IMPROVING HYDROGEN PEROXIDE BLEACHING OF ASPEN CTMP BY USING AQUEOUS ALCOHOL MEDIA

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Preliminary tests of a new hydrogen peroxide bleaching procedure for mechanical pulps were performed in a bleaching medium comprised of water and an alcohol, which is characterized by good miscibility with water, poor solvency for hemicelluloses, and good solvency for lignin. As compared with a conventional bleaching method, this modified process is aimed at reducing the removal of hemicelluloses while moderately increasing the dissolution of lignin. Results showed that an aspen CTMP pulp can be bleached to a target brightness with less bleaching chemicals and/or with a higher pulp yield. The laboratory studies demonstrate that this new bleaching process offers substantially enhanced efficiency and selectivity over the conventional peroxide bleaching. Overall, the brightness increased by about 5 ISO units for a given peroxide consumption and the yield increased by 2 to 3 percent at the same target brightness.

Keywords: Aspen; Mechanical pulp; CTMP; Bleaching; Hydrogen peroxide; Brightness; Yield

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INTRODUCTION

Hydrogen peroxide bleaching is the predominant bleaching method used in the manufacture of mechanical pulps, such as BCTMP. The process results in not just a brightness increase, but also in the development of pulp physical properties (Pan 2004). The bleaching operation contributes, to a great extent, to the total manufacturing cost; therefore, there is an interest in improving the peroxide bleaching process in order to improve the economy of bleached mechanical pulp production.

Hydrogen peroxide bleaching, however, is affected by critical limitations in terms of efficiency and selectivity, which are not overcome in a conventional manner. Bleaching efficiency is here defined as units of pulp brightness gain per amount of hydrogen peroxide consumed. Hydrogen peroxide bleaching has a typical profile, as follows, of brightness development with dependence on bleaching chemical consumption: Initially, with an increasing hydrogen peroxide dosage coupled with an adequate amount of alkali, the gain in brightness is rapid. Then the brightness rise slows down, and finally reaches a plateau.

A bleaching process occurring under conditions corresponding to the slow-down phase or to the plateau phase is characterized by low efficiency. In this bleaching phase, the brightness gain magnitude is smaller, while consuming larger amounts of bleaching chemicals. The brightness level of such a "brightness ceiling" varies, depending on the lignocellulosic species contained within a pulp substrate. Numerous approaches have been investigated as possible means to improve the bleaching efficiency and overcoming the "brightness ceiling", including sequential bleaching processes involving the use of other oxidants (Li et al. 1997; Pan et al. 2001; Wong et al. 1995) and peroxide activation (Sain et al. 1997).

A second aspect associated with peroxide bleaching is bleaching selectivity, which is here defined as pulp yield loss vs. brightness gain. In most cases, bleaching is accompanied by pulp yield loss (Pan 2002). The yield loss reflects dissolution of components from the pulp fibres into a water-containing phase of a bleaching medium. In conventional peroxide bleaching, alkalinity is the most important parameter that determines the magnitude of yield loss (Pan 2002). Selecting the lowest possible charge of sodium hydroxide for a given amount of peroxide is a quite common practice for reducing yield loss in mechanical pulp bleaching. Typically, the degree of yield loss is much more pronounced when pulp is bleached to high brightness. To minimize pulp yield loss during bleaching, lowering and buffering the bleach liquor pH by employing alternate alkali sources, such as sodium carbonate, magnesium oxide, and magnesium hydroxide, has been widely studied (Suess et al. 2002; He and Ni 2008; Hou et al. 2010). While yield conservation is evident, pulp brightness is often compromised.

In order to find more effective ways for addressing the above-mentioned selectivity and efficiency limitations in the peroxide bleaching of aspen mechanical pulps, this study investigated a novel approach by using an alternative peroxide bleach liquid system (medium). Hemicelluloses and lignin are the two major pulp components that are dissolved and contribute to yield loss in bleaching (Holmbom et al. 1991); however, their removal from fibers by bleaching results in different consequences. The removal of hemicelluloses is nothing but a contribution to yield loss. Besides contributing to yield loss, the lignin removal has some positive effects, including pulp brightening and strengthening. Furthermore, hemicelluloses have a higher tendency to alkaline solubilization/hydrolysis than lignin. For hardwood (such as aspen) pulps, in particular, the hemicelluloses content is high; therefore, it is even more critical to reduce the removal of hemicelluloses in order to decrease pulp yield loss in bleaching processes in alkaline condition.

In the present investigation, aspen CTMP was bleached with hydrogen peroxide in an aqueous medium containing an organic solvent characterized by good miscibility with water, poor solvency for hemicelluloses, and good solvency for lignin. Such organic solvents include ethanol, propanol, butanol, and ethylene glycol. This paper presents the effects of adding each of these alcohols on the peroxide bleaching performance of aspen CTMP.

EXPERIMENTAL

Materials

Aspen CTMP (62.5 ISO brightness and 480 CSF) supplied by a pulp mill in Western Canada was employed in this study. All organic solvents and bleach chemicals are commercial products and were used as received.

Methods

All the bleaching experiments, except when otherwise described, were performed in polyethylene bags using various amounts of H_2O_2 and NaOH under the following conditions: 20 g pulp (dry weight), 15% pulp consistency, 70 ^{o}C for 2 hours, 3% Na_2SiO_3, 0.05% $MgSO_4$, and 0.1% DTPA. Duplicate experiments were performed for each bleaching condition. The high consistency (25%) bleaching trials were carried out in a Quantum mixer. The bleaching chemicals were charged on the basis of o.d. pulp. After the required retention time, the spent bleach liquor was separated from the pulp by filtration in a Buchner funnel. The bleached pulp was washed and acidified to about a pH of 5 by sodium metabisulfite prior to preparation of the brightness pads.

The concentration of hydrogen peroxide in the collected spent bleach liquors was determined iodometrically. The brightness values were recorded in a Technibrite Micro TB-1C instrument. The pulp yields were calculated from gravimetric measurements using pulp consistency and total weight before and after bleaching. The total lignin content consisted of two parts: acid-insoluble lignin (TAPPI standard method T 22os-74) and acid-soluble lignin determined by UV absorption at 205 nm.

The amounts of dissolved organic substances were determined as total organic carbon (TOC) on a Dorhman DC-80 TOC analyzer. The inorganic carbon was determined by the reaction with nitric acid to produce CO_2 that was detected by an IR detector. The total carbon analysis was performed by combustion of the sample at 800 ^{o}C in an atmosphere of oxygen and detection of the CO_2 liberated. The TOC content of the sample was calculated from the difference between the total carbon value and the inorganic carbon content.

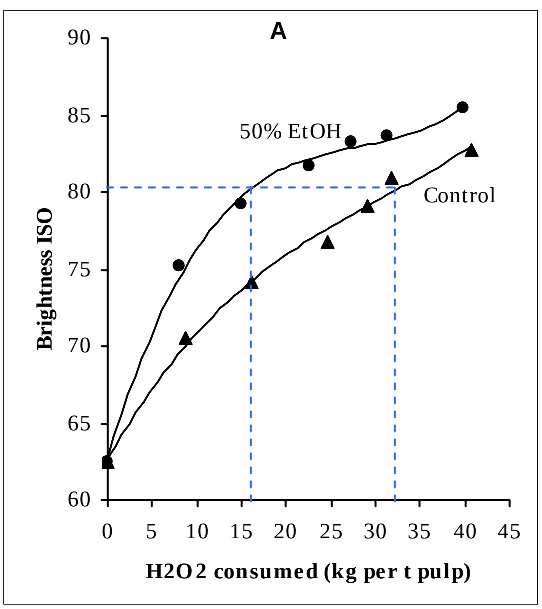
RESULTS AND DISCUSSION

Table 1 summarizes the results of the bleaching experiments with three peroxide dosages as a function of ethanol content in the aqueous organic solvent medium. At a given bleaching chemical dosage the pulp brightness increased with an increase in the rate of ethanol substitution for water in the bleaching medium. At the same time, the peroxide consumption decreased or increased by a smaller magnitude, depending on how much ethanol was used for substituting water in the bleaching medium. It appears that there existed a more efficacious range of ethanol substitution. As shown in Table 1, bleaching at a substitution rate of around 50% ethanol resulted in significantly higher pulp brightness while reducing the peroxide consumption. Combining the brightness gain and the peroxide consumption leads to an interesting observation that the alcohol-based bleaching process offered substantially enhanced bleaching efficiency over the conventional peroxide bleaching. This observation can be more clearly demonstrated by Fig. 1A. It can be seen that for a brightness target of 80 ISO the bleaching with 50% ethanol substitution reduced the peroxide consumption by approximately 50%. It appears that bleaching efficiency improvement was greater when the pulp was bleached with a lower peroxide charge. For instance, for the 2% peroxide bleaching experiments the 75% ethanol substitution resulted in a brightness increase of 6.2 ISO units by consuming a similar peroxide as compared to the conventional method.

As Table 1 shows, at given bleaching chemical dosages the pulp yield increased with an increasing rate of ethanol substitution for water in the bleaching medium. In other words, the alcohol-based bleaching process substantially improved bleaching selectivity over the conventional peroxide bleaching. Figure 2B demonstartes that when the pulp was bleached to a brightness target of 80 ISO, the 50% ethanol substitution resulted in a pulp yield gain of approximately 3 percentage points.

Table 1. Bleaching Experiments with Aspen CTMP (initial brightness 62.5 ISO)

EtOH (% v/v)	0	25	50	75
2% H_2O_2 and 1.5% NaOH				
Initial pH	10.8	11.2	11.5	11.5
End pH	8.4	8.3	8.7	9.3
H_2O_2 consumed (% on pulp)	1.50	1.35	1.38	1.51
Brightness (ISO)	73.0	76.9	78.2	79.2
Yield (%)	94.1	95.0	94.5	96.2
4% H_2O_2 and 3% NaOH				
Initial pH	11.3	11.5	11.7	12.1
End pH	8.7	8.8	9.1	9.6
H_2O_2 consumed (% on pulp)	2.80	2.40	2.54	2.98
Brightness (ISO)	78.0	81.0	82.2	82.8
Yield (%)	93.3	94.1	94.2	94.8
6% H_2O_2 and 4.5% NaOH				
Initial pH	11.5	11.6	12.2	12.4
End pH	9.7	9.6	9.8	10.1
H_2O_2 consumed (% on pulp)	3.76	3.33	3.55	4.78
Brightness (ISO)	81.3	83.5	84.7	85.0
Yield (%)	90.6	91.2	91.3	92.1



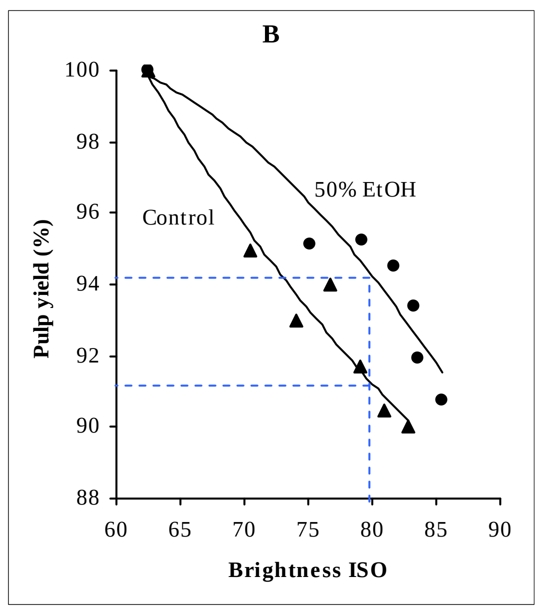


Fig. 1. Improvement of bleaching efficiency (A) and bleaching selectivity (B) by ethanol substitution in peroxide bleaching of aspen CTMP

To confirm the promising results presented above, high consistency scale-up bleaching experiments were peformed using 500 g (o.d.) of pulp per trial. For the purpose of comparison, the pulp was bleached to a similar brightness for both the conventional process and the alcohol-based process according to the brightness versus peroxide consumption curve obtained earlier. As seen in Table 2, for a brightness target of 84 ISO the bleacing with 50% ethanol substitution offered a peroxide savings of 19% and increased pulp yield by 1.8 percentage points

Table 2. High Consistency Scale-up Bleaching Experiments with Aspen CTMP

	Control	50% EtOH substitution
Bleach chemical (% on pulp)	6% H_2O_2 and 4.5% NaOH	4.5% H_2O_2 and 3.4% NaOH
Brightness ISO	83.9	84.2
H_2O_2 consumed (% on pulp)	4.3	3.5
Pulp yield (%)	89.9	91.7

Bleaching experiments using other alcohols were also performed to evaluate the effect of their substitution for water in the bleaching medium on bleaching efficiency and selectivity. The alcohols used here included n-propanol, n-butanol, and ethylene glycol. Overall, these alcohols enhanced bleaching performance, which is similar to what was observed for ethanol. As illustrated in Fig. 2, n-propanol and ethylene glycol were more effective in enhancing bleaching efficiency than n-butanol; however, the latter improved pulp yield in a similar or greater magnitude as compared to the former. While the cause for these differences among the alcohols investigated in the present study is yet to be understood, it could be concluded that the 2-4 carbon alcohols are beneficial in improving the performance of peroxide bleaching and that their partial substitution for water in the bleaching medium significantly increases pulp brightness and yield.

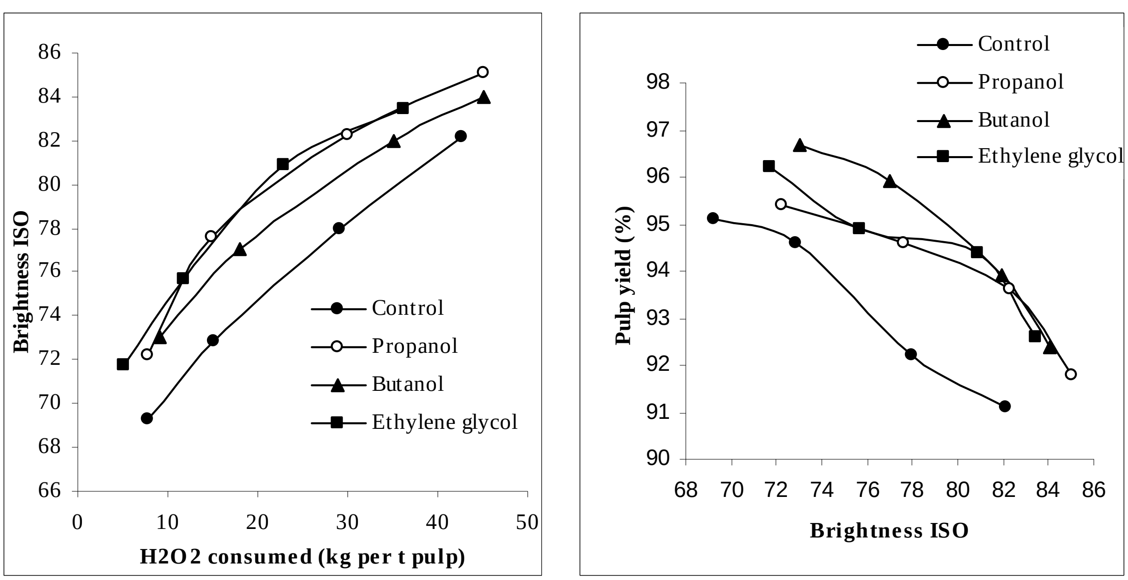


Fig. 2. Comparison of bleaching efficiency and selectivity for peroxide bleaching of aspen CTMP in media containing other alcohols at 50% v/v

In order to better understand how the dissolution of hemicellulose and lignin contributed to the improved bleaching efficiency and selectivity, samples of spent bleaching liquors and bleached pulps were submitted for further analysis. It is a general belief that hemicellulose and lignin are the two major organic substances dissolved in alkaline peroxide bleaching of mechanical pulps **(**Holmbom et al. 1991). As seen in Fig. 3, the amount of total organic substances decreased with an increase in the rate of ethanol substitution for water in the bleaching medium, which is in good agreement with the increased pulp yield (Table 1). In fact, there is a strong correlation between pulp yield and amount of dissolved organic substances in peroxide bleaching of mechanical pulps (Pan 2002). On the contrary, the dissolution of lignin increased by increasing the rate of ethanol substitution to around 50% and then leveled off or decreased slightly. Combination of the two graphs in Fig. 3 allows for presuming that the increased pulp yield in the ethanol-based bleaching resulted from the reduced dissolution of hemi-celluloses to a greater extent.

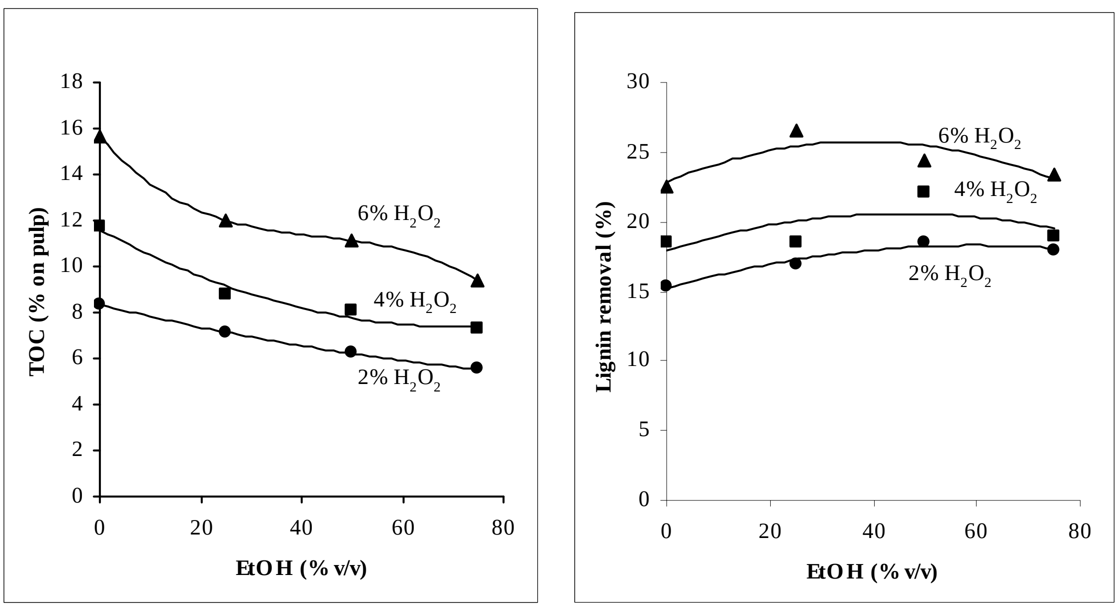


Fig. 3. Effect of ethanol substitution for water in bleaching medium on the amount of total dissolved organic substances (TOC) and the rate of lignin dissolution in bleaching conditions described in Table 1

This observation demonstrates that the inclusion of ethanol in the bleaching medium is quite effective in preventing severe hemicellulose loss, a technical challenge in conventional alkaline peroxide bleaching of mechanical pulp. As Fig. 3 shows, the degree of lignin dissolution reached a maximum at the rate of ethanol substituion of around 50% and afterward leveled off or decreased slightly. On the other hand, the pulp brightness increased with the ethanol substitution rate throughout the entire range (Table 1). This result implies that the bleaching efficiency enhancement was not only due to the increased removal of lignin but also to the improved accessibility of chromophoric substances as well.

CONCLUSIONS

The laboratory studies demonstrated that mechanical pulps can be bleached by hydrogen peroxide in an aqueous alcoholic medium to a target brightness with a higher pulp yield and/or with a reduced consumption of bleaching chemicals. This new bleaching process offers substantially enhanced efficiency and selectivity over the conventional peroxide bleaching. Overall, the brightness is increased by about 5 ISO units for a given peroxide consumption, and the yield increased by 2 to 3 percentage points at the same target brightness. It is tentatively suggested that the yield increase (selectivity improvement) mainly results from the reduced dissolution of hemicelluloses. On the other hand, the bleaching efficiency enhancement is not just due to the increased removal of lignin, but to the improved accessibility of chromophoric substances. Further experiments are needed for process optimization and mechanistic study.

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