Improved penetration of pulping reagents into wood

ABSTRACT

Pretreating hardwood chips or sticks with alkali increased the permeability of the wood and the rate of diffusion of water-soluble materials. Commercial-size hardwood (aspen, red alder, and red oak) chips were pulped with peroxymonosulfuric acid solutions to give bright pulps with very low lignin content, high viscosity, and kraft quality strength.

The enhanced penetration effect was demonstrated using uniformly cut pieces of wood (primarily aspen, but also other species). The homogeneity of delignification through the wood structure was analyzed using the acetyl bromide procedure for lignin. Penetration and delignification were much more uniform for the pretreated specimens than for water-soaked controls. The mechanism of enhanced penetration is considered from the standpoint of chemistry and the effects on wood microstructure. The primary chemical action was probably saponification of esters. The intercellular region in wood was weakened preferentially.

INTRODUCTION

The use of peroxymonosulfuric acid as a delignifying reagent was studied recently at the Forest Products Laboratory /1/. In the initial work, ground aspen wood was the substrate. In later studies, chemimechanical (cold soda) pulp, high-temperature thermal-refiner mechanical pulp (hardboard fiber), and restructured aspen wood were the substrates /2/. These materials were selected to minimize diffusion problems and fiber damage. The pulps prepared from these substrates had properties that would make them suitable for many fiber products, but they had less strength than kraft pulps from chips of the same wood species.

In chemical delignification of wood chips, the following sequence of events occurs: (a) the pulping reagent diffuses to the reaction site within the wood chip, (b) the reagent reacts with the lignin, and (c) the reaction products diffuse out of the wood structure into the bulk liquid. If the reaction within the wood structure is rate controlling, the pulping is homogeneous and a uniform pulp is obtained. With most oxidative reagents, the diffusion of the oxidant to the reaction site is rate controlling. The slow water solution mass transfer rates are even more hindered by the rapid consumption of active oxidant in the outer regions of the chip. Thus, the outer fibers are extensively delignified before the inner core has had an opportunity to react.

When wood chips were pretreated with alkali, the rate of diffusion into and out of the internal wood structure was greatly increased. This achieved a much more uniform pulping. Starting with chips, pulps of kraft strength were easily bleached without use of chlorine-containing reagents. This paper reports the results of pulping alkaline-pretreated wood with peroxymonosulfuric acid and other acidic oxidative pulping reagents. Experiments were performed to clarify the mechanism of the alkaline pretreatment.
RESULTS AND DISCUSSION

Pretreatment of wood sticks

The relative importance of reaction and diffusion rates was studied using matchstick-sized pieces of wood that had across-sectional thickness (3 mm) close to that of a 1/2-in. chip and a length (40 mm) such that the more rapid longitudinal diffusion would not dominate. The sticks were pretreated with alkaline solutions, washed with water, and pulped with acidified peroxymonosulfate solutions. The pulped sticks were extracted with 1% NaOH to remove degraded lignin products. Water-soaked sticks were used as controls. The pulped fibers were separated from the incompletely pulped core by suspending the stick in water, pressing, and stirring with a glass rod. This test for extent of fiberization was subjective, but it was adequate for this study because of the large difference between the results for the alkaline-pretreated sticks and those for the untreated hardwood sticks. The liberated fibers (referred to as fiber in the tables) and the unfiberized cores were each analyzed for their residual lignin content.

Pretreating aspen (Populus tremuloides) sticks with alkali significantly improved the rate and uniformity of the peroxymonosulfate pulping reaction compared to that for untreated wood (Table 1). The pretreated sticks were completely fiberized in less than 39 h at room temperature. At 24 h, even though the pulped stick could be separated into fiber and an unfiberized core, the difference in lignin contents between the 39-h and 24-h pulping times was not large. By contrast, the pulped controls were only 20% fiberized after 48 h and there was a large gradient of lignin concentration between the outer fibers and the inner core.

Other wood species were also examined (Table 2). With red oak (Quercus rubra), the pretreatment had positive effects even though the pulping of the pretreated oak was somewhat slower than that of pretreated aspen. After 48 h at room temperature, the pretreated oak was completely fiberized and had a lignin content of 7.1%. After the same period, the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core. The pretreatment effect was 9.4% in the controls still had an unfiberized core.

Table 1. Effect of pretreatment on peroxymonosulfate pulping of aspen.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Pulping time (h)</th>
<th>Extent fiberized (%)</th>
<th>Lignin content (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>15</td>
<td>0</td>
<td>&gt;15.5</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>54</td>
<td>6.2 (core)</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>100</td>
<td>3.6 (fiber)</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>100</td>
<td>4.6</td>
<td>62</td>
</tr>
<tr>
<td>Water soak</td>
<td>48</td>
<td>20</td>
<td>12.0 (inner core)</td>
<td>77</td>
</tr>
<tr>
<td>(control)</td>
<td></td>
<td></td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.1 (fiber)</td>
<td></td>
</tr>
</tbody>
</table>

1 Temperature, 21°C. 2 Ambient temperature, 24; 5% concentration.

Table 2. Effect of pretreatment on peroxymonosulfate pulping of various species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Pulping time (h)</th>
<th>Extent fiberized (%)</th>
<th>Lignin content (%)</th>
<th>Yield (%)</th>
<th>Lignin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red oak</td>
<td>48</td>
<td>55.1</td>
<td>7.1</td>
<td>69.3</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>53.7</td>
<td>100</td>
<td>64.1</td>
<td>55</td>
</tr>
<tr>
<td>Honey locust</td>
<td>24</td>
<td>100</td>
<td>7.5</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>164</td>
<td>90</td>
<td>3.1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Pine</td>
<td>72</td>
<td>100</td>
<td>15.5</td>
<td>0</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-</td>
<td>13.7</td>
<td>0</td>
<td>18.3</td>
</tr>
</tbody>
</table>

1 Ambient temperature, 24 h; 5% concentration. 2 1.5- by 1.25- by 50-mm sticks. 3 White outer fibers; most of the stick was hard and dark. 4 Sicks were soft and could be easily fractured but did not separate into fibers and a core.
times are excessively long. Table 4 shows the result of pulping pretreated aspen sticks at 35 °C and 50 °C. At 50 °C, the pulping reaction was too fast for diffusion; the outer fibers became pulped while the inner fibers remained lignified. Pulping was more uniform at 21 °C, but it required more than 24 h (Table 1). The optimum temperature to balance diffusion with reaction rate for aspen was near 35 °C. After 9 h at 35 °C, the stick was soft and could be fiberized, though not easily. The core was not clearly defined, but the inner fibers were slightly more yellow than the outer fibers. The fiberization point occurred at the same stage of delignification that is observed for other chemical pulping processes (6% to 7% residual lignin).

The core was not clearly defined, but the inner fibers were slightly more yellow than the outer fibers. The fiberization point occurred at the same stage of delignification that is observed for other chemical pulping processes (6% to 7% residual lignin).

Table 4. Effect of temperature on peroxymonosulfate pulping of pretreated aspen.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Extent fiberized (%)</th>
<th>Lignin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>9</td>
<td>69</td>
<td>100&lt;sup&gt;2&lt;/sup&gt;</td>
<td>6.7&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>67</td>
<td>100&lt;sup&gt;2&lt;/sup&gt;</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>–</td>
<td>53</td>
<td>4.0 (fiber)</td>
</tr>
</tbody>
</table>

<sup>1</sup> Ambient temperature, 24 h: 5% NaOH.
<sup>2</sup> Not easily fiberized (see text).
<sup>3</sup> Inner fibers.
<sup>4</sup> Untreated specimens had 5% fiberization.

The alkaline pretreatment should effectively improve the penetration and the rate of pulping of wood. Table 5 shows the result of alkaline pretreatment on the penetration of waterborne reagents. Alkaline pretreatment improved the rate and uniformity of the pulping of acidic pulping reagents. Alkaline pretreatment improved the rate and uniformity of acidic sodium chlorite delignification of aspen sticks (Table 5). Alkaline-pretreated birch sawdust pulps faster by the acid chloride process than untreated white birch /3/. At 70 °C, nitric acid as a pulp reagent had good penetration into wood even without alkaline pretreatment. The rate of the pulping reaction was slow enough that the reagent was not depleted as it moved into the wood interior. If the nitric acid pulping reaction was accelerated by raising the temperature to 97 °C, the positive effect of alkaline pretreatment on penetration was observed (Table 5).

### Chip pulping

Because of the increased penetration achievable with an alkaline pretreatment, direct pulping of wood chips seemed feasible. The details of chip pulping are given in the experiments section, and the results are shown in Table 7. Aspen chips [19 mm (0.75 in.)] were pretreated by an overnight soak in 5%, NaOH. Subsequently, the alkaline-pretreated chips could be pulped in 3 days at room temperature with peroxymonosulfuric acid. The results showed that the diffusion rate of water-soluble material through the acidic pulping reagent into the wood may be reversed partially but not completely by decreasing the pH from 13 to 3 /5/. The superswollen state is regained by raising the pH. The positive effect of the pretreatment could not be reversed by extensive washing with water or washing with acid to remove bound sodium ions (Table 3).

Thus, the sodium ions did not play a significant role in the penetration of the acid reagent. The Donnan effect has been evoked to explain the initial swelling in alkali /6/. The lack of a sodium ion effect plus the high proton and salt concentration of the pulping solution suggests that the Donnan effect was not a major contributor during peroxymonosulfate pulping reagent penetration.

The increased permeability of wood chips caused by alkaline pretreatment might be due to (a) increased access to the individual wood fibers through the gross wood structure or (b) increased permeability of the individual fiber walls. Increased permeability may be due to both of these factors as well. To test this question, the delignification of fiberized aspen wood pretreated with alkali was compared with the effect of identical pulping conditions on untreated fiberized aspen. In this experiment, the gross wood structure was destroyed and the change in permeability of the individual fiber walls as a result of alkaline pretreatment was studied.

Aspen hardboard fiber was used in this experiment /7/. The results of the comparison are shown in Table 6. Both the residue yield and the lignin content of the alkaline-pretreated fiber were fewer than that of the controls. This indicates that alkaline pretreatment increased the permeability of the individual fiber walls. These results are similar to the faster rate of acid chlorite delignification observed with alkaline-pretreated birch sawdust /3/. Alkaline treatment of hardwoods was studied in connection with improved digestibility by ruminants /5/. The results showed that the diffusion rate of water-soluble material through the cell walls increased severalfold with sodium hydroxide treatment. Also, the water permeability of air-dried pretreated hardwoods was considerably greater than that of corresponding controls. The authors attributed these observations and the superswelling effect of alkali to a saponification of "cross-linking" uronic acid esters of the 4-O-methylglucuronoxylans. There was no evidence of glu-
Table 5. Effect of pretreatment on other acidic oxidative pulping.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Pulping method</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Extent fiberized (%)</th>
<th>Lignin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Acid chlorite</td>
<td>24</td>
<td>25</td>
<td>74</td>
<td>55</td>
<td>Fiber: 5.4 Core: 7.8</td>
</tr>
<tr>
<td>5% NaOH</td>
<td>Acid chlorite</td>
<td>24</td>
<td>25</td>
<td>63</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Water</td>
<td>Nitric acid</td>
<td>1</td>
<td>97</td>
<td>43</td>
<td>78</td>
<td>Fiber: 5.8 Core: NA</td>
</tr>
<tr>
<td>5% NaOH</td>
<td>Nitric acid</td>
<td>1</td>
<td>97</td>
<td>45</td>
<td>100</td>
<td>&gt;10.9</td>
</tr>
</tbody>
</table>

Table 6. Results of peroxymonosulfate pulping of chips.

<table>
<thead>
<tr>
<th>Species</th>
<th>Total yield (%)</th>
<th>Screenings (Percent of wood)</th>
<th>Viscosity (mPa-s)</th>
<th>Lignin content (%)</th>
<th>Canadian standard freeness (ml)</th>
<th>Tear index (mN-m²/g)</th>
<th>Tensile index (N-m/g)</th>
<th>Brightness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspen A</td>
<td>64.2</td>
<td>14.8</td>
<td>28</td>
<td>0.8</td>
<td>665</td>
<td>7.7</td>
<td>93</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>485</td>
<td>6.5</td>
<td>119</td>
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<td></td>
<td></td>
<td>325</td>
<td>6.4</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>Aspen B</td>
<td>58.4</td>
<td>2.7</td>
<td>48</td>
<td>0.4</td>
<td>680</td>
<td>5.7</td>
<td>77</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>565</td>
<td>6.2</td>
<td>88</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>370</td>
<td>6.1</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Aspen (control)</td>
<td>76.1</td>
<td>64.2</td>
<td>47</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aspen kraft (control)</td>
<td>52.5</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>615</td>
<td>6.2</td>
<td>52</td>
<td>33</td>
</tr>
<tr>
<td>Red oak</td>
<td>46.8</td>
<td>14.7</td>
<td>43</td>
<td>1.0</td>
<td>710</td>
<td>8.8</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>550</td>
<td>11.1</td>
<td>72</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>395</td>
<td>10.2</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>Red alder</td>
<td>53.1</td>
<td>18</td>
<td>29</td>
<td>1.1</td>
<td>725</td>
<td>5.1</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>525</td>
<td>7.5</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>430</td>
<td>6.7</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>Bleached aspen B</td>
<td>-</td>
<td>-</td>
<td>56</td>
<td>-</td>
<td>660</td>
<td>5.6</td>
<td>28</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>505</td>
<td>8.1</td>
<td>82</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>380</td>
<td>7.1</td>
<td>97</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Effect of alkaline pretreatment on delignification of aspen hardboard fiber.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Residue yield (%)</th>
<th>Lignin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>63</td>
<td>8.0</td>
</tr>
<tr>
<td>NaOH</td>
<td>61</td>
<td>4.1</td>
</tr>
</tbody>
</table>

1 See Experimental for conditions.
2 Chips for kraft pulping taken from same sample as chips for peroxymonosulfate pulping.

curonoxylan involvement. The identity of the cell wall polymer that contributed the alcohol function to the ester was not determined, but it was postulated to be lignin or another xylan. The importance of breaking the ester bond was supported by the fact that ammonolysis with liquid ammonia was also effective in increasing the swelling capacity of the wood.

Diffuse reflectance Fourier transform infrared (DRIFT) spectra were obtained directly from the surface of aspen sticks (Fig. 1). The interior surface was examined by splitting the sticks longitudinally through the center. In all examples reported, the spectra from the interior surfaces were the same as those from the exterior surface. A strong band at 1,730 cm⁻¹ was observed in the spectrum from untreated wood. This band was assigned to ester carbonyl stretching and may have a large contribution from acetate groups. The band disappeared upon alkaline pretreatment and was replaced by increased infrared absorption in the 1,550- to 1,700-cm⁻¹ region and decreased absorption at 1,260 cm⁻¹, which could be ester C-O stretching. The increased absorption is in the region characteristic of ionized carboxyls. Treatment of the saponified wood with acid should result in an increase in the absorption frequency. Indeed, curve C was obtained after washing the alkaline pretreated wood with acid (curve B). In addition, the acid wash apparently produced some reesterification or lactonization. Treatment of aspen wood with liquid ammonia under pressure also essentially eliminated the 1,740-cm⁻¹ band (curve E). A strong band centered at 1,670 cm⁻¹ appeared in the spectrum of aspen pretreated with gaseous ammonia under conditions that would not be expected to produce many amide functional groups (curve D).

Liquid penetration into wood occurs on a scale observable by electron microscopy. The main mode of liquid transport into hardwoods is through the vessels and then into other wood cells through the pits. A thin pit membrane covers the opening between the pits of two adjacent cells. By scanning electron microscopy, we did not observe any disruption of the pit membranes caused by alkaline pretreatment. However, after air drying the membranes of the treated wood
Phenolic hydroxybenzoates, which and peroxymonosulfate were possibly in the lignin polymer. Cross-linked acids. Some of the intercellular regions as possible cross-linking acids. The band at 1,740 cm\(^{-1}\) appeared at 1,670 cm\(^{-1}\). The band at 1,260 cm\(^{-1}\) had been eliminated and a pronounced band that the 1,740 cm\(^{-1}\) band had been reduced compared with that of controls. Although some limited movement of xylan polymers could have occurred during the ammonia gas treatment, cleavage of the ester bonds apparently is more important than removal of xylan to the improvement in penetration.

### EXPERIMENTAL

**Stick penetration**

Matchstick-shaped samples (40 by 3 by 3 mm) were cut from sapwood in the bole of mature trees. The length appeared more wrinkled than those of air-dried controls. We observed a more dramatic effect by splitting air-dried sticks in the axial direction. If the wood was not pretreated, the splitting occurred with a tearing of the vessel walls. In alkaline-pretreated wood, the splitting occurred primarily between cell walls. This is probably related to the decrease in the relative torsional modulus reported in birch treated with 10 g/L NaOH /7/. These observations imply that the opening of the wood structure takes place in the middle lamella as well as in the fiber wall. Therefore, saponification of pectic substance uronic acid esters, in addition to saponification of xylan uronic acid esters, is probably important. Lignin of the poplar species contains phydroxybenzoates, which could conceivably exist as cross-link structures /8/.

Liquor analysis from the pretreatment stage showed that most of the dissolved material was xylan. Removal of xylan was reported as the reason for the increases in median pore width and pulping rate when alkaline-pretreated white birch sawdust was delignified with acid chlorite /3/. We sought to determine if xylan removal was the cause of improved penetration of acidic pulp reagents into larger wood particles. Aspen sticks with a moisture content of 22% were treated with ammonia gas by exposing them to the vapors over ammonium hydroxide for 3 days. After treatment, excess gas was removed with vacuum, and peroxymonosulfate pulping reagent was added without any washing. The results were essentially the same as those for sodium hydroxide pretreatment (100% fiberized, 2% lignin remaining after peroxymonosulfate pulping for 48 h at 21°C). The DRIFT spectrum showed that the 1,740 cm\(^{-1}\) band had been eliminated and a pronounced band appeared at 1,670 cm\(^{-1}\) (Fig. 1, curve D). The band at 1,250 cm\(^{-1}\) was also reduced compared with that of controls. This treatment can be used before pulping with acidic, oxidative reagents, such as peroxymonosulfuric acid, to increase the homogeneity and overall pulping rate. With this pretreatment, a preliminary fiberization step before pulping is not necessary, and strong pulps can be obtained directly from wood chips.

The mechanism of improved pulping reagent penetration was probably a cleavage of ester bonds as proposed by Tarkow and Fast /5/. The 4-O-methyl-glucuronic acids of hardwood xylans may have been forming ester cross-links with other wood polymers that, when broken, allowed the wood structure to swell beyond the waterswollen state. Penetration both into the wood microstructure and through the micropores of the fibril wall was improved. The observation that the middle lamella structure seemed to weaken from alkaline pretreatment implicated the galacturonic acids of pectin and other pectic polysaccharides that exist in those intercellular regions as possible cross-linking acids. Some of the carboxylic acid portion of the esters were possibly in the lignin polymer.

### CONCLUDING REMARKS

Pretreating hardwood chips or sticks with alkali increased the permeability of the wood and increased the rate of diffusion of water-soluble materials. This treatment can be used before pulping with acidic, oxidative reagents, such as peroxymonosulfonic acid, to increase the homogeneity and overall pulping rate. With this pretreatment, a preliminary fiberization step before pulping is not necessary, and strong pulps can be obtained directly from wood chips.

Chip pulping

Mixed 19-mm aspen chips (screened only to remove fines, large knots, and oversized pieces) (400-g oven-dry basis, 34% moisture) were soaked in 3,500 ml of 5% NaOH solution overnight. The alkali was removed by filtration and the chips were washed twice with a solution composed of 896 g Oxone, 320 ml concentrated H\(_2\)SO\(_4\), and 5 l water. After 50 h at room temperature (Aspen A), the acidic pulping liquors were removed, and the chips were washed twice with water and extracted for 24 h at ambient temperature with 4 L of 1% NaOH solution. The alkali was removed by filtration, and the softened chips were washed with hot water and fiberized with a large excess of hot water in a vigorously stirred mixing tank. A second batch of aspen chips (Aspen B) was treated in the same manner ex-
cept that the room temperature pulp-
ing was continued for 72 h. Red oak
and red alder chips were similarly
pulped for 72 h at room temperature.
The control aspen chips (no pretreat-
ment) were pulped for 72 h.

Aspen peroxymonosulfate pulp
with a residual lignin content of 0.4%
and a brightness of 74% (relative to
magnesium carbonate) was bleached
with hydrogen peroxide. The pulp
was first treated with 0.5% DTPA, then
washed and bleached with 0.5% H₂O₂
on pulp at 11% consistency with a stan-
dard magnesium and silicate buffer.
After 45 min at 75°C, the pulp was
rinsed with a dilute bisulfite-thio-
sulfate solution followed by distilled
water. The pulp brightness was 79%.1
A second treatment with 0.28% H₂O₂
on pulp raised the brightness to 85%.

Handsheets were formed and
tested by TAPPI Test Methods T205
om-88 and t220 om-88. Tensile index
measurements were performed on
necked-down specimens and calculat-
ed on a volume basis. Viscosities
were determined by TAPPI Test
Method T230 om-82.

Hardboard fiber comparison

Aspen hardboard fiber used in previ-
ous studies /2/ was soaked for 16 h in
a 1.0% NaOH solution at 10% consist-
ency and then drained. It was then
delignified at room temperature
(22°C) for 3 days using a 2.7% solution
of peroxymonosulfuric acid acidified
to pH 0.30 with sulfuric acid at a 10%
consistency. An untreated sample
was also delignified under identical
conditions. The sodium hydroxide left
in the drained fibers was neutralized
by adding an equivalent amount of
sulfuric acid to the peroxymonosul-
fate treating solution. To remove the
degraded lignin, both samples were
extracted with 1.0% NaOH at 50°C for
3 h.

DRIFT spectra

The diffuse reflectance Fourier trans-
form infrared (DRIFT) spectra were
obtained using a Nicolet Instrument
Corporation (Madison, Wisconsin) Se-
tries 6000 Fourier Transform Spectro-
meter with a Harrick (Ossining, New
York) “praying mantis” diffuse reflect-
ance attachment. Spectra were re-
corded from external or internal sur-
faces of air-dried stick samples. There
was no additional sample prepara-
tion.

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