**ABSTRACT**

High-temperature (HT)-peroxide bleaching of a thermomechanical pulp made of Norwegian spruce was investigated; to that end, one-stage reference bleaching at 70°C and one- and two-stage bleaching at 105°C at different total alkali charges (TAs) using a wing defibrator as a mixer were performed.

Two-stage HT peroxide bleaching produces a brighter pulp than one-stage HT peroxide bleaching does. The TA should be kept low (10–15 kg/t) and the total alkali/peroxide ratio should be low in the first stage to minimize the COD load and obtain higher residual peroxide. Increased TA does not improve brightness. The bleaching time in HT bleaching at 105°C can be short, since the maximum brightness is reached after only 2.5 min.

Preimpregnation of the pulp with hydrogen peroxide before a two-stage alkali addition can produce a pulp with a brightness and residual peroxide comparable to those obtained in conventional one-stage peroxide bleaching at the same hydrogen peroxide charge and at a low TA. The COD load was, however, higher than in conventional bleaching.

**INTRODUCTION**

In bleaching mechanical pulps, hydrogen peroxide or sodium dithionite are the common bleaching agents. Conventional bleaching includes a chelating step in which detrimental metal ions, such as manganese, are removed and hydrogen peroxide and alkali are added to the pulp. Bleaching is usually performed in a bleaching tower at temperatures of 60–80°C for a bleaching time of 2–4 h.

High-temperature (HT)-peroxide bleaching of mechanical pulps can be performed by adding the bleaching chemicals to the refiner eye or the blow line of the refiner. The disadvantages of refiner or blow-line bleaching are that heavy metal management is usually quite poor and the temperature very high, resulting in lower brightness for a given hydrogen peroxide charge than with conventional tower bleaching [1, 2]. In recent years, HT-peroxide bleaching technology for manufacturing mechanical hardwood and, to some extent, softwood pulps has been further developed [3, 4]. In the alkaline peroxide mechanical pulping (APMP) process, the wood chips are impregnated in one or two steps with chelating agents and bleaching chemicals before refining [5, 6].

HT-peroxide bleaching under slightly steam-pressurized conditions should have some advantages over conventional bleaching. The main features of this method are a short bleaching time and low alkali charges; under such conditions, the darkening of the pulp due to alkali and temperature effects negligible.

In this investigation, one- and two-stage HT-peroxide bleaching processes were studied at various total alkali charges (TAs) and with various bleaching periods; ISO brightness (R457), chemical oxygen demand (COD) load, residual peroxide, and final pH were determined.

**MATERIALS AND METHODS**

DTPA-treated and washed industrially manufactured thermomechanical pulp (TMP) made of Norwegian spruce with an initial ISO brightness of 60.9, freeness of 95 mL and manganese content of 1.5 ppm was used in the experiments.

A modified wing defibrator consisting of a double-mantled vessel (see Appendix) was preheated to 105°C. Then, 150 g of pulp (o.d.) was placed inside the wing defibrator and heated with steam to approximately 100°C for 2 min. The mixing was started and the chemicals (peroxide, silicate, and sodium hydroxide) were added (12 L/min) to the defibrator vessel via a nozzle. Mixing was done at 1750 rpm for 45 s (one-stage bleaching) or 2 × 30 s (two-stage bleaching). The pulp remained in the defibrator for either 5 or 10 min in the one-stage bleaching and for 2 × 1.25, 2 × 2.5, or 2 × 5 min in the two-stage bleaching.
In the hydrogen peroxide preimpregnation experiments, the pulp was mixed separately with hydrogen peroxide at room temperature and then placed in plastic bags in a 70°C water bath for 45 min. The pulp was placed in the defibrator and the alkali was added in one or two steps.

For the reference bleaching experiments conducted at 70°C, the defibrator was used as a mixer and the pulp was put in plastic bags after mixing the chemicals. The bags were placed in a 70°C water bath for 2 h.

The bleaching reaction was rapidly quenched in cold water, and the ISO brightness (R 457), pH, COD load, and residual peroxide were then determined. The hydrogen peroxide charge was 40 kg/t and the silicate charge was 30 kg/t in all experiments.

RESULTS AND DISCUSSION

One-Stage Peroxide Bleaching

The one-stage reference bleaching was performed at 70°C for 2 h. The total alkali charge (TA) was 10–35 kg/t. It was possible to obtain an ISO brightness (R457) of 79 using 30 kg/t TA (see Figure 1). The HT bleaching was performed at 105°C for 5 and 10 min with the same chemical charges as for the reference. The maximum brightness was 75 using a TA of 20 kg/t. The hydrogen peroxide charge was 40 kg/t and the silicate charge was 30 kg/t in all the experiments.

The maximum brightness obtained with HT bleaching was noticeably lower than that obtained with the reference bleaching performed at 70°C. Since the brightness was approximately the same for both 5 and 10 min of bleaching, no further increase in brightness would be obtained by further prolonging the bleaching time. The lower brightness achieved with HT bleaching could be because alkaline darkening reactions compete with the bleaching reactions in the initial bleaching stage. Alkaline darkening is a fast and irreversible reaction, and the chromophores that are formed are resistant to peroxide [7-10]. One way to reduce the darkening effect of the alkali should thus be to preimpregnate the pulp with hydrogen peroxide before alkali addition. Preimpregnation of the pulp with 40 kg/t of hydrogen peroxide before alkali addition increased the brightness at low alkali charges; at higher alkali charges, however, the effect was small. Preimpregnation obviously prevents some of the alkali darkening reactions.

The residual peroxide at low alkali charges was high because the pH was close to neutral (see Table 1 and Figure 2). The residual peroxide levels in the HT experiments were in the same range as those of the reference, though the brightness was generally higher for the reference (see Figure 2). However, after preimpregnation, the brightness achieved with HT bleaching at low alkali charges approached that of the reference, and the residual peroxide was slightly higher than in the HT bleaching with no preimpregnation. Not even the increased consumption of peroxide with the addition of more alkali improved the brightness. The COD load was approximately the same for the HT bleaching with hydrogen peroxide preimpregnation and the reference (see Figure 3). The alkali charge affected the COD load more than the temperature did.

Figure 1. R457 (ISO brightness) versus total alkali charge (TA) for one-stage peroxide bleaching performed at 70°C for 2 h (reference), 105°C for 5 or 10 min, and 105°C for 5 or 10 min with hydrogen peroxide preimpregnation at 70°C for 45 min.
Table 1. pH measured in approximately 2% pulp concentration (p.c.) after one-stage peroxide bleaching with total alkali charges (TAs) of 10, 20, and 30 kg/t.

<table>
<thead>
<tr>
<th>TA kg/t</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 70°C, 2 h</td>
<td>6.8</td>
<td>7.6</td>
<td>9.0</td>
</tr>
<tr>
<td>105°C, 5 min</td>
<td>6.9</td>
<td>9.0</td>
<td>9.5</td>
</tr>
<tr>
<td>105°C, 10 min</td>
<td>6.6</td>
<td>8.3</td>
<td>9.7</td>
</tr>
<tr>
<td>105°C, 5 min (Pre. imp.)</td>
<td>7.1</td>
<td>8.6</td>
<td>9.7</td>
</tr>
<tr>
<td>105°C, 10 min (Pre. imp.)</td>
<td>6.3</td>
<td>8.0</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Figure 2. R457 versus residual peroxide for one-stage peroxide bleaching performed at 70°C for 2 h (reference), 105°C for 5 or 10 min, and 105°C for 5 or 10 min with hydrogen peroxide preimpregnation at 70°C for 45 min.

Figure 3. R457 versus chemical oxygen demand (COD) load for one-stage peroxide bleaching performed at 70°C for 2 h (reference), 105°C for 5 or 10 min, and 105°C for 5 or 10 min with hydrogen peroxide preimpregnation at 70°C for 45 min.
The sodium hydroxide charge was chosen so that the TA in the first stage was ¼, ½, or ¾ of the TA added in both stages together. The bleaching time was 2.5 min in each of the first and second stages, for a total bleaching time of 5 min. A low alkali/peroxide ratio (¼ of TA) in the first stage produced a higher final brightness (see Figure 4). A high alkali/peroxide ratio in the first stage reduced the brightness, probably due to alkaline darkening of the pulp. The residual peroxide was approximately the same independent of the alkali addition strategy (see Table 2). The COD load was lower in the samples for which ¼ of the TA was added in the first stage.

Table 2. COD load, residual peroxide, and final pH (2% p.c.) for the two-stage bleaching experiments at 105°C and 2 × 2.5 min at 10, 20, and 30 kg/t of TA. The TA in the first stage was ¼, ½, or ¾ of the TA in both stages together.

<table>
<thead>
<tr>
<th>TA kg/t</th>
<th>COD, kg/t</th>
<th>Residual peroxide, kg/t</th>
<th>Final pH, 2% p.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>¼ of TA charge in first stage</td>
<td>25</td>
<td>31</td>
<td>59</td>
</tr>
<tr>
<td>½ of TA charge in first stage</td>
<td>19</td>
<td>54</td>
<td>25</td>
</tr>
<tr>
<td>¾ of TA charge in first stage</td>
<td>19</td>
<td>54</td>
<td>29</td>
</tr>
<tr>
<td>¼ of TA charge in first stage</td>
<td>25</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>½ of TA charge in first stage</td>
<td>25</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>¾ of TA charge in first stage</td>
<td>29</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

Time

The sodium hydroxide charge was chosen so that the TA in the first stage was ¼ of the TA in both stages together. The bleaching time was 2 × 1.25, 2 × 2.5, or 2 × 5 min, giving total times of 2.5, 5, or 10 min. After 2 × 1.25 min the brightness was 74–75; prolonging the bleaching time to 2 × 2.5 min did not increase the brightness significantly, and bleaching for 2 × 5 min slightly lowered the brightness (see Figure 5). This indicates that the bleaching reaction is fast and that prolonging the bleaching time does not increase the brightness. At low alkali charges, the residual peroxide was high and the final pH was low (see Table 3) and again; prolonging the bleaching time will not improve the brightness. At higher alkali charges, the peroxide consumption and final pH were higher but the brightness was not improved, maximum brightness being reached after only 2 × 1.25 min. The COD loads for the three different total bleaching times were similar, indicating that COD formation is fast and that time is less important in this regard, than the alkali charge is (see Table 3). A short bleaching time and low TA will produce good brightness at a high residual peroxide level and lower COD load.
Figure 5. R457 versus time for two-stage peroxide bleaching performed at 105°C for 2 × 1.25, 2 × 2.5, and 2 × 5 min. The TA in the first stage was ¼ of the TA in both stages together. The dotted line indicates the average for all samples at the given time.

Table 3. COD load, residual peroxide, and final pH (2% p.c.) for the two-stage bleaching experiments at 105°C and 2 × 1.25, 2 × 2.5, and 2 × 5 min at 10, 20, and 30 kg/t of TA. The TA in the first stage was ¼ of the TA in both stages together.

Preimpregnation

To increase the brightness still further, the pulp was preimpregnated with 40 kg/t of hydrogen peroxide at room temperature; the pulp was then preheated for 45 min at 70°C to ensure good penetration of the hydrogen peroxide into the fiber. The pulp was heated with steam and alkali was added in two stages: ¼ of the TA (including 30 kg/t of silicate) was added in the first stage and the rest of the sodium hydroxide in the second stage. The total bleaching time was 2 × 2.5 min.

Preimpregnation improved the pulp brightness slightly at low TAs (see Figure 6). The effect was, however, not as significant as in one-stage bleaching, because conditions in two-stage bleaching (no preimpregnation) with a low alkali/peroxide ratio (¼ of TA) in first stage in themselves improved the brightness compared to that achieved in one-stage bleaching.

The COD load was higher for the preimpregnated pulps (see Table 4), and the residual peroxide and pH levels were slightly higher as well; this is probably because the alkali requires time to penetrate into the fiber and react with the peroxide.
Comparison of Bleaching Methods

Two-stage HT peroxide bleaching produces a brighter pulp than one-stage HT peroxide bleaching does (see Figure 7). Preimpregnation of the pulp with hydrogen peroxide before alkali addition improves the brightness. Two-stage HT bleaching with a low alkali/peroxide ratio (¼ of the TA) in the first stage produces a pulp with a brightness comparable to that obtained in one-stage HT bleaching with hydrogen peroxide preimpregnation. Preimpregnation of the pulp with hydrogen peroxide before a two-stage alkali addition can produce a pulp with a brightness and residual peroxide comparable to those obtained in conventional one-stage peroxide bleaching. The COD load was, however, higher.
CONCLUSIONS

Two-stage HT peroxide bleaching produces a brighter pulp than one-stage bleaching does. The total alkali/peroxide ratio should be low in the first stage, for example, ¼ of the TA. The total alkali charge (TA) should be kept low (10–15 kg/t) to minimize the COD load and increase the residual peroxide. Surprisingly, increased TA does not improve brightness. The bleaching time can be short, since maximum brightness was reached after only 2.5 min. To achieve the highest possible brightness with HT-peroxide bleaching, other measures than increasing the alkali charge and prolonging the bleaching time must be taken. Preimpregnation of the pulp with hydrogen peroxide before a two-stage alkali addition increases the brightness. HT-peroxide bleaching under these conditions can produce a pulp with a brightness and residual peroxide comparable to those obtained in conventional one-stage peroxide bleaching at a low TA.

ACKNOWLEDGEMENTS

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REFERENCES


**APPENDIX**

**Modified Wing Defibrator**

![Modified Wing Defibrator Diagram](image-url)