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KRAFT PULPING OF *Juniperus communis* RESULTS IN PAPER WITH UNUSUALLY HIGH ELASTICITY

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Juniper (*Juniperus communis*) is a slowly growing softwood species that has unusually high elasticity. To demonstrate the utilization of the material properties of juniper, conventional kraft pulping was used to prepare juniper pulp, whose handsheet and fiber properties were subsequently analyzed. A large number of uncooked fiber bundles remained after pulping, the screened yield was low, and kappa number high. Also the viscosity value of juniper pulp was lower than that of common industrial softwood pulps, due to the harsh pulping conditions required. Juniper fibres had thicker cell walls, smaller diameters, and shorter lengths than those of the more conventional softwood species, while the microfibril angle, which was measured by X-ray diffraction, was significantly higher (22-37°). Moreover, the strength properties of juniper pulp handsheets were lower than those of common softwood pulps. The intriguing elastic properties of juniper wood, however, were apparent in the handsheet properties. Tensile stiffness was determined to be merely half of the value typical for softwood pulps, whereas the breaking stretch was more than twice higher. Although a large-scale industrial use of juniper is not possible, one can speculate that it may be feasible to mimic its properties via transgenic modification to faster growing species.

**Keywords:** *Juniperus communis;* Kraft pulping; Microfibril angle; Paper properties

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INTRODUCTION

Juniper (*Juniperus communis*) is a small tree whose growth rate is much too slow to justify its utilization for industrial manufacturing of wood and, in particular, paper products. Probably for this reason, we are not aware of any previous reports dealing with chemical pulping of juniper. Yet the unusual mechanical properties of juniper wood coupled with its exceptional fiber structure suggest that a network of delignified juniper fibers could result in paper with rather extraordinary strength properties. Although out of reach for the industrial use, one could envisage that if modern transgenic modifications could enable the tailoring of a species with juniper-like qualities with higher growth rates, these strength properties would be useful for certain applications in the first place. With this in mind, the aim of this article is to elucidate the fundamental properties of kraft pulped juniper fibers.
Despite the intriguing characteristics of juniper, there is little information on its properties or ultrastructure (Kantola and Seitsonen 1961; Kantola and Kähkönen 1963). The distinctive scent of juniper has probably been one of the main reasons for the abundance of studies on its extractives from wood, berries and needles, which have also been shown to have some medical applications (Agrawal et al. 1980; Chatzopoulou et al. 2002; Gordien et al. 2009; Inatomi et al. 2005; Shahmir et al. 2003). There are very few known applications of juniper. It has traditionally been used in decorative purposes in knife handles and butter knives and as material for toy bows. Juniper has also been proposed as a possible material for bone implants (Gross and Ezerietis 2002). Maybe the most well-known use for juniper is in gin, whose taste is predominantly derived from juniper berries (Willkie et al. 1937).

Fiber properties of juniper were examined by pulping with conventional kraft cooking and testing the handsheets produced from pulp. The peculiar elastic properties of the wood were visible as a high elasticity of handsheets. Although the tear and tensile strength of juniper handsheets were low when compared to softwood pulp values, they showed exceptionally high stretch and low tensile stiffness.

**EXPERIMENTAL**

**Pulping**

Juniper stem was obtained from Mikkeli, Finland. Only straight parts of the stem were used for pulping throughout their entire cross sections. Juniper was debarked and sawn into 5 mm thick discs, which were split in two for better packing of the material in bombs. An oil bath with rotating bombs was used for pulping. Chips and cooking liquor were added into cold bombs, and therefore the heating-up time can be considered the impregnation time. Pulping conditions and pulp properties are shown in Table 1. Pulping was done using industrial grade NaOH and Na$_2$S.

<table>
<thead>
<tr>
<th>Table 1. Conditions for Kraft Pulping and the Resulting Pulp Properties</th>
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<tbody>
<tr>
<td><strong>Cooking time</strong></td>
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<tr>
<td><strong>Temperature</strong></td>
</tr>
<tr>
<td><strong>Liquid : Wood - ratio</strong></td>
</tr>
<tr>
<td><strong>Active alkali</strong></td>
</tr>
<tr>
<td><strong>Sulfidity</strong></td>
</tr>
<tr>
<td><strong>Screened Yield</strong></td>
</tr>
<tr>
<td><strong>Reject</strong></td>
</tr>
<tr>
<td><strong>Kappa number</strong></td>
</tr>
<tr>
<td><strong>Intrinsic Viscosity</strong></td>
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</table>

Subsequently, pulp was washed with deionized water, defibrated in a Wennberg disintegrator, and fractionated using a flat screen (Mänttä, Finland) device with a 0.17 mm screen.
Handsheet and Fibre Testing

Kappa number and viscosity were determined according to SCAN-C 1:00 and SCAN-CM 15:99, respectively. The pulp was further analyzed using Kajaani FiberLab equipment (Metso Endress+Hauser Oy, Finland), giving the cumulative length weighed projectile fiber length distributions according to ISO16065-1:2001. Handsheets were prepared according to ISO 5269-1. Stiffness, stretch, and tensile strength and tear indices were measured according to SCAN-P 38:80 and SCAN-P 11:73 standard methods, respectively.

Chemical Characterisation of Pulp

Air-dry juniper pulp was ground using a Wiley mill. About 10 g of ground pulp was extracted with acetone. Subsequently, the acetone was evaporated using a rotary evaporator to determine the extractive content. Klason lignin was determined from the acetone-extracted ground pulp using the T 222 om-98 TAPPI standard.

Carbohydrate composition was determined using total acid hydrolysis. About 0.3 g of acetone-extracted ground pulp was hydrolysed with 72% sulphuric acid (0.3 mL) at 30°C for 1 hour. The hydrolyzate was mixed with 84 mL of water and sterilized in an autoclave at 120°C. Subsequently, the solution was cooled and diluted to 200 mL. Two 50 mL parallel samples were taken from the solution, and 2 mg rhamnose internal standard was added. Solution was neutralized by mixing it with anion exchange resin (IR-45, 20-50 mesh). After reaching pH 4, the solution was evaporated dry and diluted to about 2 mL volume. Then 60 mg of sodium borohydride was added to the solution, which was left to stand overnight. Sodium ions were removed using cation exchange resin (2-3 mL, Dowex W-X 8, H+-form, 50-100 mesh). After 5 minutes, the solution was filtered with a sintered glass filter (G1). The sample was evaporated dry, and 10 mL of methanol was added to remove the boric acid. Subsequently, the sample was evaporated dry and esterified by refluxing for 4 hours at 120°C with 2 mL of a 1:1 mixture of acetic anhydride and pyridine. After cooling, the samples were analysed using gas chromatography.

The used GC device was HP 5890 (USA). The capillary column NB-1701 (HNU-Nordion, Espoo, Finland) was used to determine monosaccharides as their alditol acetate derivates. Samples were analysed by isothermal temperature program (oven temperature 210 °C, 15 min). The injector and detector temperatures were 260 °C.

XRD Measurements

X-ray diffraction (XRD) measurements were conducted for the handsheets made of juniper pulp and the solid pieces of juniper wood. Using a scalpel, four wood samples were cut tangentially between approximately 0.5 cm radial spacing from the pith to the bark from the stem, whose radius (without bark) was 2.5 cm. The size of the pieces was 0.1 cm (radially) × 1 cm (tangentially) × 1 cm (longitudinally). The microfibril angles (MFA) were determined for juniper wood from the azimuthal intensity profiles of the cellulose reflection 004 measured using the symmetrical transmission geometry. The setup consisted of a Huber 420/511 four-circle goniometer, a sealed Cu-anode x-ray tube, and a NaI(Tl) scintillation counter. CuKα1 radiation (wavelength 1.541 Å) was obtained using a ground and bent germanium monochromator. The MFAs were determined by fitting a pair of Gaussian functions into the profile (Sarén et al. 2001). For the juniper
pulp handsheets, the width of cellulose crystallites was determined by measuring the cellulose reflection 200 using this same set-up in symmetrical reflection mode. The length of crystallites in juniper pulp handsheets was determined by measuring the reflection 004 in symmetrical transmission mode. The crystallite dimensions were obtained using the Scherrer equation (Andersson et al. 2000).

RESULTS AND DISCUSSION

A large number of uncooked fiber bundles that remained after pulping were removed using the 0.17 mm flat screen in the fractionation of pulp. Probably the high amount of branches in juniper was one reason for the large amount of uncooked fibers, which can be seen in the low yield.

The yield and the viscosity were low, whereas the kappa number was high (Table 1) compared to other unbleached softwood pulps that usually exhibit viscosity values around 1000 to 1300 and kappa numbers within the range of 15 to 30 (Sjöholm 2000; Kontturi et al. 2005; Kontturi and Vuorinen 2006; Joutsimo et al. 2005; Robertsén and Joutsimo 2005).

The high kappa number resulted from slow delignification, which was also evident according to the composition of the pulp (Table 2). The low viscosity, however, would indicate that the pulping conditions were harsh, leading to subsequent degradation of cellulose. Since pulping was not the main focus of this research, the parameters were not optimized further.

Table 2. Composition of Juniper Pulp

<table>
<thead>
<tr>
<th>Compound</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates</td>
<td>87.7</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>10.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.2</td>
</tr>
<tr>
<td>Acid-soluble Lignin</td>
<td>0.2</td>
</tr>
<tr>
<td>Extractives</td>
<td>0.5</td>
</tr>
</tbody>
</table>

In order to evaluate the potential of pulp as a paper material, one must understand how different factors affect the pulp quality. In general, the pulp properties that determine its suitability for various end-uses can be divided in two categories: chemistry (Rydholm 1985; Koljonen et al. 2004) and morphology of the fibers (Page 1969; Seth and Page 1988).

The carbohydrate composition of juniper kraft pulp and the literature values for softwood pulps are presented in Table 3. Juniper pulp had a higher amount of hemicelluloses than conventional softwood pulp. The amount of glucose correlated with the lowest values found in literature (Table 3).
Table 3. Carbohydrate Composition of Juniper and Pine (Rydholm 1985; Sjöholm et al. 2000; Hult et al. 2001) Kraft Pulp

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Juniper</th>
<th>Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinose (%)</td>
<td>0.4</td>
<td>0.1-1</td>
</tr>
<tr>
<td>Xylose (%)</td>
<td>9.4</td>
<td>4.5-9.4</td>
</tr>
<tr>
<td>Mannose (%)</td>
<td>6.9</td>
<td>5.0-5.9</td>
</tr>
<tr>
<td>Galactose (%)</td>
<td>0.3</td>
<td>0.0-0.5</td>
</tr>
<tr>
<td>Glucose (%)</td>
<td>83.1</td>
<td>83.6-90.3</td>
</tr>
</tbody>
</table>

The main hemicelluloses in softwoods are galactoglucomannan (GGM) and arabinoglucuronoxylan (AGX) (Sjöström 1993; Timell 1967). GGM consists of a linear backbone made of β-D-glucopyranose and β-D-mannopyranose units with α-D-galactopyranose branches. AGX, in turn, has a β-D-xylopyranose backbone with 4-O-methyl-α-D-glucuronic acid and α-L-arabinofuranose groups. Ratios of the monomeric units vary between wood species and even within a tree (Sjöström 1993). Although the exact amount of GGM and AGX cannot be calculated from the carbohydrate composition of pulp, rough estimations can be done from the amounts of hemicellulose backbone units, mannose and xylose.

The galactose:mannose ratio, 0.047 (in softwood pulp about 0.07), showed that GGM in juniper pulp contained significantly lower amounts of galactose than GGM in conventional softwood pulps. The arabinose:xylose ratio, 0.04, on the other hand, was much lower in juniper pulp than in AGX of conventional softwood pulp (ca. 0.1). Arabinose is known to be easily cleaved during alkaline pulping (Rydholm 1985), which partially explains the low arabinose:xylan ratio of juniper pulp, particularly when considering the harsh pulping conditions that led to the aforementioned low viscosity (Table 1).

The DP of the cellulose was about 2600, as calculated from the viscosity value, taking into account the amount of hemicelluloses (da Silva Perez and van Heiningen 2003). That DP value is much lower than the corresponding values for other unbleached softwood pulps, which usually have a cellulose DP in the order of 4000 (Sjöholm et al. 2000; Hult et al. 2001). The low DP of juniper pulp indicated that pulping had degraded fiber components to such extent that it possibly affected the fiber strength properties in the manner demonstrated by Gurnagul et al. (1992). However, since the DP of cellulose in the original juniper wood is unknown, conclusions on the effect of cooking should be considered with reservations.

The XRD patterns of juniper pulp handsheets corresponded to those of more common softwood species (Andersson et al. 2003) implying that the structure of cellulose in them was similar (Fig. 1). The width of cellulose crystallites was determined to be 4.0 ± 0.1 nm, and the length of the cellulose crystallites was 16 ± 2 nm. Typically, the cellulose crystallite width increases and the length decreases due to pulping (Leppänen et al. 2009), and further experiments with XRD on juniper wood are currently underway to clarify whether this is the case for juniper as well. The results will be published later elsewhere.
The handsheet and fiber properties of juniper pulp are presented in Table 4. The fibers in juniper pulp had thicker cell walls and smaller diameters and were significantly shorter than most common softwood pulp fibers. However, they somewhat resemble compression wood fibers, which are known for their shorter fiber lengths and increased cell wall thicknesses (Timell 1982; Westing 1965). It is unlikely, however, that these common features originate from the fact that the juniper wood used for pulping possessed vast amounts of compression wood. Indeed, as pointed out by Timell (1983), there are several genera of wood whose normal fibers bear resemblance to compression wood fibers in other species, *Juniperus* being one of them.

### Table 4. Handsheet and Fiber Properties of Juniper and Industrially Used Softwoods

<table>
<thead>
<tr>
<th>Handsheet properties</th>
<th>Juniper kraft pulp</th>
<th>Softwood kraft pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tens. Index (Nm/g)</td>
<td>36.9</td>
<td>36-120 ^c,d,a,e</td>
</tr>
<tr>
<td>Stretch (%)</td>
<td>5.4</td>
<td>2.7-3.3 ^c</td>
</tr>
<tr>
<td>Stiffness (kNm/g)</td>
<td>3.4</td>
<td>7.5-9.6 ^c,e</td>
</tr>
<tr>
<td>Tear Index (Nm/kg)</td>
<td>9.4</td>
<td>13-30 ^c,d,e</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>584</td>
<td></td>
</tr>
<tr>
<td>Fibre properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber diameter (μm)</td>
<td>21</td>
<td>23-56 ^g,h</td>
</tr>
<tr>
<td>Cell wall thickness (µm)</td>
<td>3.9</td>
<td>2.8-3.8 ^g,j</td>
</tr>
<tr>
<td>Mean length (mm)</td>
<td>0.83</td>
<td>1.5-3.6 ^g,h,i,k</td>
</tr>
<tr>
<td>Coarseness (µg/m)</td>
<td>97</td>
<td>130-300 ^l</td>
</tr>
<tr>
<td>Curl (%)</td>
<td>21.5</td>
<td>16.4-22.9 ^l</td>
</tr>
<tr>
<td>Microfibril angle (*)</td>
<td>37</td>
<td>5-20 ^a,b</td>
</tr>
</tbody>
</table>

Microfibril angle is one of the most important factors that determine the fiber properties. The strength properties of fibers depend more on the microfibril angle than on the type of fibers (early and late wood) or wood species (Page et al. 1972). Increase in the MFA has been shown to decrease the tensile strength of fibers. MFA also significantly affects the elastic modulus by increasing it when the MFA decreases. Even large differences in the chemistry of fibers have been shown to have almost no impact on the elastic modulus of fibers with the same microfibril angle (Page et al. 1977).

The MFA of juniper fibers was significantly higher than that in other conventional softwood fibers (Table 4). The growth rate of the tree has, in some instances, been shown to affect the microfibril angle (Herman et al. 1999). As the growth rate decreases, also the MFA has been reported to decrease in several softwood species (Donaldson 2008, Mäkinen et al. 2002). The high microfibril angle of juniper thus cannot be explained by its extremely slow growth rate. Besides, the growth rate does not necessarily affect the MFA (Francis et al. 2006). Here, the analogy between juniper fibers and compression wood fibers in common softwoods is again relevant: compression wood fibers have been reported to possess a higher microfibril angle than normal wood fibers (Kantola and Seitsonen 1961; Westing 1965; Paakkari and Serimaa 1984; Donaldson 2008). The high MFA is known to increase the elasticity of the fibers. Thus, as expected, similar values for elastic properties as the ones of juniper pulp fibers have been reported for compression wood fibers of spruce. In this respect, juniper fibers are similar to the fibers of another curious wood species, ginkgo (Ginkgo bilota L.) (Burgett et al. 2004). Fibers in ginkgo genus, like juniperus, are known to possess a structure that resembles compression wood fibers (Timell 1983).

The elastic properties of handsheets correlate well with the elasticity of individual fibers. As Page and Seth (1980a) have shown, the modulus of random sheets is proportional to one-third of the modulus of their component fiber in a well-bonded handsheet. The MFA is the most dominant factor determining the elastic modulus of fibers (Page et al. 1977). Decrease in elastic modulus of paper with increase in the MFA has been shown by Courchene et al. (2006).

In addition to bonding and elasticity of a single fiber, other fiber properties that affect the handsheet elasticity are fiber dimensions, curl, and microcompressions (Page and Seth 1980a; Page and Seth 1980b). When comparing to commercial pulps, a lower amount of microcompressions can be anticipated to occur during the relatively gentle process of laboratory pulping. The curl value 21.5% corresponds to those from commercial softwood kraft pulp, and the fiber length is lower than in common softwoods (Table 4), which normally would indicate high elastic modulus values (Page and Seth 1980a). The juniper pulp, however, resulted in the exceptionally low tensile stiffness and high stretch for handsheets, suggesting that mostly the fiber ultrastructure was the main contributor to the elasticity.

We can conclude that the intriguing elastic properties of the juniper pulp handsheets are mainly due to compression wood like properties, especially the high MFA. Although the high hemicellulose content could possibly increase the mobility of microfibris with respect to each other, their contribution to elasticity is only marginal (Salmén 2004).
The tensile strength of juniper pulp handsheets was significantly lower than the values for softwood handsheets from the literature (Table 4). It has been shown by Page (1969) that the tensile strength of the handsheets depends on the fiber length, fiber strength, relative bonded area, fiber dimensions in cross section, and bond strength. In the case of juniper pulp, fiber length and fiber dimensions were lower than those for common softwood kraft pulps (Table 4), which might be partially the reason for low tensile strength values. The high MFA of juniper is likely to decrease fiber strength, which in turn decreases the handsheet tensile strength. The tensile strength values are also affected by the relatively low density (Table 4) which reflects a low degree of interfiber bonding in the sheet (Page 1969). As for the tear strength (Table 4), juniper fibers have lower coarseness, shorter fiber length, and presumably lower fiber strength due to the high MFA than softwood fibers commonly. These properties are likely to be the cause of the relatively low tear index of the handsheets (Seth and Page 1988; Page 1994).

We emphasize that the kappa number of the pulped juniper was very high (56) in this study because the pulping conditions were not optimized. Therefore, direct comparison to the literature values of fiber and papermaking properties for conventional unbleached softwood pulps (Table 4) should be considered with reservations. Yet the deviations of juniper pulp handsheets from the handsheet properties of other softwood pulps can be ascribed largely to the higher MFA of juniper, which is an intrinsic property of juniper wood fibers, not juniper pulp per se. The high MFA is particularly influential on the handsheets’ elastic properties, which can be regarded as the most important result of this study. Optimization of the pulping conditions, together with beating experiments, would ultimately result in optimized material properties. Moreover, the response of juniper pulp to bleaching would be interesting to explore the scope of possible applications for high MFA fibers. Unfortunately, these experiments are outside the scope of this preliminary study.

Juniper wood itself is surely not a potential industrial fiber source. However, its intriguing fiber properties could be mimicked at a larger scale via biotechnology. Although the biotechnological research of natural fibers has so far been mainly focusing on the lignification, for example, to decrease the chemical consumption of processes (Chapple and Carpita 1998; Grima-Pettenati and Goffner 1999), the alteration of the structural features of the cell wall, such as the microfibril angle, could be of interest in the future (Donaldson 2008). For example, materials with high elasticity are used for certain packaging products that require high bursting strength, and nowadays plastics are commonly applied for this purpose. The use of wood fibers for such products would be in line with the current trend to reduce our dependency on the fossil-based chemicals. Moreover, natural fibers with novel properties are set to create new kinds of applications in the natural fiber reinforced composite field.

CONCLUSIONS

1. Strength properties of juniper pulp handsheets were lower than those of common industrial softwood pulp, while the elasticity was significantly higher. This was
considered to result primarily from the high microfibril angle (MFA), since the other fiber properties were considered to decrease the elasticity.

2. Juniper pulp fibers were shorter and had thicker cell walls and smaller diameters than softwoods commonly used in pulp and paper industry. The MFA in juniper fibers was significantly higher than in other softwoods.

3. The yield of juniper pulp turned out to be rather low, possibly due to the high amount of branches, which is also supported by the high lignin content of pulp. The low viscosity and the low DP of cellulose indicated that fibers had been possibly overcooked and fibers had been degraded severely.

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