⁵⁻¹⁸

A primary approach to attain this goal involves a proper modification of the cooking conditions, to make them more suitable for the first-thinning wood material. For example, it has been reported that a higher chemical charge is needed, for the same target kappa number, to delignify Norway spruce¹⁹ and American aspen²⁰ juvenile wood as compared to mature woods. Furthermore, some recent studies suggest that the kraft pulp yield of first-thinning Scandinavian softwood is lower than that of industrial pulpwood.^{8,17,21} In addition, it has been noted that extended cooking of softwood from kappa number 30 to 15 lowers pulp yield by 3.4 percent units.²¹

The main objective of the present study was to establish the influence of the basic cooking parameters (alkali charge, sulfidity and time) on the common pulp properties (screened yield, amount of reject and kappa number) in the kraft pulping of Scots pine (*Pinus sylvestris*) from first-thinning. In addition to these general trends, some strength properties of the pulps, tested under two proposed cooking conditions, were determined. The study is part of a more extensive project, aiming at a more effective utilization of fiber sources based on firstthinning. In our earlier studies,^{14,17,18} the suitability of different fractions of firstthinning wood material, especially for the pulp components of the fine paper products, has been investigated.

EXPERIMENTAL

Wood raw materials

Two Scots pine (*Pinus sylvestris*) trees were harvested from a first-thinning stand from the district of Leppävesi in Central Finland. The first tree (age: 27 years, height: 11 m, and diameter at breast height: 11 cm) was used to examine the effect of the cooking conditions on wood delignification. In a subsequent stage, the influence of the cooking conditions on the strength and optical properties of the obtained pulps was studied. To this end, the second firstthinning tree (age: 28 years, height: 12 m, and diameter at breast height: 13 cm) was cooked under two proposed cooking conditions. In both cases, the wood material was chipped after manual debarking with a pilot chipper.

Kraft pulping

In the first cooking series, the first-thinning pine was delignified under the cooking conditions shown in Table 1. In a separate, second experiment, the first-thinning pine was delignified under the same cooking conditions as those used in cookings 7 and 10 (Table 1). All these conventional kraft cooking experiments were carried out in 1 L rotating stainless steel autoclaves heated in an oil bath, each of them charged with 130 g of oven-dried (o.d.) chips. The liquor-to-wood ratio was 4.5 L/kg and the heating time, from 80 °C to a maximum cooking temperature of 170 °C, was of 90 min.

After each cooking, the pulps were thoroughly washed with tap water, disintegrated at low consistency, sieved on a vibrating flatslotted laboratory screen with 0.2 mm slots, centrifuged and homogenized. The total pulp yield, the amount of screened reject and the kappa number (SCAN-C 1:77) were determined. Pulp yield was calculated on the basis of chips and pulp dry solids. The Kappa number was converted³¹ to the lignin content by multiplying by 0.153. The handsheets of the second series of kraft pulps were made according to SCAN-C 26: 76 and analyzed for their physical properties: density (SCAN-P 7:75), Bendtsen roughness (SCAN-P 21:67), strength (SCAN-P 38:80 tensile and SCAN-P 11:73 tear) and optical properties (ISO 2469). In addition, the kraft pulps were characterized in terms of fiber length and coarseness, on a Kajaani FS-200 fiber length analyzer, according to standard TAPPI T-271 pm-91.

RESULTS AND DISCUSSION

For the sake of clarity, only certain examples were provided on the "limiting conditions" suitable for a satisfactory delignification degree of the first-thinning softwood, for elucidating only some general trends, rather than thoroughly optimizing the cooking procedure.

In the experiments, an increase in sulfidity from 25 to 40%, at both active alkali (AA) charge levels (25 and 30%) accelerated lignin removal (*i.e.*, about 10% more lignin was removed) at short cooking time periods (45 and 60 min) and maximum cooking temperature, while the difference leveled off during prolonged cooking (Fig. 1). When comparing the content of residual lignin in pulp after short and long delignification time periods, an approximate decrease of 40% was found at both AA charge levels.

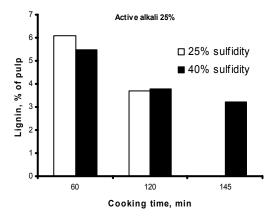
As expected based on a previous study,²² a shorter cooking time was needed to reach the same target kappa number, when increasing the AA charge (Table 1); cf. kappa number ≈38 (AA 25%, cooking time 60 min) $\rightarrow \approx 32$ (AA 30%, cooking time 45 min) and ≈ 24 (AA 25%, cooking time 120 min) $\rightarrow \approx 19$ (AA 30%, cooking time 85/95) min). Generally, 30-35% more lignin was dissolved at a higher AA charge level, for the same cooking time - between 60 and 100 min (Fig. 2). During kraft pulping, the hydrogen sulfide ions primarily react with lignin, whereas the carbohydrate reactions are affected only by alkalinity (*i.e.*, hydroxide ions).²³⁻²⁷ As seen in Figure 3, a relatively low yield was observed for all cooking experiments performed. In addition, mainly due to the enhanced peeling reactions of hemicelluloses,²⁴⁻²⁸ an increase in the AA charge from 25 to 30% typically decreased the pulp yield by 4-6%, at the same cooking time (60-100 min).

The results also confirmed that the variation in sulfidity at both AA charge levels (*i.e.*, changes in the relative portions of HO⁻ and HS⁻ ions) had no significant effect on the pulp yield during deligni-fication (Fig.

4). Furthermore, the results indicated a slight formation of reject only in the "undercooked" cases, corresponding to short cooking times (45 or 60 min).

c x	Ū	Table 1
Cooking data on the	kr	aft pulping of first-thinning pine

Cooking no.	Active alkali, % (as NaOH)	Sulfidity, %	Time, min	Screened yield, % on wood	Reject, % on wood	Kappa number
1	25	25	60	44.8	1.55	39.7
2	25	25	120	43.7	0.15	24.1
3	25	40	60	45.7	0.42	36.2
4	25	40	120	44.0	0.10	24.9
5	25	40	145	42.4	0.05	21.1
6	30	25	45	45.0	0.25	33.9
7	30	25	95	40.5	0.01	18.8
8	30	25	105	42.0	0.08	18.5
9	30	40	45	45.4	0.21	30.0
10	30	40	85	42.3	0.03	19.2
11	30	40	105	42.8	0.03	18.7



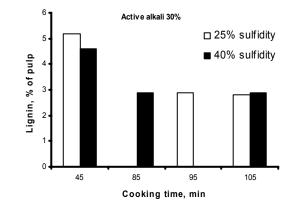
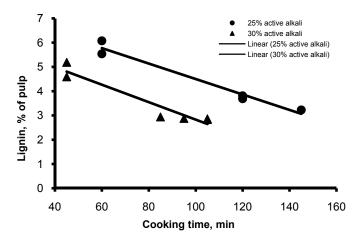


Figure 1: Lignin content in the first-thinning pine kraft pulps obtained at two AA charges and sulfidity levels



25% active alkali 47 30% active alkali Total pulp yield, % on wood Linear (25% active alkali) 46 Linear (30% active alkali) 45 44 43 42 4 40 40 60 80 100 120 140 160 Cooking time, min

Figure 2: Lignin content in the first-thinning pine kraft pulps, as a function of cooking time, at two AA charge levels (sulfidity 25% or 40%)

Figure 3: Total pulp yield *versus* cooking time for the kraft pulping of first-thinning pine

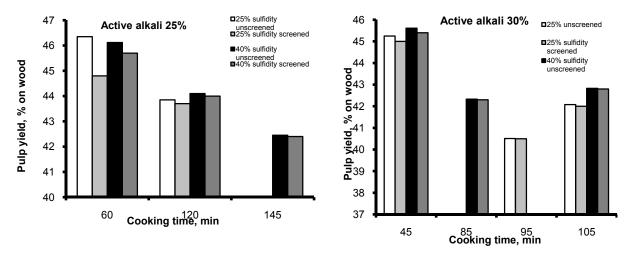


Figure 4: Pulp yields obtained for the kraft pulping of first-thinning pine under varying conditions

Figure 5 provides pulp yield data for all cooking experiments plotted against kappa number. This single relationship suggested that a rather sharp yield drop occurred below a kappa number of ≈ 22 . This increase in non-selectivity was, however, not attributed to a significant loss in the brownstock physical

properties, shown in Table 2, for two slightly "overcooked" pulps (*cf.* cookings 7 and 10, Table 1).

The results obtained were similar to those of previous studies,³⁰⁻³² showing that tensile strength decreased and tear index increased, along with an increase in

coarseness. For our pulps, the tensile index decreased when sulfidity increased, which was contrary to a slight tensile strength benefit when sulfidity increased³¹ from 30 (AA 25%) to 40% (AA 26%) in the full-scale kraft pulping of pine chips, at a constant effective alkali level of 21%.

In addition, the tear index increased only slightly $(14.8 \rightarrow 15.5 \text{ mNm}^2/\text{g})$ compared to the values obtained by Paavilainen³¹ (15 \rightarrow 17 mNm²/g) – if sulfidity is generally increased during kraft pulping.

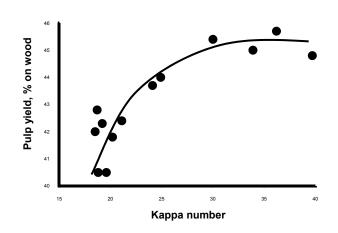


Figure 5: Pulp yield vs. kappa number for all cooking sessions under study

Table 2Properties of kraft pulps obtained at two sulfidity levels:25% (I) and 40% (II) (active alkali charge as NaOH 30% on wood)

Description	Ι	II
Kappa number	19.6	20.2
Pulp yield, % on wood	40.5	41.8
Fiber length, mm	1.91	1.92
Coarseness, mg/m	0.147	0.158
Brightness, % ISO	18.5	16.9
Density, g/dm ³	608	599
Bulk, cm ³ /g	1.64	1.67
Tear index, mNm ² /g	14.8	15.5
Tensile index, Nm/g	45.9	36.8
Roughness, mL/min	681	663
Opacity, %	94.5	96.1
Light-scattering coefficient, m ² /kg	15.6	15.9

CONCLUSIONS

First-thinning Scots pine (Pinus sylvestris) was delignified by conventional kraft pulping to clarify the "sensitiveness" of the pulp properties to the common cooking parameters. Generally, regardless of the sulfidity levels (i.e., 25 and 40%) tested, it was found out that a rather high active alkali charge had to be used to obtain a satisfactory delignification degree. In addition, it seemed that an increase in the active alkali charge from 25 to 30% resulted in pronounced yield loss, as compared to the overall benefits for an accelerated lignin removal. The strength properties were somewhat lower than those typical of industrial pulps. The cooking data laid a firm foundation obtained for forthcoming studies, analyzing in more detail the suitability of first-thinning softwoodderived materials for the production of fine paper.

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REFERENCES

¹ K. Mielikäinen and P. Hakkila, in "Wood Fuel from Early Thinning and Plantation Cleaning: An International Review", edited by D. Puttock and J. Richardson, The Finnish Forest Research Institute, 1998, pp. 29-35.

² J. Heikkilä, M. Sirén and O. Äijälä, *Biomass Bioenerg.*, **31**, 255 (2008).

³ B. Zobel, *Wood Sci. Technol.*, **18**, 11 (1984).

⁴ P. Hakkila, Acta For. Fenn., 207, 1 (1989).

⁵ P. Hakkila, *Procurement of Timber for the Finnish Forest Industries*, The Finnish Forest Research Institute, Research Paper 557, 1995, p. 73.

⁶ P. Hakkila, in "Forest Resources and Suitable Management", edited by S. Kellomäki, Fapet Oy, 1998, pp. 117-185.

⁷ M. Sirén and H. Aaltio, *Int. J. Forest Eng.*, **14**, 39 (2003).

⁸ D. H. Kim, L. Allison, B. Carter, Q. Hou, C. Courchene, A. J. Ragauskas and J. Sealey, *Tappi J.*, **4**, 21 (2005).

⁹ A. Asikainen, *Int. J. Forest Eng.*, **15**, 11 (2004).

¹⁰ P. Jylhä, *Int. J. Forest Eng.*, **15**, 35 (2004).

¹¹ K. Kärhä, E. Rönkkö and S.-I. Gumse, *Int. J. Forest Eng.*, **15**, 43 (2004).

¹² H. Ovaskainen, J. Uusitalo and K. Väätäinen, *Int. J. Forest Eng.*, **15**, 67 (2004).

¹³ T.-J. Toivanen and R. Alén, *Cellulose*, **13**, 53 (2006).

¹⁴ R. Rautiainen and R. Alén, *Cellulose*, **16**, 349 (2009).

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¹⁵ I. Duchesne, L. Wilhelmsson and K. Spångberg, *Can. J. Forest Res.*, **27**, 790 (1997).

- ¹⁶ P. Kärenlampi and H. Suur-Hamari, *Pap. Puu*, **79**, 404 (1997).
- ¹⁷ R. Rautiainen and R. Alén, *Holzforschung*, **61**, 8 (2007).

¹⁸ R. Rautiainen and R. Alén, *Pap. Puu*, **89**, 294 (2007).

¹⁹ M. Yngvesson, *Procs. Pulping Conference*, Atlanta, November 1-3, 1993, pp. 87-94.

²⁰ G. C. Myers, R. A. Arola, R. A. Horn and T. H. Wegner, *Tappi J.*, **79**, 161 (1996).

²¹ M. Svedman, P. Tikka and M. Luhtanen, *Tappi J.*, **81**, 157 (1998).
²² R. Aurell and N. Hartler, *Svensk Papper-stidn.*,

²² R. Aurell and N. Hartler, *Svensk Papper-stidn.*, **68**, 97 (1965).

²³ P. J. Kleppe, *Forest Prod. J.*, **20**, 50 (1970).

- ²⁴ J. Gierer, *Wood Sci. Technol.*, **14**, 241 (1980).
- ²⁵ O. Pekkala, *Pap. Puu*, **65**, 251 (1983).

²⁶ E. Sjöström, in "Wood Chemistry, Fundamentals and Applications", Academic Press, 1993, pp. 140-161. ²⁷ R. Alén, in "Forest Products Chemistry", edited by P. Stenius, Fapet Oy, 2000, pp. 58-104.

²⁸ D. Clayton, D. Easty, D. Einspahr, W. Lonsky,
 E. Malcolm, T. Mcdonough, L. Schoroerder and

N. Thompson, in "Pulp and Paper Manufacture",

Vol. 5: "Alkaline Pulping", edited by T. Grace,

B. Leopold, E. Malcolm and M. Kocurek, Tappi & CPPA, 1989, pp. 1-128.

²⁹ G. W. Legg and J. S. Hart, *Pulp Pap. Mag. Can.*, **61**, T299 (1960).

³⁰ R. S. Seth and D. H. Page, *Tappi J.*, **71**, 103 (1988).

³¹ L. Paavilainen, *Pap. Puu*, **71**, 356 (1989).

³² L. Paavilainen, *Pap. Puu*, **75**, 343 (1993).