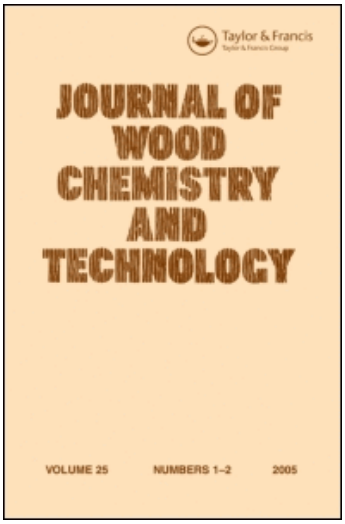

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The Effect of Wood Drying on Crystallinity and Microfibril Angle in Black Spruce *(Picea mariana)*

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The Effect of Wood Drying on Crystallinity and Microfibril Angle in Black Spruce *(Picea mariana)*

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Abstract: The effect of drying on wood cellulose crystallinity, crystallite size, and microfibril angle was investigated using wide angle X-ray diffraction. Forty replicated specimens of black spruce (*Picea mariana*) wood were dried at constant temperatures of 40°C and 80°C and relative humidities of 34% and 47% in attempts to attain samples possessing final moisture content of 15% and 8% at each temperature. X-ray evaluation of wood specimens, comparing individual samples pre- and post-drying, revealed that both the mass fraction of crystalline cellulose and crystallite width increased with drying. In contrast, mean microfibril angle of the wood was not significantly affected by drying. It was also apparent that the changes in wood ultrastructure resulting from drying were not influenced by the drying conditions, including temperature, relative humidity, and final moisture contents.

Keywords: Black spruce, cellulose, crystallinity, crystallite width, microfibril angle, X-ray diffraction

INTRODUCTION

Black spruce *(Picea mariana)* is an important species for the pulp and paper industry in eastern and central Canada and the Great Lakes States of the United States.[1] The wood of this species is also highly valued as lumber. Despite the industrial significance of black spruce, to-date there has been little research focused on the effects of drying on its ultrastructural properties such as crystallinity or microfibril angle.

The ultrastructural properties of wood are very critical in determining their industrial application and utility. Any variation in cell wall architecture, including crystallinity, and thus crystallite size, during processing could have significant impact on the resulting mechanical properties of the wood.[2]

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Similarly, the angle between the cellulose fibrils and the longitudinal cell axis, the microfibril angle (MFA), has been shown to be a crucial factor that influences the modulus of elasticity and the dimensional stability of wood.[3,4] Therefore, structural studies aimed at understanding pre-processing conditions like drying are essential for tailoring the properties of wood products.

Crystallinity is defined as the weight fraction of crystalline material in wood, whereas the size of the crystallite refers to the dimensions of ordered regions in the cellulose crystals. Estimation of wood crystallinity has been carried out using several analytical techniques, including X-ray diffraction,[5,6] solid state ^{13}C NMR spectroscopy,[7,8] and FT-IR Spectroscopy[8,9] to name only a few. Crystallinity depends on several factors including age, cell type, and chemical composition. Earlier studies have shown that the mass fraction of crystalline cellulose increases slightly with distance from the pith,[10] whereas the crystallinity and the thickness of cellulose crystallites were found to be approximately the same at the pith and near the bark.[11] Newman[12] indicated that the crystallinity of cellulose within the same tree can vary from 48–54%. On the other hand, studies suggest that crystallite sizes in softwood ranges from 25Å–36Å in thickness and 65Å–311Å in length.[4,13–16]

Microfibril angle, the major angle of the cellulose fibrils in S_2 layer of the secondary cell wall, has been shown to vary significantly from pith to bark and between trees.[17–21] The secondary cell wall of gymnosperm tracheids consists of S_1, S_2, and S_3 layers. In which each layer consists of a cellulose fibrils (microfibril) as a framework, oriented at a different angle in reference to the cell's long axis. The thickest layer, S_2, of the secondary cell wall plays an important role with regard to mechanical support, and has a significant role in mechanical properties of the wood formed.[22,23] MFA has been shown to be generally higher in softwoods compared to hardwoods.[24] Evans et al.[25] have shown that MFA decrease from the inner to outer growth rings at all heights in the stem, displaying angles ranging from 20–30° near the pith and then remaining constant (near 10°) in older wood near the bark. In addition, a decreasing trend in MFA was observed with height with respect to a defined growth ring. Several techniques have been applied in the past to quantify MFA, including polarized microscopy, iodine staining, and near-infrared spectroscopy (NIR).[19,26–29] X-ray diffraction, however, has recently become a common method of measuring MFA.

There have been numerous studies in the past that examined the effect(s) of thermal treatment on the ultrastructure of both softwood and hardwood species. It has been observed that crystallinity and crystallite size are among the parameters that change during thermal modification.[3,4,9] Bhuiyan et al.[30] observed an increase in crystallinity at the initial stages of thermal treatment, which then decreased in later stages. The authors concluded that the initial increase in crystallization occurs in the quasi-crystalline region, and is due to a rearrangement of cellulose molecules and lower stresses in wood (relaxation) at high moisture content. Wikberg et al.[31,32] studied the changes in the

chemical structure induced by thermal modification (steam) in spruce (*Picea abies*), birch (*Betula pendula*), aspen (*Populus tremula*), and oak (*Quercus robur*), and showed that in all cases some degradation of the less-ordered carbohydrates (i.e., hemicelluloses and amorphous cellulose) occurs during the thermal modified treatment, which consequently resulted in an overall increase in the cellulose (wood) crystallinity.

Generally, wood components are relatively stable at temperatures lower than 100°C and up to 48 hours of treatment.[33] The decomposition of cellulose crystals starts at approximately 210°C, and proceeds rapidly at 270°C.[34] Chow and Pickeles[35] studied softening and thermal degradation of wood, and presented X-ray diffraction patterns demonstrating decay of cellulose crystals between 250–400°C. Although many researchers have also studied the crystallinity of cellulose and its changes during steam treatments, there is a noticeable gap in similar research evaluating the changes in cellulose crystallinity during dynamic drying conditions.[36–38]

In the present study, changes in crystallinity, crystallite width and MFA of black spruce were investigated following various drying regimes. Unlike previous studies, the experiments were conducted at comparatively lower temperatures, namely 40 and 80°C with targeted moisture content of 8% and 15% in each drying regime. Variations in the crystallinity, crystallite size, and microfibril angles were compared between the green and dried wood, and also with respect to the difference in the drying temperature and final moisture content.

MATERIALS AND METHODS

Six black spruce (*Picea mariana*) trees were randomly selected and felled from a British Columbia coastal forest. Sections 550 mm in thickness were cut from each tree at breast height (1.3 m). Two planks were then cut from each section along the diagonal in a north-to-south direction. A total of eighty square specimens measuring 45 mm × 45 mm × 504 mm in length were subsequently cut from the planks. Fifty-mm-thick end-sections were removed from the ends of each specimen for the gravimetric determination of the initial moisture content (M_i). A further 2-mm section was then cut from each green specimen to measure initial wood crystallinity and MFA before drying. The final dimensions of the specimens employed for the drying experiments were therefore 45 mm × 45 mm × 402 mm in length. Following the completion of each drying regime, an additional 2-mm-thick section was removed from the adjacent end where the original section was cut to quantify the post-drying crystallinity and MFA. The cutting pattern of the specimens is shown in Figure 1.

Once the initial weight and M_i of the eighty test specimens was determined, the samples were subsequently dried in two climate controlled chambers (40 specimens in each) that were pre-set at two different temperatures; 40°C

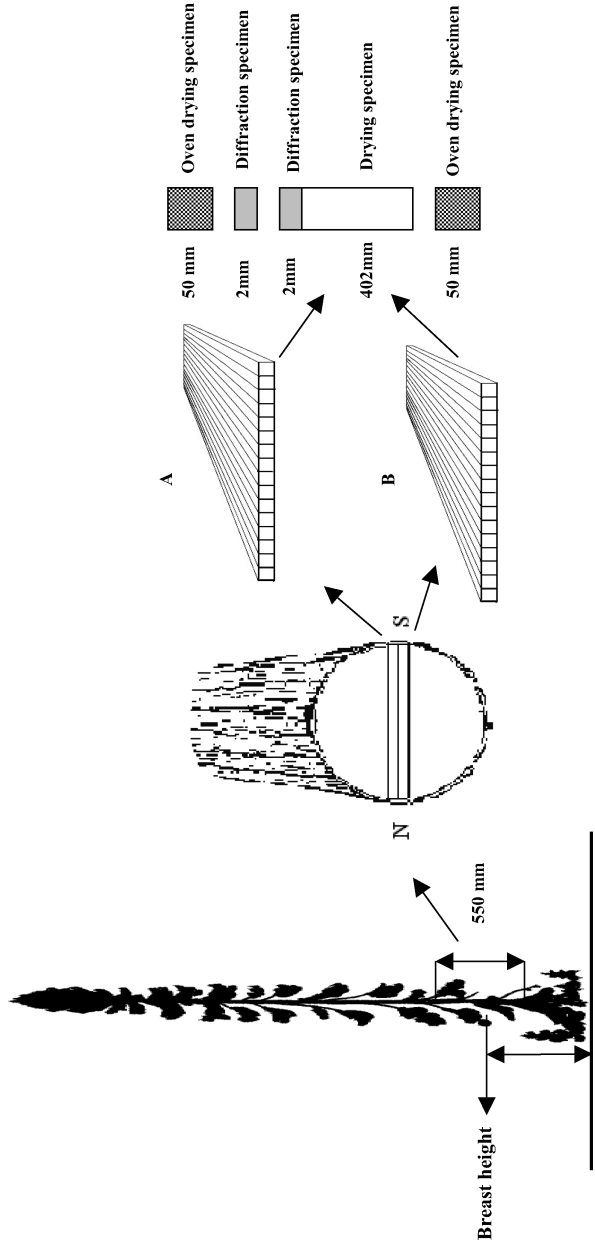

Figure 1. Schematic diagram of the specimen sampling protocol.

and 80°C at relative humidities of 34% and 47% for each temperature level. The mean M_i value was 37.6% with a standard deviation of 9.2% for the 40°C run, and 34.4% with a standard deviation of 4.6% for the 80°C run. An aluminum rack was manufactured for each chamber to hold the specimens and for ensuring equal air-flow between the specimens. The weight of each specimen was monitored daily with an electronic balance and twenty specimens were removed from each chamber when they reached a pre-calculated weight corresponding to 15% moisture content. The remaining twenty specimens were left in the controlled climate chamber to continue to dry until they reached the second target moisture content of ~8%.

A 1.68-mm cant was precision cut from each of the 80 test specimens using a twin-blade pneumatic saw. MFA was measured on the earlywood portion of three independent growth rings from each of the 45 mm × 2 mm × 1.68 mm cant specimens, representing a growth ring at both the left and right ends, and one in the center of the test specimen.[23] The 002 diffraction arc T-values were collected using a Bruker D8 Discover X-Ray diffraction unit equipped with an area array detector (GADDS) on the radial face of each earlywood portion of individual growth rings. The schematic representation of T-value determination is represented in Figure 2. Wide-angle diffraction was used in the transmission mode, and the measurements were performed with CuKα_1 radiation ($\lambda = 1.54$ Å), and the X-ray source fit with a 0.5 mm collimator and the scattered photon collected by the GADDS detector. Both the X-ray source and detector were set to theta = 0°. The average T-value of the two 002 diffraction arc peaks was used to calculate MFA as per Ukrainetz et al.[39].

Cell wall crystallinity was determined using the same X-ray unit and conditions, with the exception of the position of source, which was set to 17.5°. The main issue in such a process is the separation of the crystalline peaks from

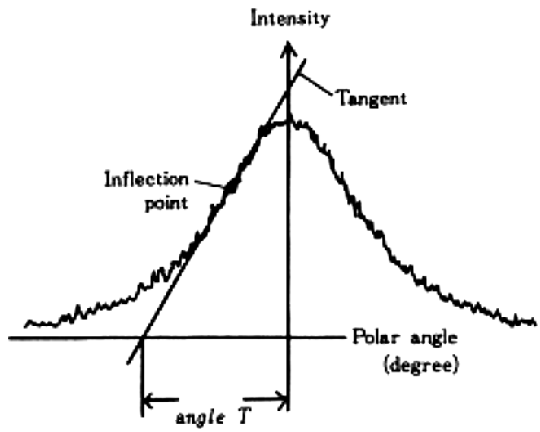

Figure 2. Measurement of *t*-value from (002) arc diffraction.

the background of amorphous scattering, thus it requires knowledge of the shape of the diffraction curve of the amorphous phase in those regions where the crystallinity peaks are superimposed. For this the lowest points of the peaks were selected assuming that these are the lowest point of the crystalline peaks, and the amorphous regions were separated from the crystalline domains, using the computerized programming technique for the determination of crystallinity as described by Vonk.[40] The width of the crystals was determined by the Scherrer formula:

$$\text{Width of crystal } (t) = \frac{K x \lambda}{B \cos \theta}$$

where K is the Scherrer constant (0.9), λ is the wavelength of the X-ray (1.542 Å), B is the full width half max (FWHM) of the reflection (in radians), and θ is the Bragg angle in degrees.

Significant change in the aforementioned parameters after drying was analyzed using Analysis of Variance using the SPSS software. In some cases a t-test was also performed to reveal the difference between them using Microsoft Excel.

RESULTS AND DISCUSSION

The crystallinity of green and dried black spruce specimens was measured and a paired t-test analysis was employed to evaluate differences. The mean crystallinity value of the green wood specimens was calculated to be 45.5% with a standard deviation (SD) of 3.8%, whereas the mean crystallinity for the eighty dried specimens was found to be 55.5% with a SD of 3.7%. The crystallinity data concur with values previously published for softwoods,[10] and statistical analyses indicated there is a significant difference between green and dried specimens ($p \leq .05$).

The temperature effect on changes in cell wall crystallinity were subsequently analyzed for the specimens dried at 40°C and 80°C, irrespective of their final moisture content, and were compared with their corresponding paired green values. Figure 3 demonstrates that the average crystallinity of green specimens that were dried at 40°C was found to be 45.6%, whereas after drying the average crystallinity value increased to 55.2%. In the case of the specimens that were dried at 80°C, these values were 45.3% and 54.9%, respectively. A paired t-test demonstrated that there are significant differences between green and dried crystallinity of the specimens dried at both temperatures ($p \leq .05$); however, there is no difference for final crystallinity when comparing drying temperature. Similar results have been reported by Futoshi et al.[41] evaluating Japanese softwoods, where it was shown that crystallinity increased after heat treatment, and the authors suggested that the increase in crystallinity was due to

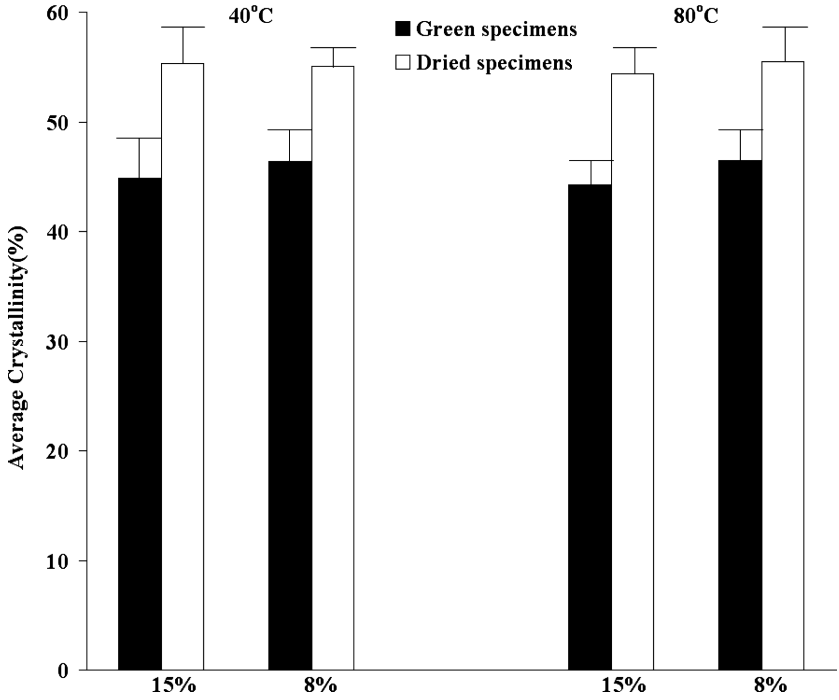

Figure 3. Average crystallinity of green and dried black spruce specimens at different temperatures and final moisture contents. Error bars represent standard deviation of 20 individual test specimens.

a reduction in the amorphous region caused by thermal decomposition in addition to the crystallization of the amorphous cellulose. More recently, Bhuiyan et al.[30] also found an increase in crystallinity both in Sitka spruce (*Picea sitchensis*) and in Buna tree (*Fagus crenata*) after heat treatment in both dry and moist conditions. These authors suggested that the increase in crystallinity was due to crystallization of the amorphous regions caused by rearrangement or reorientation of cellulose molecules. The authors also suggest that both the xylan and mannan components in the wood undergo crystallization as a result of the heat treatment, which results in an overall more crystalline wood.

In the current study, crystallinity changes of the specimens dried at 15% and 8% moisture content, irrespective of their drying temperatures, were also compared. At 15% moisture content the mean crystallinity values were found to be 54.9%, while the average crystallinity of the corresponding green samples was 44.6%. The corresponding additional forty specimens dried to 8% moisture content showed an average crystallinity of 55.5%, from a starting green crystallinity of 46.4%. Paired t-test analyses suggest that the average crystallinity after drying was again significantly different from the crystallinity of the green

samples. However, the average crystallinity values of the dried specimens at 15% moisture content showed no difference in comparison with those dried to 8% moisture content.

The variations within and between treatment groups were also analyzed by ANOVA in an attempted to detect any significant differences. In each case there were no significant differences observed between and within the treatment groups. The average crystallinity of dried specimens at 15% and 40°C was not significantly different from the average crystallinity of specimens dried at 8% and 40°C. Similar findings were also observed with the specimens dried at 80°C, and furthermore, this was also the case between the treatment groups. The average crystallinity of the 15% and 40°C specimens was observed to have no significant difference from the 8% and 80°C samples. Therefore, the observed changes in crystallinity were found to be independent of both target moisture content and drying temperature.

A similar trend was also observed in the calculated crystallite width of the samples. In the green samples, the crystallite width, determined by Scherrer formula, ranged from 15.5 to 23.3 Å with an average of 20.5 Å for green samples, whereas the dried samples ranged from 14.3 to 18.2 Å with average crystallite width of 16.2 Å. A paired *t*-test showed significant variation between conditions. The average crystallite width obtained in this study was lower than the crystallite width determined by others; however, none of the previously reported values were for black spruce. Marton et al.[13] observed a crystallite width of 30–35 Å for Norway spruce grown in Syracuse (New York, USA) and also observed that the width in compression wood was smaller than that of normal wood. Washusen and Evans[42] studied Tasmanian blue gum (*Eucalyptus globulus*) and found the width to be 36 Å in tension wood and 32 Å in normal wood. In Japanese red pine (*Pinus densiflora*) a crystallite width of 28–32 Å was reported by Nomura and Yamada.[14] The lower crystallite width in this study may be due to the difference in the method of measurement and type of specimens used. However, it is also possible that the dimensions are reflective of growing region, but this requires further investigation.

The effect of temperature and final moisture content on crystallite width was also analyzed, and in both the cases there does not appear to be any significant variation between treatment groups ($p \leq .05$).

The mean MFA was found to decrease as a consequence of drying, decreasing from an average of 16.3° with a SD of 5° to 15° with a SD of 3.9°. This small decrease is not statistically significant, and it seems that the removal of free water from wood under mild drying regimes, as used herein, has little influence on MFA. This trend was also observed by Andersson et al.[10] who evaluated thermal modification of Scots pine (*Pinus sylvestris*) and showed that the MFA distributions for thermally modified and reference samples were almost equal. The authors concluded that thermal modification did not markedly affect the orientation of microfibrils in the wood cell walls.

Average MFA values of the specimens dried at 40°C and 80°C, irrespective of final moisture content, were also compared with their green values. The average MFA of the green specimens was found to be 16.5°, whereas it was determined to be 14.9° after drying at 40°C. The specimens that were dried at 80°C showed an average MFA of 15.9° for the green specimens and 15° after drying (Figure 4). Paired t-test analysis indicated that there is no significant difference between the green and dried MFA values of the associated specimens dried at these two different temperatures ($p \leq .05$). It was also observed that the average MFA values of the specimens dried at 40°C showed no significant difference with the values of those dried at 80°C. The same trend was apparent when the green and dried MFA values of test specimens dried to 15% and 8% target moisture content were determined, irrespective of their drying temperatures. Although mean MFA decreased slightly after drying for each final moisture content group, they are not statistically significant, and therefore one cannot conclude that there is a difference in MFA of the dried and green

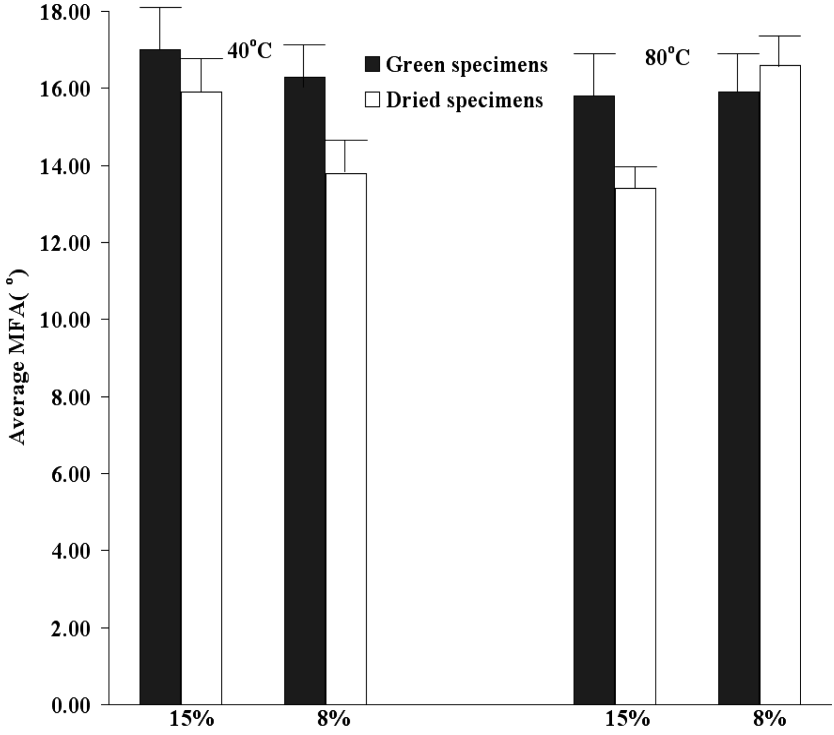

Figure 4. Average microfibril angle (MFA) of green and dried black spruce samples at different drying temperature and final moisture contents. Error bars represent standard deviation of 20 individual test specimens.

specimens. The comparison was also carried out between the dried specimens of two different moisture content groups, and also showed no significant differences. A second analysis was performed using the dried specimens to evaluate whether differences in average MFA between and within the treatment groups exist, that is, both between the drying temperatures and also between the final moisture content. In each case there was no significant differences observed between the MFA values.

The MFA values of the specimens, as a function of their tree cross-section location, were also analyzed. The MFA increased with distance from the bark towards the pith. The MFA values of the dried specimens closer to the pith and the bark were also compared with their corresponding green values. In both specimen groups it was apparent that there is significant variation in MFA between the dried and green specimens. However, a comparison of MFA of the dried outer and inner specimens revealed a significant difference which indicates that the MFA values of the specimens that are closer to the pith are more significantly affected by drying than the specimens near to the bark, which is accordance with the previous findings.[25]

CONCLUSIONS

The effect of drying on the average S_2 cell wall crystallinity and MFA in black spruce wood samples was studied using X-ray diffraction. The study clearly supports the following conclusions:

- The average crystallinity of dried black spruce was 55.5%, and are statistically different from the corresponding green samples (45.5%). However, differences were not observed between the average crystallinity values of the dried specimens compared at different drying regimes.
- Average dried crystallinity values were independent of temperature and target moisture content.
- The crystallite width of the green black spruce samples ranged from 15.5–23.3 Å with an average of 20.5 Å, whereas in dried samples the values ranged from 14.3–18.2 Å with average crystallite width of 16.2 Å.
- Average dried crystallite widths were independent of temperature and target moisture content.
- Average MFA of green black spruce was 16.4° and after drying was reduced to 15.3°. Although the MFA tends to decrease slightly after drying, no statistical significance was observed between wet and dried specimens.
- Average MFA values were independent of temperature and target moisture content.
- MFA increases from bark to pith in a tree cross-section.

- In both wet and dried specimens, the average MFA closer to the pith showed higher values than the ones closer to the bark.
- Following drying, the average MFA value of specimens closer to the pith showed a significant difference from the MFA value obtained in specimens near the bark.

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