A HIGHER BRIGHTENING OF MECHANICAL PULPS

HAO REN* and SHIGETOSHI OMORI

**NanJing Forestry University, Department of Light Industry and Science*
NanJing, JiangSu Province 210037, China
State University of New York, College of Environmental Science and Forestry,
Department of Paper and Bioprocess Engineering, Syracuse, NY 13210, USA

Received September 28, 2011

Enhanced utilization of mechanical pulp is an ideal strategy for countries such as China, whose supply of wood and of other high quality biomass is limited. The objective of this study was to minimize the brightness difference between hydrogen peroxide (H_2O_2) bleached mechanical pulps and bleached chemical pulps. The relationships between alkalinity and brightness, alkalinity and H_2O_2 consumption, H_2O_2 application and brightness, H_2O_2 application and its consumption, maximum brightness *versus* H_2O_2 consumption, and extinction coefficient *versus* bleaching time were investigated.

The investigation was conducted on Norway spruce (*Picea abies*) thermomechanical pulp (TMP). A bleached brightness of 81.1% was obtained with H_2O_2 application of 4.0% on pulp for 3.0 h at 30.6% consistency and 60 °C. The optimization of the sodium hydroxide application dose was the key to such a high final brightness. Preliminary results suggest that a higher brightness could be obtained if two-stage bleaching with liquor recycle was used. However, the concentrations of TOC and calcium in the recycled liquor have to be carefully controlled.

Keywords: mechanical pulp, alkalinity, hydrogen peroxide, pulp consistency, brightness

INTRODUCTION

Developing environmentally compatible industrial processes based on renewable resources is an important social goal. High-yield pulps, such as mechanical pulp (MP), thermo-mechanical pulp (TMP), chemi-thermo-mechanical pulp (CTMP) and semi-chemical pulp (SCP) are attractive, due to their efficient utilization of lignocellulosic materials. In addition, bleaching of these pulps does not require the removal of lignin and therefore, it does not generate toxic chlorinated waste products. Furthermore, these pulps have attractive bulk, optical absorbency, and printing properties. Although they are inferior to chemical pulps in brightness and strength, improvements in bleaching and refining technology have shown that mechanical pulps can replace part of the chemical pulp component in high-value paper products, such as business forms, copying papers and writing papers. The characteristics of mechanical pulp are different from those of chemical pulp; reducing these differences will allow for an increased usage of mechanical pulp in both new and existing applications. Since mechanical pulping processes are high-yield and environmentally friendly (compared to chemical pulp), they will allow for better utilization of natural resources and contribute to a cleaner global environment. As, with today's technology, mechanical pulp cannot completely replace chemical pulp, it is viable as a partial substitute. The percentage that can be substituted depends on the brightness characteristics of the mechanical pulp. The more brightness of mechanical pulp can be increased, the higher will be the percentage of chemical pulp it can replace.

The constituents and qualities of the wood used are very important. The higher the original brightness of wood and pulp, the higher will be the resulting brightness after bleaching. Significant research has been performed on the relationship between wood species and bleachability, some of which contradictory. For example, there are studies which show that several softwoods can be bleached by hydrogen peroxide, while others conclude that the extractives in softwood prevent bleaching.[1,2] Significant differences have been observed in the bleachability of various hardwoods.[3] There is also a report that shows that the age of a tree can affect its bleachability, younger trees exhibiting a higher brightness gain.[4] Pulp brightness can be also degraded when the wood chips used to make it are contaminated by bark. For instance, brightness decreases with 9-11% when the pulp is contaminated with 3% bark, depending on the steaming temperature of the chips.[5-7] Also, when healthy wood chips are contaminated with decayed ones, the degradation caused by fungi produces an enzyme that decomposes hydrogen peroxide.[8] The transition metals present in wood can also have a negative influence on peroxide bleaching.

Although several methods for adjusting the individual characteristics of a raw material are in use (for instance, a chelating agent can be used to remove transition metals), it is not realistic to try and adjust all the above mentioned properties and differences.

The development of a new, all-encompassing brightening technique is difficult, given the significant differences in the properties of various woods. This study was conducted exclusively on spruce wood, to maintain consistency among trials.

The present study attempted at improving the brightness of mechanical pulp to a level close to that of chemical pulp, to promote mechanical pulp as a viable substituent. The following relationships have been investigated and discussed: alkaline concentration *vs*. brightness, alkaline concentration *vs*. consumption of hydrogen peroxide, additive amount of hydrogen peroxide *vs*. brightness and consumption of hydrogen peroxide, maximum brightness *vs.* hydrogen peroxide consumption, absorption coefficient *vs*. bleaching time, influence of pulp consistency on brightness during bleaching, etc.

EXPERIMENTAL

Pulp preparation

The pulp was made from fresh spruce chips prepared within one year of cutting. The chips were treated with a 2% sodium sulfite solution, at a liquor-to-solid ratio of 7, a pH of 10.5, at 95 °C, for 25 min. The heated chips were refined at 175 kPa in the first stage and at atmospheric pressure in the second stage, respectively.

Pulp pretreatment

The pulp (CTMP) prepared as described above was pretreated with 0.5% Na_5DTPA at 2% consistency, a pH of 4.5, for 30 min, to remove the transition metal before bleaching.

Pulp bleaching

The pretreated pulp was bleached with 1-12% hydrogen peroxide, 1-10% sodium hydroxide, 5% sodium silicate and 0.05% magnesium sulfate ($MgSO_4 \cdot 7H_2O$) at a 10-35% pulp consistency, for 10-180 min at 60 °C.

Measurement of residual hydrogen peroxide

After bleaching, as described above, a part of the bleached liquid was taken out and acidified with 2N sulfuric acid, followed by the addition of potassium iodide and a few drops of a saturated solution of ammonium molybdate, after which the iodine produced was titrated with a 0.01 N sodium thiosulfate solution.

Measurement of brightness and specific absorption coefficient

The pulp bleached according to the procedure described above and adjusted to pH 5 with sodium bisulfite or sodium metabisulfite solution, was washed with water, after which handsheets were prepared and dried overnight in a controlled humidity room. The brightness and absorption coefficients were measured with a brightness meter.

RESULTS AND DISCUSSION

Final pulp brightness is affected not only by bleaching, but also by pulping. Some of these effects are discussed below. A high brightness pulp achieves a higher final brightness through the bleaching procedure. Factors like temperature, chemical concentration and contamination by transition metals are also reflected in final brightness. If the pretreatment temperature is too high and the holding time too long, brightness is generally lower.[5,6,9] A study[10] devoted to the preparation of TMP from black spruce and Loblolly pine demonstrates that refining pressure, steaming hold time and the presence/absence of presteaming do not affect pulp brightness. However, the same parameters were shown to have a negative effect on both brightness and physical properties when the same experiments were repeated using Appalachian pine. In the process of TMP preparation from black spruce, the negative effects of the steaming and refining pressure are compensated by shortening of the presteaming time. The optimum refining temperature on brightness is 120 °C, at a 5 min presteaming time. The negative effect on brightness is 2-3% lower if increasing the refining temperature in the peroxide treatment stage.[6] To counteract the negative effect of metals on brightness during refining, Gellerstedt *et al.*[11] added DTPA to the sodium silicate solution in the pretreatment of spruce chips. The resulting brightness increased by about 8%, compared to the reference, as due to a synergistic effect. Maximum brightness was obtained at pH 7, and around half of the trials contained 2% peroxide residue after bleaching.[12] Comparable results were obtained with mixed hardwood. Even if the influence of pulping is not clear in the case of pulps, as a commercial CTMP pulp was used in this study, it is advisable to keep these negative effects to minimum.

Alkaline concentration and brightness

It is widely known that, in pulp bleaching, alkalinity is an important factor that influences its brightness.[13] When alkalinity is adjusted to an appropriate level, total alkalinity has to be sufficient to assure enough concentration of the peroxide anion (OOH^-), which is an active bleaching species produced by the following equilibrium reaction throughout the bleaching process:

$$H_2O_2 + OH^- \rightleftharpoons OOH^- + H_2O$$

At the same time, alkalinity has to be kept at a level permitting to minimize peroxide degradation and the chromophore formation reaction, occurring at a high pH, as described by many researchers.[14,15]

Excess alkaline addition has a negative effect, as confirmed by our experiments. Figure 1 shows the effect of alkaline concentration on brightness during peroxide bleaching. It is obvious that the optimum alkaline concentration changes with the amount of peroxide addition, namely, it increases with incremental addition of peroxide. This suggests that the amount of alkaline addition is decided by the amount of peroxide addition.

pH and brightness

In Figure 2, the alkaline concentration plotted in Figure 1 is expressed as pH, the optimum alkaline concentration being at around a pH of 11, despite the amount of peroxide addition. From this trend, the alkaline concentration should be adjusted by changing the pH instead of changing the amount of alkali addition.

pH and hydrogen peroxide consumption

Figure 3 shows the relation between peroxide consumption and pH. It can be seen that peroxide consumption increases rapidly beyond a pH of 11. That is, the optimum pH (pH 11) occurs at the same point in which peroxide consumption begins to increase dramatically. An excess of alkali addition accelerates self-decomposition, prevents brightening and reduces its effect.

Brightness around 2% hydrogen peroxide consumption

Figure 4 shows the relation between hydrogen peroxide addition and brightness gain, around a peroxide consumption of 2%. Near this point, if peroxide addition exceeds 8%, a high brightness gain of over 80% will be achieved, as shown in the figure. Therefore, we can conclude that bleaching cost can be controlled by recycling the excess peroxide, which remains in the bleaching process, by maintaining a peroxide consumption level of 2% or less.

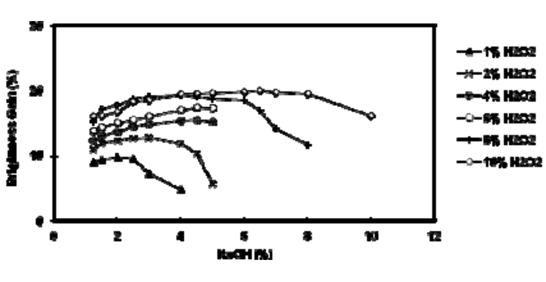

Figure 1: Effect of alkali charge on brightness gain

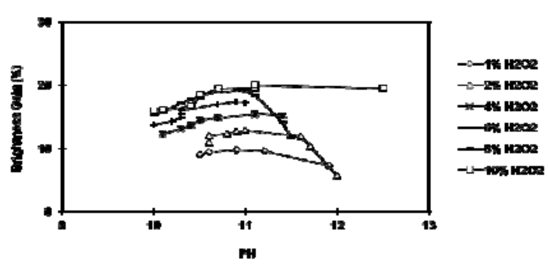

Figure 2: Effect of pH on brightness gain

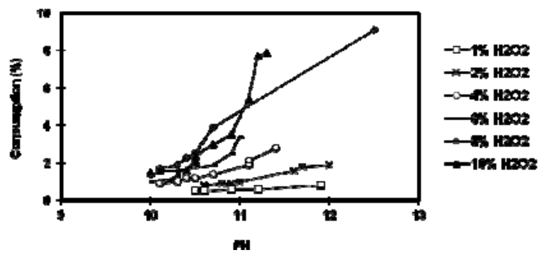

Figure 3: Effect of alkali charge on peroxide consumption

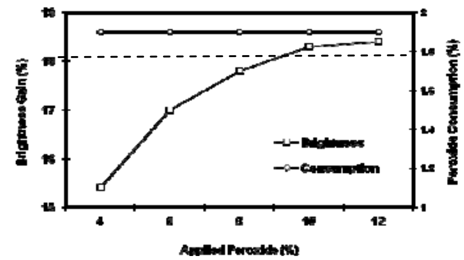

Figure 4: Effect of peroxide application on brightness gain at fixed peroxide consumption (2%)
(--- 80% brightness line)

However, controlling the consumption rate becomes problematic when peroxide is recycled, as the peroxide consumption rate increases with each recycling. For instance, when the sample was bleached with 10% peroxide, peroxide consumption was 2.3%. The consumption in the first recycle was of 4.1%, in the second recycle, it was of 7.0% and in the third recycle – of 9.7%. During the third recycling, almost the entire 10% of the supplied peroxide was consumed.

There are two reasons for this trend. One is that the amount of low molecular weight organic materials increased in the recovered peroxide liquor. The TOC test showed that almost 0 ppm of such materials in the original bleaching liquor increased to 2791 ppm in the first recycling, to 3861 ppm in the second recycling and to 4587 ppm, respectively, in the third recycling stage. Peroxide consumption was tested using recycled liquor prepared with sodium silicate free alkaline 10% hydrogen peroxide. When the organic material was of 0, 500, 1000, 2000 and 4000 ppm, peroxide consumption was of 0.05, 0.28, 0.67, 1.13 and 1.17%, respectively. It can be concluded that, when recycling this organic source, the consumption of peroxide will greatly increase. However, when the recycled liquor containing more than 2500 ppm organic material was kept overnight in a refrigerator, the organic materials precipitated and the supernatant did not contain harmful organic peroxides in the liquor. That is, the organic contaminants in the recycled bleaching liquor (caused by peroxide consumption) can be removed easily by keeping the liquor in the refrigerator overnight.

Another factor causing an increased peroxide consumption may be calcium (Ca). Although calcium generally stabilizes hydrogen peroxide, a direct relationship was observed between calcium concentration and consumption. A possible explanation to this may be related to the reaction between the calcium and silicon present in the liquor. In a controlled trial, it was observed that the calcium content in recycled liquor increases from approximately 0 to 7.9, 20.4 and 35.0 ppm in the first, second and third recycle, respectively. On the other hand, silica in the liquor decreased from 1377 ppm (mg/L) to 855, 551.0 and 513.1 ppm. The silica content of the pulp after bleaching (prepared to 761.6 ppm (mg/kg pulp) for all three trials) decreased to 591.3, 596.8 and 560.2 ppm in the first, second and third recycling trials. These results show that silica is lost in both pulp and recycled liquors. One possible explanation is that when calcium increases in the recycled liquor, the soluble sodium silicate (which acts as a peroxide stabilizer) is converted to insoluble calcium silicate, being lost as scale on the walls of the bleaching system. As a result, peroxide consumption increases rapidly.

Supporting experimental data for this trend have been found in an experiment that used calcium and magnesium, showing that the consumption of peroxide rises rapidly, proportionally to the amount of calcium in the bleaching liquor.[16]

Consumption of hydrogen peroxide and maximum brightness

Figure 5 shows the relation between peroxide consumption and brightness gain when maximum brightness is obtained under optimum alkali conditions (pH 11). As one may see, peroxide consumption increases linearly with peroxide addition. Brightness also increases linearly with peroxide addition, beginning to level off at approximately 8% peroxide. Increasing peroxide concentration beyond 8% results in lower returns, showing that the brightness gain due to peroxide addition has reached a limit.

Absorption coefficient and bleaching time

Figure 6 plots the absorption coefficient as a function of bleaching time. A decreasing light absorption coefficient is indicative of the removal of chromophore groups. The absorption coefficient response shows strong performance in the 4-10% peroxide addition range, and less performance in the 1-2% range.

Influence of pulp consistency on brightness

Existing studies have shown that, in the peroxide bleaching of mechanical pulp, brightness can be increased by increasing pulp consistency.[17,18] For instance, spruce/fir TMP with 30% pulp consistency was able to achieve the same brightness as the pulp with 12-20% consistency, at only half peroxide and alkaline concentration.[19] The same study showed that a pulp consistency of 35-40% gave a brightness gain of 4-5%, compared[19] to a pulp consistency of 25%. It can be postulated that more peroxide enters the fibers in which the bleaching reaction occurs.

Another possible explanation is that, when pulp consistency is increased, peroxide concentration also increases. As a result, the bleaching reaction is more intense than the alkali darkening reaction.[20] Figure 7 shows the relation between pulp consistency and brightness *via* a peroxide addition of 4-10%, the data being listed in Table 1.

To achieve 80% brightness, 6% or more peroxide addition is required at 10.7% pulp consistency. However, the peroxide demand is 4% or less, when pulp consistency records 21 and 31% levels, which suggests that 80% or higher brightness can be attained.

It is difficult to remove calcium (which accelerates peroxide consumption) without incurring significant extra cost by decomposition and loss. Without establishing a simple and low-cost method to remove calcium, it seems that peroxide recycling is not financially viable. Instead of recycling peroxide, it is more realistic to maintain the peroxide concentration at 4% or less, and to raise pulp consistency as high as possible. By this methodology, pulps with a brightness of 80% or higher can be achieved.

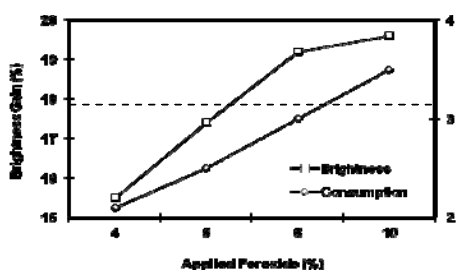

Figure 5: Effect of peroxide application on brightness gain and peroxide consumption at optimum alkali concentration (----80% brightness line)

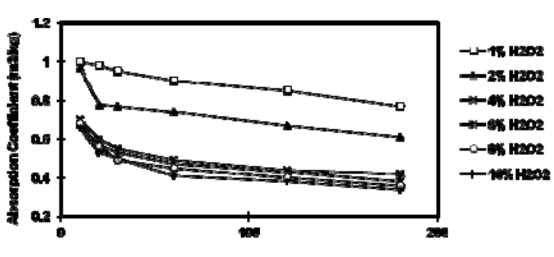

Figure 6: Decrease rate of light absorption coefficient (K) at varying application of peroxide

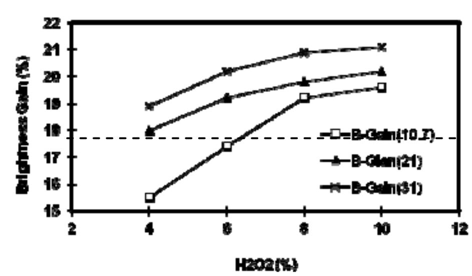

Figure 7: Effect of consistency on maximum brightness achieved in CTMP bleaching with varying peroxide application (----80% brightness line)

Table 1
Brightening effects of peroxide application and pulp consistency

Peroxide concentrations (%)	Pulp consistency (%)					
	10.7		21.3		30.6	
	B	ΔB	B	ΔB	B	ΔB
4	77.5	15.5	80.2	18.0	81.1	18.9
6	79.6	17.4	81.4	19.2	82.4	20.2
8	81.4	19.2	81.6	19.4	83.1	20.9
10	81.8	19.6	82.4	20.2	83.3	21.1

B: Brightness (%), ΔB: Brightness gain (%)

CONCLUSIONS

The present investigation attempted at improving the brightness of mechanical pulps, bringing it closer to that of chemical pulps. The attempt to attain brightness levels of 80% or higher led to the following conclusions:

1) It is important to maintain an optimum alkali condition (pH 11).
2) For economical reasons, peroxide consumption should be controlled by setting alkaline concentration accordingly.
3) When performing high concentration peroxide bleaching, peroxide recycling is not realistic without removing calcium from the recycled liquor.
4) A realistic method to achieve high brightness with a relatively low cost is to keep peroxide concentration below 4% and to raise pulp consistency as high as possible.
5) To achieve maximum brightness, it is important to set optimum alkaline concentration according to peroxide concentration. Therefore, high peroxide consumption (and therefore a high cost) is unavoidable when trying to attain maximum brightness.
6) High concentration peroxide addition and high pulp consistency are important for achieving high brightness. The amount up to which pulp consistency can be raised depends strongly on the mixing technology.
7) To achieve high brightness pulps, neither high peroxide addition nor high peroxide consumption can be avoided. Even if alkaline concentration is optimized and pulp consistency is maximized, it is still not feasible for mechanical pulp to reach 90% brightness in the near future.

ACKNOWLEDGEMENTS: The financial support of this study by the 973 National Basic Research Program of China (No. 2010CB732205) and Natural Science Funding of NanJing Forestry University (No. 163105017) is gratefully acknowledged.

REFERENCES

[1] T. P. Shcherbakova, V. A. Demin and A. I. Mikhailov, *Russian J. Appl. Chem.*, **77**, 1725 (2004).
[2] X. Q. Pan, D. Lachenal, C. Lapierre, B. Monties *et al.*, *Holzforschung*, **48**, 429 (1994).
[3] E. David, J. Estebe, C. Dulion *et al.*, *Japan Tappi J.*, **41**, 474 (1987).
[4] N. B. Clark, *Appita J.*, **43**, 208 (1990).
[5] V. Loras, J. Carles and G. Papageorges, *ATIP Rev.*, **30**, 322 (1976).
[6] V. Loras, *Tappi J.*, **59**, 99 (1976).
[7] T. A. Hagglund and L.-P. Lindstrom, *Tappi J.*, **68**, 82 (1985).
[8] P. Joyce and D. M. Mackie, *Preprints of the 1979 International Pulp Bleaching Conference*, CPPA, Toronto, Canada, p. 107.
[9] G. Gellerstedt *et al.*, *Svensk Papperstidn.*, **88**, R68 (1985).
[10] J. D. Sinkey, *Pulp Pap. Mag. Can.*, **80**, T75 (1975).
[11] G. Gellerstedt *et al.*, *Svensk Papperstidn.*, **86**, R204 (1983).
[12] J. Blackburn *et al.*, *Pulp Pap.-Can.*, **84**, 63 (1983).
[13] Y. H. Ni, *Can. J. Chem. Eng.*, **83**, 610 (2005).
[14] K. G. Ryrber, *Pulp Pap. Int.*, **20**, 47 (1978).
[15] S. Moldenius, *J. Pulp Pap. Sci.*, **10**, J172 (1984).
[16] W. C. Froass, S. Omori *et al.*, *Tappi J.*, **76**, 111 (1993).
[17] S. Moldenius, *Svensk Papperstidn.*, **85**, R116 (1982).
[18] A. Guerra, R. Mendonca and A. Ferraz, *J. Wood Chem. Technol.*, **25**, 203 (2005).
[19] V. B. Degteva, E. A. Pribytkovskaya and F. V. Borisova, *Bumazh. Prom.*, **9**, 21 (1979).
[20] S. Moldenius and B. Sjogren, *J. Wood Chem. Technol.*, **2**, 447 (1982).