Alkaline Peroxide Mechanical Pulping of Wheat Straw

Part 1: Factors Influencing the Brightness Response in Impregnation

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ABSTRACT

The present investigation has gained an insight into the roles of process parameters in the alkaline peroxide impregnation of wheat straw. Preparation of the fiber material by chopping and hot water wash was found to be an important step to enhance the efficiency of the subsequent alkaline peroxide treatment. The pulp brightness and yield were highly dependent on the application levels of both peroxide and caustic soda. Nevertheless, a compromise should be reached in order to balance brightness increase and yield loss. Other variables, such as sodium silicate, magnesium sulfate, peroxide activation, temperature and retention time, had only a little or moderate effect on the brightness response.

KEYWORDS

Wheat straw (*Triticum aestivum*), mechanical pulping, bleaching, impregnation, peroxide, alkali, brightness, yield

INTRODUCTION

There is growing interest in using agricultural residues for pulping and papermaking. Wheat straw has been used for pulp and paper production for a long time and remains one of the major raw materials in many developing countries. To date, almost all of the commercial straw pulping processes are based on chemical pulping technology. However, one of the most serious problems associated with straw chemical pulping is a high silica content of the fibers, which makes conventional chemical recovery difficult. Alternatively, mechanical pulping seems to be suitable for wheat straw since it is easily disintegrated by mechanical process. The process generates a minimal volume of effluent, thus reducing the environmental impact.

Alkaline peroxide mechanical pulping (APMP) has been a successful pulping method for low-density hardwoods like aspen. Its advantages over conventional CTMP processes include good pulp quality, elimination of a bleach plant and energy savings [1]. The APMP process is based on the incorporation of peroxide bleaching into chemical impregnation and refining stages in which bleaching action takes place not only to eliminate alkali-darkening of wood chips but to brighten them to certain brightness levels as well. Similar to sulfonation, carboxylation of lignin by alkaline peroxide results in easier fiber separation during refining and improved fiber bonding in papermaking. Adaptation of the wood APMP process to agricultural fibers has been proven successful for kenaf [2], hemp [3] and bagasse [4]. Nevertheless, the fundamentals of wheat straw APMP have not been described in the literature.

The objective of our research is to develop a wheat straw APMP process to produce bleachable pulps for printing grade papers. The proposed process would allow a pulp production that leads to minimal environmental impact, as resulted from its high-yield, non-sulfur pulping and chlorine-free bleaching. In this new process, alkaline peroxide impregnation stage is similar to conventional peroxide bleaching in many respects. The process variables that influence pulp bleaching have a comparable effect on the performance of the new process. This paper describes our investigation into the effects on brightness, peroxide consumption, and pulp yield of process variables in chemical impregnation stages, including chemical charge, peroxide activation, temperature and time.

EXPERIMENTAL

Materials

All chemicals are commercial products and were employed as received. Wheat straw collected at the University of Alberta farm was comminuted by a hammer mill into a length of 10 –15 mm and screened to remove fines and dusts.

Impregnation

Each trial used approximately 10 g (o.d.) of wheat straw. Chemical impregnation was conducted in polyethylene bags. Prior to this, the cut wheat straw was washed with hot water in the absence or presence of diethylenetriaminepentaacetic acid (DTPA) under the following conditions.

a) Pre-washing: 20:1 of water-straw ratio, 70^{o}C, 1 hour

b) DTPA pre-treatment: 40:1 of water-straw ratio, 0.5% DTPA (on o.d. wheat straw), pH 4.5. The mixture of cut straw and water was stirred mechanically at 70^{o}C for 1 hour. The treated straw was filtered off and washed to neutral pH.

The charges of all chemicals were based on the o.d. straw weight before the wash. As they varied from one trial to another, the chemical charges will be specified individually throughout the paper. The general condition was: 6:1 of water-straw ratio, 70^{o}C, 2 hours. The impregnated wheat straw was then defibrated in a Waring blender. The resulting pulps were washed with distilled water and acidified to pH 5.

Testing and analysis

The concentration of hydrogen peroxide was determined iodometrically. Handsheets were prepared following the TAPPI standard method T-218. Brightness values were recorded in a Technibrite Micro TB-1C instrument.

RESULTS AND DISCUSSION

Raw Material Preparation

In the present investigation, hammer milling was used for comminuting/screening wheat straw. **Table I** shows that the hammer milled wheat straw and the internodal material had a comparable pulp yield, considerably higher than that of the whole wheat straw. This indicates that the hammer milling process was effective in removing certain non-fibrous materials that would be turned into fines and eventually removed in later stages. Supporting evidence is that the whole wheat straw had a greater material loss by hot water washing, 7% compared to 3% for the hammer milled sample. In addition, the hammer milling offered a moderate reduction in peroxide consumption. However, there was no significant difference in brightness. The internodal pulp was a little brighter than two others. This study would suggest that the hammer milling is effective in upgrading the quality of wheat straw for pulping.

Sample	Pulp yield %	H_2O_2 consumption %	Brightness ISO
Whole wheat straw	83.8	76	50.0
Internodal	89.3	64	51.6
Hammer milled	89.6	72	50.2

Table I. Comparison of Different Wheat Straw Preparations in Alkaline Peroxide Impregnation (pre-washed, 3% NaOH, 3% H_2O_2, 2% Na_2SiO_3, 0.05% $MgSO_4$, and 0.1% DTPA)

The cut wheat straw was washed with hot water (70^{o}C) prior to chemical impregnation. This pretreatment not only softened the material but also removed impurities as well as wheat straw components which could consume chemicals in the subsequent impregnation stage. While the extent to which such components as metal ions, extractives and lignin were solubilized in hot water will be discussed in the following paper [5], the importance of wheat straw pre-washing is clearly demonstrated by the result in **Table II**. The benefits of this pretreatment include a remarkable decrease in peroxide consumption and a substantial increase in brightness, while producing pulps of comparable yields. When the wheat straw was directly impregnated, the residual peroxide was almost nil, and alkali-darkening may offset brightness gain. Hence, pre-washing wheat straw is highly recommended to maximize the response of peroxide brightening.

Sample	Pulp yield %	H_2O_2 consumption %	Brightness ISO
Non-washed	90.4	98	45.6
Pre-washed	89.6	72	50.2

Table II. Effect of Wheat Straw Pre-washing on Alkaline Peroxide Impregnation (3% NaOH, 3% H_2O_2, 2% Na_2SiO_3, 0.05% $MgSO_4$, and 0.1% DTPA)

To examine the effect of extractives on peroxide bleaching, a wheat straw sample, extracted in a Soxhlet apparatus with acetone, was used in an impregnation trial. Although the acetone extraction removed 2% of extractives from the wheat straw, part of which were yellow material (the acetone extract was yellowish), this pretreatment was hardly beneficial in terms of peroxide consumption and pulp brightness. The brightness of the resulting pulp was 50.5, compared to 50.2 for the pulp made from the non-extracted straw.

Peroxide Charge and Alkalinity

APMP is a flexible process to be used in a variety of applications. For example, it allows the production of a fully bleached CTMP with no need to install a separate bleach plant [1]. In general, for a given peroxide charge, a proper ratio of alkali to peroxide is required to maximize the response of peroxide bleaching [6, 7]. As illustrated in **Figure 1**, an overall similar trend was observed for the three levels of peroxide application, i.e., 3%, 6%, and 9%. As the alkali charge increased, both the pulp brightness and the peroxide consumption increased, and, on the contrary, the pulp yield decreased. Overall, the pulp yields were relatively low, mostly around 85%. At high levels of alkalinity (e.g. over 6% NaOH), further increasing alkali charge caused a dramatic drop in pulp yield. This is not surprising because wheat straw contains appreciable amounts of low-molecular-weight lignin and hemicellulose, which are easily solubilized in alkaline medium [8]. Moreover, alkaline peroxide is able to delignify wheat straw to a high degree [9].

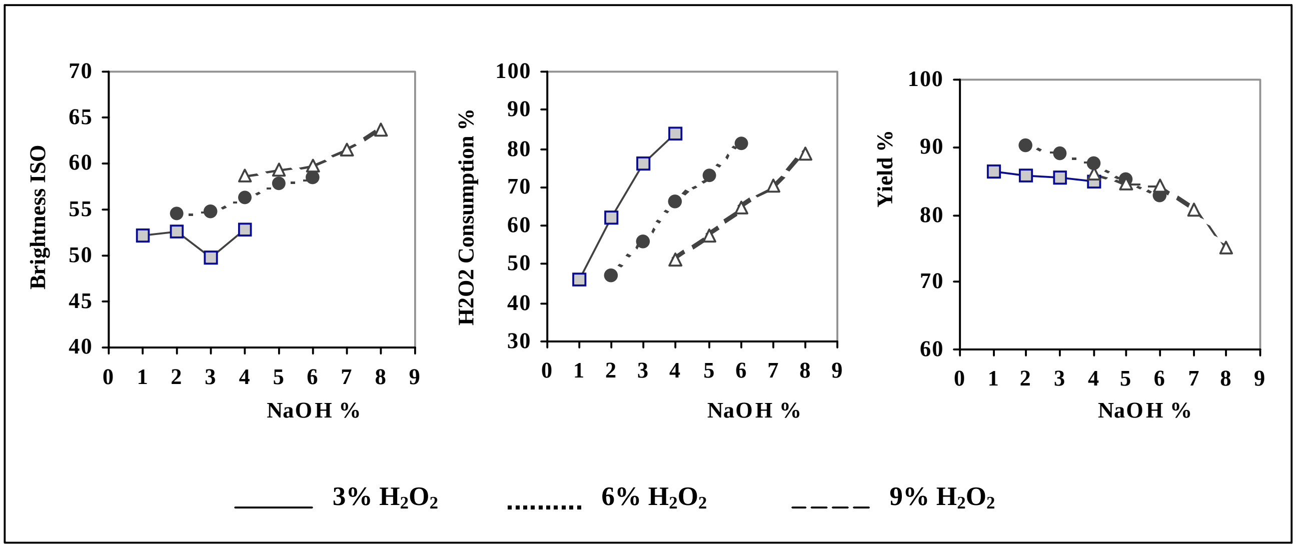

Figure 1. Effect of H_2O_2 and NaOH charges on brightness, peroxide consumption and pulp yield in the alkaline peroxide impregnation of wheat straw (DTPA-pretreated, 2% Na_2SiO_3, 0.05% $MgSO_4$)

As shown in Figure 1, increasing either peroxide charge or alkalinity offered a positive effect on the brightness development. Comparatively, increasing the alkali charge seemed to have greater effect on brightness than increasing the peroxide charge. Generally, the pulp brightness was relatively low, 50 – 60 ISO % except when 9% H_2O_2 and over 6% NaOH were used. Hydrogen peroxide does not appear to be an effective oxidant to brighten wheat straw. Presumably, wheat straw contains certain colored substances that are inert to alkaline peroxide. On the other hand, the great influence of alkali charge on the brightness response could be more likely due to delignification than brightening reaction. In other words, delignification to some degree may help remove chromophores and enhance brightness gain. Nevertheless, a too high alkali charge may cause substantial yield loss. For example, 9% H_2O_2 and 8% NaOH produced a pulp of 64 ISO brightness but the yield was only 75%.

Based on the above observation, the selectivity of brightness gain versus yield loss would be a key factor in selecting peroxide and alkali charges as process variables in the wheat straw APMP. In mechanical pulping it is important to produce a pulp of high brightness without substantial sacrifice in pulp yield. To meet this criterion, a more selective bleaching is highly needed.

Role of Sodium Silicate and Magnesium Sulfate

It is well established that hydrogen peroxide is highly susceptible to catalytic decomposition, especially in the presence of transition metals [10]. In addition to using chelating agents for pulp treatment or during bleaching, bleach liquor may be stabilized to control the metal-induced decomposition of peroxide. Sodium silicate is widely used as an efficient stabilizer for alkaline peroxide bleaching. It significantly reduces peroxide decomposition and enhances the brightness response [6, 7]. It is also reported that adding magnesium sulfate to the silicate in peroxide bleaching further enhances the brightening effect, possibly due to the adsorption of metal ions by a colloidal suspension of magnesium silicate [11].

Figures 2 and 3 show the changes in brightness and peroxide consumption at varying levels of both Na_2SiO_3 and $MgSO_4$. In Figure 2, a slightly improved brightness response by increasing the Na_2SiO_3 addition was more likely due to an increased alkalinity of the bleach liquor since the commercial Na_2SiO_3 solution contains 11.5% NaOH. This observation suggests that the addition of both Na_2SiO_3 and $MgSO_4$ may be superfluous. This is not consistent with their effectiveness in stabilizing peroxide, as observed above, and it also contradicts the widely held belief that their addition results in an enhancement of brightness response. One possible explanation could be that wood and wheat straw have different metal profiles. Wheat straw contains a much smaller amount of manganese [5], a key transition metal ion catalyzing peroxide decomposition. Alternatively, wheat straw contains large amounts of silica and magnesium [5]. It is speculated that some forms of these native silica and magnesium might provide a stabilizing effect, like the added Na_2SiO_3 and $MgSO_4$, for the alkaline peroxide bleaching. Similarly, Eroglu and Usta have reported that in oxygen pulping and bleaching of wheat straw the addition of stabilizers for metal sequestering was not necessary as the silicates in the straw acted as radical inhibitors [12].

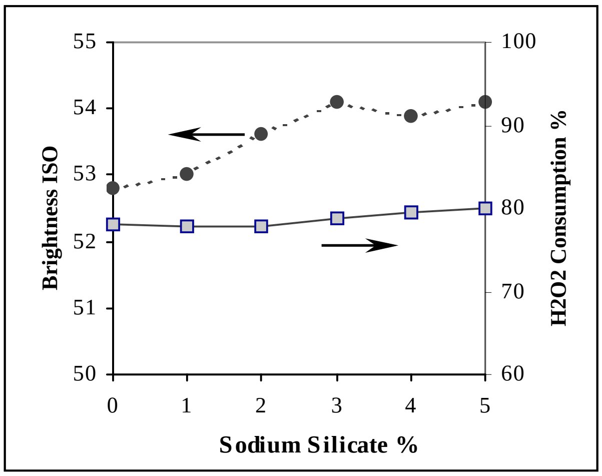

Figure 2. Effect of Na_2SiO_3 charges on pulp brightness and peroxide consumption in the alkaline peroxide impregnation of wheat straw (DTPA-pretreated, 4% NaOH, 4% H_2O_2, 0.05% $MgSO_4$)

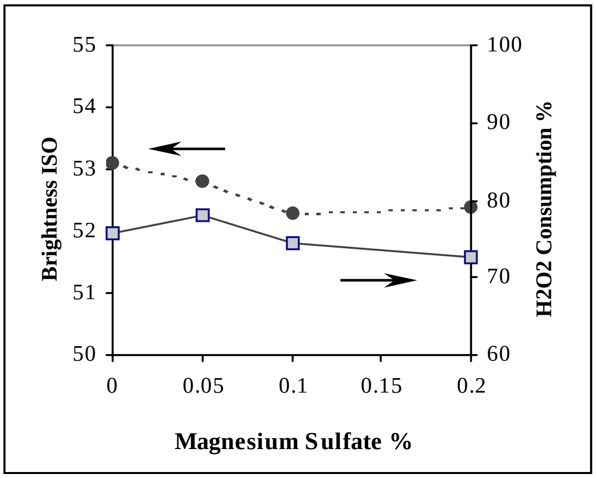

Figure 3. Effect of $MgSO_4$ charges on pulp brightness and peroxide consumption in the alkaline peroxide impregnation of wheat straw (DTPA-pretreated, 4% NaOH, 4% H_2O_2)

Temperature and Time

As shown in **Figure 4**, the peroxide consumption increased with increasing either temperature or retention time. This is because at higher temperature the reactions of both bleaching and peroxide decomposition were accelerated. On the other hand, temperature variations in the 60°C to 80°C range had only a minor effect on the brightness response. Therefore, conditions of lower temperature coupled with adequate retention time are preferable, which allow high brightness with low peroxide consumption.

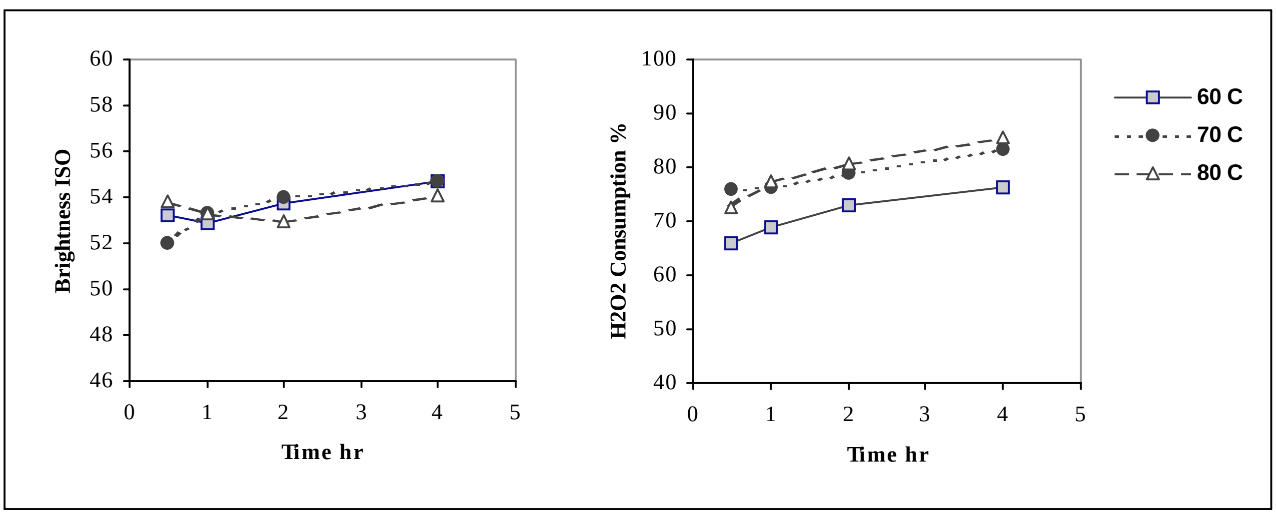

Figure 4. Effect of temperature and time on brightness and peroxide consumption in the alkaline peroxide impregnation of wheat straw (DTPA-pretreated, 4% NaOH, 4% H_2O_2, 3% Na_2SiO_3, 0.05% $MgSO_4$)

It should be noted that the initial brightness of the DTPA-pretreated wheat straw, the starting material, was 36.1% ISO. Obviously, most of both brightness development and peroxide consumption took place in the first 30 minutes of impregnation. This indicates that the bleaching reaction occurred at a fast rate.

Activation of Alkaline Peroxide Bleach Liquor

Nitrilamine and tetraacetylethylenediamine (TAED) have recently been investigated as peroxide activators in bleaching of chemical and mechanical pulps [13, 14]. Nitrilamine reacts with alkaline hydrogen peroxide to form an amino-imino peracid [13], and the perhydrolysis reaction of TAED generates a peracetic acid [15]. These two peracids are a strong nucleophile that reacts selectively with chromophores in lignin.

As shown in **Figure 5**, the presence of TAED in the impregnation liquor provided little benefit in brightening wheat straw by peroxide. Instead, there was a slight decrease in both peroxide consumption and brightness. However, adding 0.5% of nitrilamine offered a brightness gain of 1 ISO point. When the charge of the activator was increased further, the brightness decreased and the peroxide consumption increased pronouncedly. This is because the amino-imino peracid can react with a second molecule of hydrogen peroxide to form urea and oxygen. When an excess amount of nitrilamine was added, this reaction would compete with the bleaching reaction so as to undesirably consume hydrogen peroxide. On the basis of our observation, the activators had little effect on the peroxide activity of brightening wheat straw.

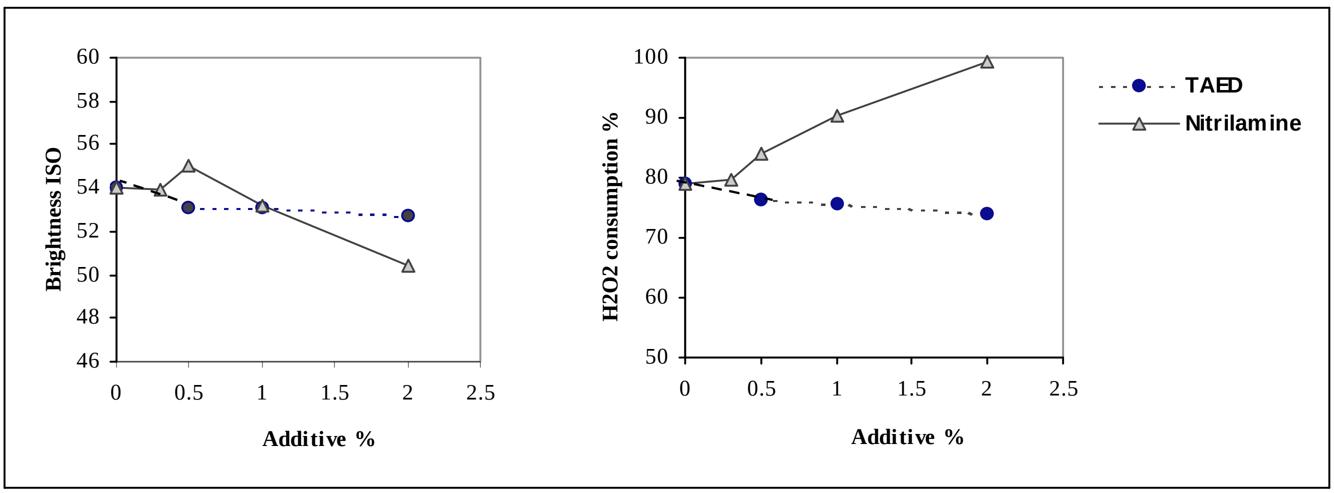

Figure 5. Effect of activators on brightness and peroxide consumption in the alkaline peroxide impregnation of wheat straw (DTPA-pretreated, 4% NaOH, 4% H_2O_2, 3% Na_2SiO_3, 0.05% $MgSO_4$)

CONCLUSIONS

Pre-washing wheat straw with hot water appeared to be remarkably beneficial to the subsequent alkaline peroxide impregnation. This pretreatment was likely to soften straw so as to improve its accessibility to the chemicals, and the removal of fines and dusts and the dissolution of wheat straw components resulted in peroxide saving and brightness gain. On the other hand, acetone extraction of wheat straw provided little effect on the alkaline peroxide bleaching.

It seemed that hydrogen peroxide was not an effective oxidant to brighten wheat straw. The presence of activators was unlikely to enhance the bleaching activity of peroxide. It is thus postulated that some of chromophores in wheat straw are not reactive to hydrogen peroxide. As a consequence, the brightness development of wheat straw by alkaline peroxide is limited, which is a technical challenge to producing high brightness mechanical pulps from wheat straw.

However, the composition of an alkaline peroxide bleach liquor used for wheat straw can be simplified, in light of our finding that it was not necessary to include sodium silicate and magnesium sulfate, which are commonly added in a conventional peroxide bleaching of mechanical pulp.

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