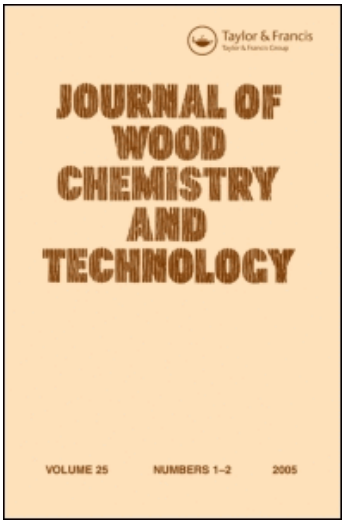

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Hossein Lohrasebi[a]; Warren E. Mabee[a]; D. N. Roy[a]
[a] Faculty of Forestry, University of Toronto, Toronto, Ontario, Canada

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CHEMISTRY AND PULPING FEASIBILITY OF COMPRESSION WOOD IN BLACK SPRUCE

Hossein Lohrasebi, Warren E. Mabee and D.N. Roy
University of Toronto, Faculty of Forestry
33 Willcocks Street
Toronto, Ontario, Canada
M5S 3B3

ABSTRACT

This research was conducted to study the organic and inorganic constituents and pulping behaviour of compression wood (CW), in comparison to normal wood (NW) and opposite wood (OW). It was found that differences in the chemical properties of OW and NW were not significant, except in alpha-cellulose and hemicellulose content; whereas both differed significantly from CW which contained more lignin and calcium and less alpha-cellulose. These chemical characteristics of CW resulted in high residual lignin and poor pulp yields, in comparison with normal and opposite woods, when different cooking times and temperatures were applied. Bleachable grade pulp could be obtained from normal wood with H-factor 2300. Using CW, however, this was not practical even under severe cooking conditions.

INTRODUCTION

Black spruce (*Picea mariana* L.) is one of the most important commercial species in Ontario with superior morphological, physical and chemical properties. However, 15% of the wood in a typical black spruce tree is composed of compression wood (CW). Compression wood, typified by high lignin contents and

short fibre lengths, is a relatively low quality pulpwood when compared to the normal wood (NW) of black spruce. The influence of wind, snow, light, or any factor causing stem deviation from the vertical is associated with CW formation.[1] The large amounts of CW within the black spruce stem and branches corresponds to 6% less pulp in the sulphite process, or to over 2.3 tons of usable pulp per hectare.[2]

The physical and chemical process conditions employed in kraft pulping, combined with the properties of the specific type of wood being cooked, determine the behaviour of the pulping system. Thus, the large morphological, physical and chemical differences between CW and NW zones within a tree should be expected to result in markedly different pulp properties. Short fibres with a rounded outline, a thick cell wall, and fewer and smaller pits are the major morphological features of dense CW,[1] which makes it less permeable to the penetration of pulping liquor and water compared with NW and opposite wood OW.

Higher amounts of residual lignin are reported in CW,[1] with different chemical structures. This may result in the redeposition of highly condensable CW lignin on the fibre. Such a rigid lignin is expected to have higher molecular weight and lower reactivity towards bleaching agents, increasing bleach requirements. The final brightness and cleanliness would also be lower than those of NW and OW pulps. The inflexible CW pulp provides fibres which are difficult to improve by beating or refining, which results in pulp with low fibrillation and freeness while suffering from extreme fragmentation.[1] The lignin remaining in CW fibres restricts the bonding ability of the fibres. The presence of undercooked bundles of fibres, i.e. shives originated from stem CW and knots, adversely affect the runnability during papermaking or printing. Further, the properties of the effluent (suspended solid and toxicity) coming from pulping and bleaching would depend on the proportion of CW in the wood supply. According to Hrutfiord and Negri,[3,4] CW lignin yields proportionally more chlorinated dioxins and furans than NW does. This, in turn, requires an optimization of recovery operation and/or effluent treatment systems.

Irrespective of the type of pulping process, CW, when cooked under normal conditions, is converted to undercooked pulp which is rejected during the deknotting and screening processes. On the other hand, if the pulping time or temperature is increased, normal wood is overcooked and degraded. Using CPPA Standard Methods[5] and statistical analysis software (SAS), this work determines the differences in the organic components of CW, NW, and OW and elucidates some previous contradictory results in these figures as noted by Timell.[1] The study also takes particular note of the inorganic composition of CW. Finally, this paper presents data on the effects of various ranges of cooking time and temperature on such variables as yield and lignin content.

MATERIAL AND METHODS

Mature black spruce was chosen for this study. Wood disks were cut at breast-height level from six leaning trees. This was carried out by Abitibi-Price (now Abitibi-Consolidated) Inc., and collected near Iroquois Falls, Ontario. Different types of wood, i.e. CW and OW, were identified on the discs and separated from the NW. The physical criteria used to identify CW were the presence of irregular growth rings featuring an abnormally large proportion of latewood, while OW was identified as the region of extremely small growth rings opposite to the CW region.[6] Then, wood samples were ground in a Wiley mill and screened to 40-mesh size. The grinding procedure was used to reduce the impact of diffusion on mass transfer, allowing the delignification to be controlled by the chemical reactions only.

Chemical Characterisation

Samples from different wood tissues were extracted following CPPA Standard G.13. After determination of extractive content, another set of extractions was run to prepare enough extractive-free wood to be used in other experiments. The carbohydrate (holocellulose) fraction of wood was isolated by

removing the lignin from extractive-free wood using the acid chlorite method. For determination of alpha-cellulose in wood, NaOH (17.5%) was applied to holocellulose, dissolving hemicelluloses. Following CPPA Standards G.8 & G.9 Klason lignin was determined by hydrolysing the carbohydrates with 72% sulphuric acid. Employing UV absorption at 205 nm, the acid-soluble lignin was also measured on the filtrate specimen. Elemental analysis on the unextracted wood samples of CW, NW and OW was performed to assess the concentration of Al, Ca, Cl, Cu, I, K, Na, Mg, Mn, Ti, V, and Zn. Applying neutron activation analysis (NAA) at the University of Toronto, a 10 kW, 5 min neutron irradiation was applied with a 2 min delay time prior to 5 min of counting. Using SAS program, the basic analysis of variance and Duncan's Test were performed for all organic and inorganic variables at $p \leq 0.05$, a 95% confidence level.

Kraft Micro-Pulping Procedure

Ground wood (2.5 g - 40 mesh) and pulping liquor (15 mL) were placed in a micro-pulping reactor (25-mL), the liquor to wood ratio being 6:1. The stock solution of the kraft pulping liquor consisted of 33 g/L active alkali (as Na_2O) and a sulphidity of 25%. The reactors were placed in a silicon oil bath which was adjusted to the desired cooking temperature by a thermal regulator. The cooking time to reach maximum temperature was constant (10 min) and was added to the cooking time at each level of cooking temperature. Wood samples were cooked isothermally at 140°, 155°, and 170°C for various times, i.e. 30, 45, 60, 90, 120, 150, and 180 min.

RESULTS AND DISCUSSION

Chemical Composition of Black Spruce Woods

Organic Components

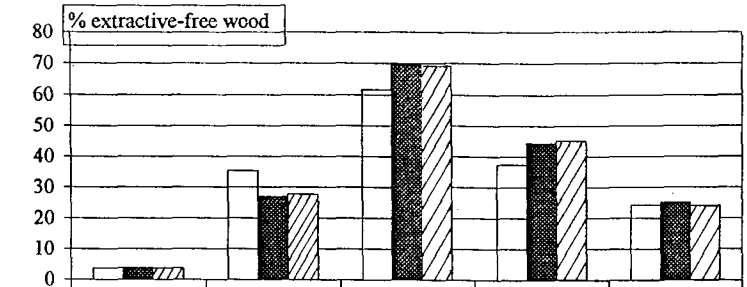
Despite significant variation in the extractive content of different trees, it was found that there is no statistically significant variation in the amount of

extractives among CW, NW, and OW. Thus, CW should not be expected to cause more pitch problems than NW during the pulping process, although an exception must be made for CW taken from knots, which has significantly higher extractive content.[7] The mean values for the chemical components of woods are illustrated in **Figure 1**. The extractive content in NW (3.8%) is in a good agreement with the general conclusion made by Timell[1] that mature xylem of both NW and CW contain 3.5-3.7% extractive. The results suggest that the extractive content in a wood tissue is tree-dependent, in addition to being species-dependent and site-specific.[8]

Substantial variation existed in the lignin content of CW and NW but much less among different trees. It was found that the observed difference between NW and OW lignin contents was statistically insignificant whereas it was significant in comparison with CW which contained about 8% more lignin at the expense of holocellulose. As with the lignin content, the difference in holocellulose content of NW and OW tissues was also insignificant, but both differed significantly from that in CW. The ratio of holocellulose:lignin was 2.5:1, 2.6:1, and 1.7:1 in OW, NW and CW, respectively. The Duncan's Test for the means of alpha-cellulose content showed that the variations among OW, NW and CW are significant at 95% confidence level and that these differences were not due to variations among individual trees. There was not much variation in the hemicellulose content of CW and OW whereas a significant difference was observed compared to NW. The possible contradiction with data reported by some investigators might originate from the methods which were applied and/or from severity of CW.[1]

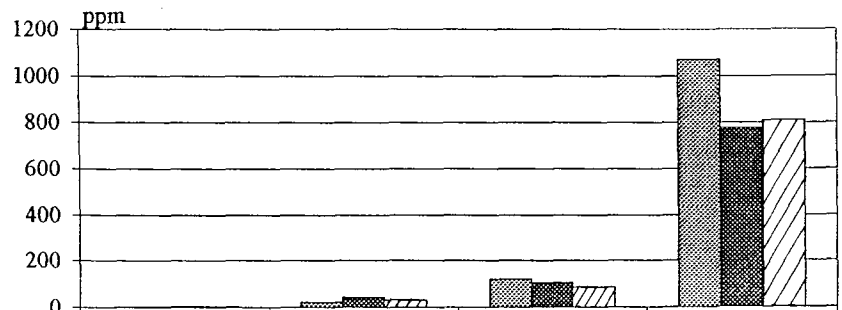
Inorganic Components

In this study, different wood types were examined for concentrations of 12 elements including: Ca, Mn, Cl, Al, Zn, K, Mg, Cu, Ti, Na, I, and V, by employing neutron activation analysis (NAA). Of the twelve elements studied, Ca was the element that exhibited the highest concentration in the woods, while Mn, Cl, and Al had very low concentrations (see **Figure 2**). It was found that the



	Extractives	Lignin	Holocellulose	Cellulose	Hemicellulose
CW	3.7	35.4	61.5	37.3	24.2
NW	3.8	27.1	69.7	44.4	25.3
OW	3.6	27.7	69.2	45.1	24.1

Figure 1. Chemical composition of CW, NW, and OW (% of extractive-free wood).



	Aluminum	Chlorine	Manganese	Calcium
CW	3	23	120	1070
NW	4	45	105	780
OW	4	32	86	810

Figure 2. Trace element concentrations in CW, NW, and OW (parts per million).

concentration of Ca differed among the wood tissues and trees. Ca had identical concentration patterns to that of lignin; this might confirm the proposal[9] that the distribution of Ca is associated with that of lignin. This, in turn, suggests that Ca plays an important role in the lignification pathway[10] likely in the formation of the highly lignified secondary wall in compression wood. Higher concentration of Ca in compression wood (1070 ppm) makes this type of wood less suitable for the pulping industry. The most immediate effect of such high inputs is at the digester[11] and subsequently during bleaching. On the other hand, the inorganic elements can affect the surface properties of fibres. Scallan and Grignon[12] observed that trace metals within pulps increase the ability of the fibres to bond extensively, i.e. confer the same beneficial effects of an appreciable amount of beating of the pulp.

The low concentration of Mn varied to a less extent compared to that of Ca. Despite insignificant variations in Mn concentration among the types of tissue, the concentration of Mn differed significantly among different trees. The data from literature were contradictory; Mn concentration in black spruce was reported to be 227 ppm,[11] 79 ppm for sapwood and 110 ppm for heartwood.[13] The recorded Mn concentration in NW (105 ppm) is in a reasonable agreement with the latter. These variations can be due to the different trees site conditions. Accumulation of Mn in a closed-cycle mill can adversely affect the quality of resulting pulp because Mn catalyses peroxide decomposition during the bleaching process.[14]

In contrast to the concentration of Ca, compression wood contained less Cl compared to normal and opposite woods, while different trees had no significant effect on the amount of Cl in either tissue type. The presence of Cl in the pulping system can cause serious problems in the operation of the recovery furnace. This leads to excessively deleterious deposits on the fireside of the superheater and boiler bank of the recovery furnace, causing plugging, fouling and corrosion damages to the heat exchange surfaces.[11,15] Thus, the lower concentration of Cl in compression wood is one of the few properties of CW which is beneficial in the pulping process. Furthermore, different tissue types contained slightly different

amounts of Al, which was present in a very low concentration. Other inorganic elements, Cu, I, K, Mg, Na, Ti, V, and Zn were not detectable by the NAA facility. This seems to be due to the presence of Ca, Cl, Mn and Al, all of which have a very high activation energy.

Kraft Pulping of the Woods

It was found that there was no significant difference between the pulping characteristics of NW and OW in black spruce. However, CW behaved differently in delignification. Thus, all comparisons are made between NW and CW.

The dissolution of any wood component was greater when CW was cooked. Over the whole range of cooking times and temperatures investigated, CW resulted in a substantially lower yield but higher residual lignin than NW. **Figure 3** shows yield and lignin content of NW and CW cooked at different times and temperatures as a function of H-factor. At the temperature usually used in industry, 170°C, a conventional NW pulp with a comparatively low lignin content was produced after cooking for 90 min. In contrast, bulk cooking of CW under this condition resulted in a pulp with 5% lower yield and a lignin content of as high as 11%. The lowest level of residual lignin in CW, equivalent to kappa number of 75, was obtained with H-factor 2770. This kappa unit corresponds to a NW cooking with H-factor 1350. To obtain pulps of similar kappa number from the two woods in kraft pulping, it was necessary to use a longer cooking time or higher temperature for CW than for NW. On prolonged cooking to lower the lignin content, a much lower yield was obtained from CW, showing noticeable carbohydrate degradation. Bleachable grades of kraft pulp (kappa no.≈30) could be achieved from NW portion of black spruce through batch isothermal micro-pulping by use of H-factor less than 2300 in yields higher than 50%. Using CW, however, this was not practical even under severe cooking conditions because of low selectivity towards delignification.

The higher residual lignin in CW pulp can partially be explained by the high degree of lignification of CW fibres, and also by the statements of Chang and

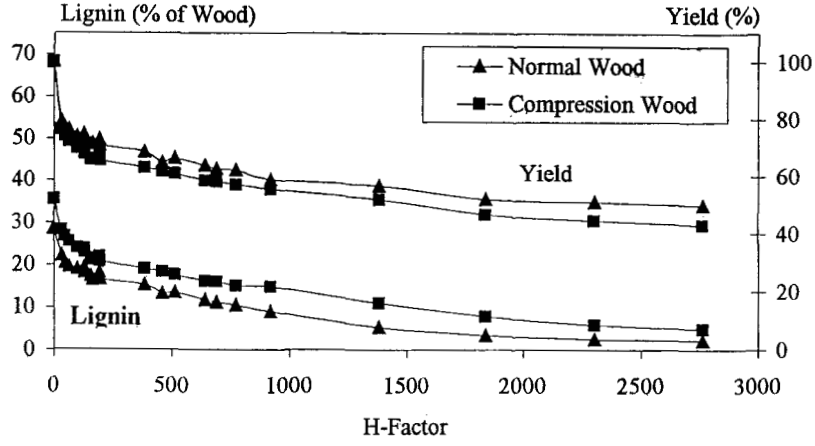


Figure 3. Percent lignin and pulp yield versus H-factor.

Sarkanen[16] who indicated a correlation between the rate of delignification and the structure of lignin (MeO/C_9 ratio). This can be applied to CW as its lignin contains more p-hydroxy and less guaiacyl phenylpropane units, i.e. less methoxyl groups, compared to NW lignin which contains a lower quantity of lignin in its fibres.[17] The unoccupied C_5-position of the benzene ring, in guaiacyl and p-hydroxy phenylpropane units, is the most reactive point of condensation,[18] and the formation of phenolic groups during the cook is likely to increase that reactivity.[19] Thus, it can result in lignin precipitation on fibres, causing an increase in kappa number. The high lignin content of the CW also corresponded to higher levels of alkali consumption.

Figure 4 indicates that yield is related to the amount of lignin remaining in the pulps, regardless of the cooking time and temperature. At all levels of maximum cooking time/temperature, total yield and residual lignin content are related by the expressions:

$$Y_{NW} = 46.974 + 1.455 \cdot L \qquad r^2 = 0.99 \tag{1}$$

$$Y_{CW} = 35.568 + 1.444 \cdot L \qquad r^2 = 0.99 \tag{2}$$

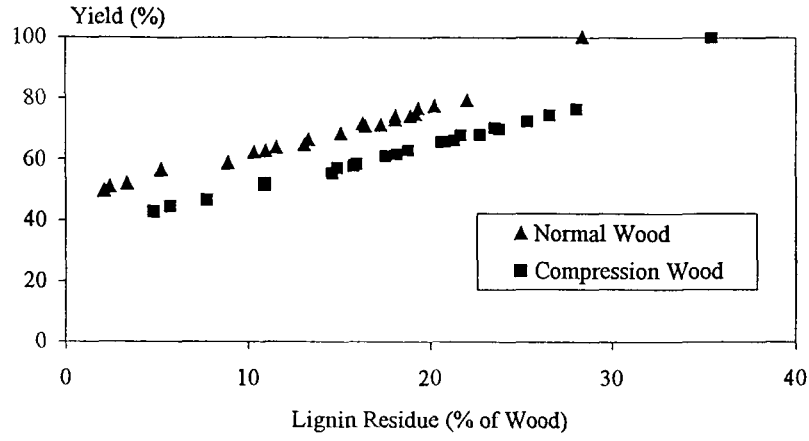


Figure 4. Plot of yield versus residual lignin content, different cooking time and temperature.

where Y = yield (%) and L = lignin content (% of wood) ({$2 \leq L_{NW} \leq 22$} and {$5 \leq L_{CW} \leq 28$})

The very high values of r^2 justify the fit of the experimental data to linear relationships in all cases. These simple linear models are in good agreement with the model proposed by Hatton[20] who showed that the general form for the dependence of pulp yield (Y) on lignin content (L) to be

$$Y = A + B(L) \tag{3}$$

where A and B are constants.

The lignin content of pulp (L) can be converted to kappa number (K) using the following equation:

$$K = \frac{100 \cdot L}{0.15 \cdot Y} \tag{4}$$

By substituting Equation 4 into Equations 1 and 2, the final expressions are made:

$$Y_{NW} = \frac{46.974}{1 - (0.002183 \cdot K)} \tag{5}$$

$$Y_{CW} = \frac{35.568}{1-(0.002166 \cdot K)} \quad (6)$$

where K = kappa number ({$28 \leq K_{NW} \leq 185$} and {$75 \leq K_{CW} \leq 245$}).

These linear models can be used as indirect methods for yield estimation, an important measure of pulp mill performance in a continuous pulping system. The precision of the yield estimates is controlled by the precision of the measured kappa numbers.[20] This method offers a time advantage in the analysis of pulp, as only kappa numbers need to be determined.[21]

Selectivity, defined as the simultaneous dissolution of lignin and carbohydrates during pulping, is of fundamental interest and economic importance. **Figure 4** implies a low delignification selectivity during the cook and thus a lower reactivity of CW lignin compared to that of NW. The selectivity of the pulping chemicals towards delignification determines the pulp yield and, to some extent, the pulp properties.[18] A low selectivity of CW pulping would result in a drop in DP and molecular weight of the cellulose polymer and in a reduction in the viscosity of the CW pulp.

CONCLUSIONS

The analyses showed that opposite wood and normal wood had the same amount of extractive, lignin, holocellulose and inorganic trace elements. Compression wood, on the other hand, possessed different chemical traits, which were drawbacks from a pulping and papermaking viewpoint. Compression wood behaved poorly in pulping. To obtain pulps of conventionally low kappa number, it was necessary to use a longer cooking time for CW. This was expected from the higher lignin content, different chemistry and distribution of lignin in CW and the need to remove considerably higher amounts in order to reach any given kappa no. Examining different cooking cycles, pulp yield of CW and NW indicated a linear relationship with residual lignin content, regardless of cooking time/temperature applied in this study.

The results of the present study indicate that CW processing would require special attention and control. If the feed stock contains some CW, conditions suitable for pulping of NW would result in non-uniform cooking and therefore in a heterogeneous pulp, i.e. some undercooked fibres. This would overload the subsequent deknotting and screening processes. Consequently, the amount of CW (and similarly knots) naturally present in a black spruce tree will also impact on the quality and price of the final product as CW requires more energy, chemicals and time for pulping. Considering the differences among the wood types, in order to produce a better pulp with higher yield and low lignin content, normal and opposite woods can be pulped together but compression wood has to be collected and processed separately, if desired at all.

Further work will concentrate on the kinetics of delignification and holocellulose dissolution, and will lead to the development of a model. Predicting final pulp properties and the required H-factor, this model will contribute to a better process control and monitoring through optimization of cooking conditions. More research and development is needed to design a screen which removes chips containing compression wood and knots, based on the chip density.

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REFERENCES

1 T.E. Timell, Compression Wood in Gymnosperms, Vol. I - III, Academic Press, San Diego, 1986.

2 J.L. Ladel, A.J. Carmichael and G.S. Thomas, Proceedings of the 8th Lake States Forest Tree Improvement Conference, September 12-13, p. 52-60 (1967).

3 B.F. Hrutfiord and A.R. Negri, Chemosphere, 25(1-2), 53 (1992).

4 B.F. Hrutfiord and A.R. Negri, Tappi J., 75(8), 129 (1992).

5 CPPA Standard Methods, Method # G.8, G.9, and G.13 (1992).

6 A.J. Panshin and C. de Zeeuw, Textbook of Wood Technology, 4th ed., McGraw-Hill Publishing Company, Toronto, 1980.

7 U. Sahlberg, Tappi J., 78(5), 162 (1995).

8 W.A. Kenney, Quantitative Genetic Aspects of Some Chemical Traits of North American Willow (*Salix* L.) Coppice, Ph.D. Thesis, University of Toronto, Faculty of Forestry, 1990.

9 U. Westermark, Wood Sci. Tech., 16(1), 71 (1982).

10 P.K. Hepler and R.O. Wayne, Annual Rev. Plant Physiol., 36, 397 (1985).

11 A. Wong, Pulp Paper Canada, 84(7), T170 (1983).

12 A.M. Scallan and J. Grignon, Svensk Papperstid. 82(2), 40 (1979).

13 J.H.E. Bailey and D.W. Reeve, J. Pulp Paper Sci., 20(3), 83 (1994).

14 T.M. Grace, B. Leopold, E.W. Malcolm and M.J. Kocurek, In Pulp and Paper Manufacture, Vol. 5, The Joint Textbook Committee of the Paper Industry, Atlanta, 1989.

15 M. Hupa, Recovery Boiler Chemical Principles: Kraft Recovery Operations Short Course, p. 170-172, Tappi Press, Atlanta, 1993.

16 H. Chang and K.V. Sarkanen, Tappi J. 56(3), 132 (1973).

17 E. Adler, Wood Sci. Tech., 11, 169 (1977).

18 E. Sjöström, Wood Chemistry: Fundamentals and Applications, 2nd ed., Academic Press, Inc. San Diego, 1993.

19 S.A. Rydholm, Pulping Processes, Interscience, New York, 1965.

20 J.V. Hatton, Tappi J. 76(3), 105 (1993).

21 D.B. Easty and E.W. Malcolm, Tappi J. 65(12), 78 (1982).