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# Effect of $H_2O_2$ bleaching with ultrasonication on the properties of thermomechanical pulp and unbleached kraft pulp

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ABSTRACT

$H_2O_2$ was used in the final stage of a multistage bleaching process to increase ISO brightness by 2–3%, because of the poor selectivity and bleachability. However, concerns about the environmental load of the bleaching process have led to the efficient use of oxygen-derived compounds, with a concomitant decrease in the quantity of chlorine-derived compounds consumed.

In this study, thermomechanical pulp (TMP) and unbleached kraft pulp (UKP) were bleached with $H_2O_2$ and ultrasonicated in order to increase the bleaching efficiency, and the effects of some bleaching conditions such as treatment time, treatment concentration, and temperature were determined.

The best bleaching efficiency of pulp was obtained using $H_2O_2$ with ultrasonication (at 20 kHz) of the pulp mixture at 45 °C for 30 min. The ISO brightness of the bleached pulp increased up to 1.9%, although the bleached pulp yield was slightly reduced to 1.5%. Magnesium sulfate was used as a bleaching stabilizer to increase the bleached pulp yield and viscosity. As a result, the bleached pulp yield and viscosity increased by 2.1% and 10%, compared with fully bleached pulp at the end of the process, respectively, despite a decrease in ISO brightness.



## 1. Introduction

In the early 1900s, $H_2O_2$ was used for bleaching precious materials, and it was indirectly used as a solid peroxide in bleaching on an industrial scale [1]. Furthermore, the commercial use of $H_2O_2$ as a delignifying agent for kraft pulp was reported in the late 1970s [2]. However, there is a limit to the improvement in the ISO brightness of pulp that can be achieved by $H_2O_2$ bleaching; therefore, $H_2O_2$ is mainly used as a supplement agent to achieve a further increase of 2–3% ISO brightness at the final stage of multistage bleaching [3]. Nevertheless, there is an increasing use of $H_2O_2$ as a total or partial substitute for chlorine-based bleaching agents with elemental chlorine-free (ECF) and totally chlorine-free (TCF) sequences because of the adverse environmental effect of the latter two compounds [4].

During chlorine-based bleaching, chlorinated compounds are produced, and these materials present significant toxicity to plants and animals, including humans. Furthermore, chlorinated compounds cause serious health problems such as low sperm count and cancer [5,6].

Because of these issues, much research has been carried out into the efficient use of $H_2O_2$ and a decreased use of chlorine-derived compounds. Kim and Yang [7] researched the effect of different chelating agents and multistage process with different pH in $H_2O_2$ bleaching. Ninawe and Kuhad reported a bleach-boosting effect when endoxylanase from thermoalkalophilic *Streptomyces cyaneus* SN32 was used in the $H_2O_2$ bleaching of wheat straw-enriched soda pulp [8]. Research on the efficiency of TCF bleaching with a laccase mediator system was conducted by Camarero et al. [9], while ultrasound-aided $KMnO_4$-acid systems for bleaching linen fabric were researched by Hebeish et al. [10].

This present study was initiated to evaluate the bleaching efficiency and energy reduction achieved by $H_2O_2$ bleaching with added ultrasonication. The ultrasonic frequency range is beyond the capacity of human hearing, that is, frequencies higher than 16 kHz (1600 cycles per second) [11]. Ultrasound can be used to perform heat transfer in liquids, and the bubbles generated by ultrasound-induced cavitation are used in cleaning applications. In addition, such ultrasound-cavitation can facilitate particle disintegration. Ultrasonication can produce morphological changes in fibers that can contribute to increased flexibility and improved bonding of the fibers during paper formation [12,13] and efficient bleaching of pulp. Therefore, the aim of this study was to investigate the effect of ultrasonication during $H_2O_2$ bleaching.

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## 2. Materials and methods

### 2.1. Pulps

Pine TMP that contained lignin was used in the $H_2O_2$/ultrasonication bleaching system. Standard methods were used to measure ISO brightness (KS M ISO 2470), klason lignin content (KS M 7045), the amount of extractives (KS M 7039), and the yield of pulp. The basic characteristics of TMP are presented in Table 1.

The viscosity of TMP cannot be measured due to an amount of lignin contents. Therefore, Eucalyptus UKP was bleached using the $H_2O_2$/ultrasonication bleaching system, and both the limiting viscosity number (KS M ISO 5351) to investigate the effect of ultrasonic energy on the cellulose degradation. The ISO brightness (KS M ISO 2470) of the pulp was measured. These basic characteristics are presented in Table 2.

### 2.2. Bleaching methods

The $H_2O_2$ bleaching process was conducted using bleach liquor consisting of 1.5% $H_2O_2$, 2% NaOH, and 1% $Na_2SiO_3$ (% on dry pulp) by mass, and the bleached pulps were further treated by an alkali process (2.5% NaOH) after the $H_2O_2$ bleaching stage. The pH was adjusted to 11 by adding NaOH.

Ultrasonication was applied during the $H_2O_2$ stage to evaluate the bleachability of pulp by the $H_2O_2$/ultrasonication bleaching system. The bleaching was carried out on the ultrasonic water bath of 20 kHz frequency (Branson, 220 V and 205 W). The bleaching temperature was varied between 45, 70, and 90 °C, and different reaction times in the range 20–60 min were tested. Furthermore, magnesium sulfate was used at a concentration of either 1% or 2% as a bleaching stabilizer to prevent the degradation of cellulose.

**Table 1**
Characteristics of TMP used in the experiment.

| | Alcohol–benzene extractives (%) | Klason lignin content (%) | ISO brightness (%) |
|---|---|---|---|
| TMP | 14.17 | 21.73 | 50.2 |

**Table 2**
Characteristics of UKP used in the experiment.

| | Viscosity (cps) | ISO brightness (%) |
|---|---|---|
| UKP | 18.85 | 23.04 |

**Table 4**
Measured items and standard methods.

| No. | Measurement items | Standard methods |
|---|---|---|
| 1 | ISO brightness | KS M ISO 2470 |
| 2 | Klason lignin content | KS M 7045 |
| 3 | Alcohol–benzene extractives | KS M 7039 |
| 4 | Viscosity | KS M ISO 5351 |

The bleaching conditions for the $H_2O_2$/ultrasonication bleaching system are shown in Table 3.

### 2.3. Analysis of fiber characteristics

The ISO brightness values of the pulps were determined according to the ISO 2470 standard using an Elrepho spectrophotometer, and the klason lignin contents and alcohol–benzene extractives, in addition to the pulp viscosity and yield, were measured by standard methods (Table 4).

## 3. Results and discussion

### 3.1. Bleaching efficiency of TMP by pulp consistency

Generally, ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human hearing. In addition, the velocity of ultrasound increases with an increase in the medium density. The trials investigated the effect of pulp consistency on the $H_2O_2$/ultrasonication bleaching system (values of 3%, 5%, and 10%).

Fig. 1 compares the percentages of alcohol–benzene extractives measured in each percent-pulp category for TMP bleached using $H_2O_2$ alone, or using the $H_2O_2$/ultrasonication bleaching system by pulp consistency. As can be seen in Fig. 1, the initial percentage of alcohol–benzene extractives in TMP is 14.2%, but this is reduced to 12.7% after $H_2O_2$ bleaching at 70 °C for 60 min. In particular, the especially low contents of alcohol–benzene extractives of TMP bleached using the $H_2O_2$/ultrasonication bleaching system are significant; these are 10.1% for 3%, 11.4% for 5%, and 12.2% for 10% pulp consistencies. The increase of pulp consistencies can decrease discharge of extractives in pulp because the highly anionic fibers of peroxide-bleached pulps absorb extractives [14–16]. Overall, there are lower amounts of alcohol–benzene extractives in the pulps bleached using the combined $H_2O_2$/ultrasonication process as compared with those for the pulps bleached using the conventional $H_2O_2$ process. It is probable that ultrasonication produced morphological changes in the fiber [13] and increased the treatment tem-

**Table 3**
Bleaching conditions for pulp.

| Lot No. | Pulp consistency (%) | $H_2O_2$ conc., % on o.d. pulp | Reaction time (min) | Temperature (°C) | $MgSO_4$ conc., % on o.d. pulp | EDTA conc., % on o.d. pulp | Ultrasonic energy (kHz) | pH |
|---|---|---|---|---|---|---|---|---|
| Non-bleached | 5 (UKP, TMP) | 1.5 | 0 | Room temperature | – | 0.03 | – | 11 |
| 1 | 5 (TMP) | | 30 | 70 | | | | |
| 2 | | | 60 | | | | | |
| 3 | | | 20 | 45 | | | 20 | |
| 4 | | | 30 | | | | | |
| 5 | | | 60 | | | | | |
| 6 | | | 30 | 70 | | | | |
| 7 | | | | 90 | | | | |
| 8 | 3 (TMP) | | | 45 | | | | |
| 9 | 10 (TMP) | | | | | | | |
| 10 | 5 (UKP) | | | | 1 | | | |
| 11 | | | | | 2 | | | |
| 12 | | | | 70 | 1 | | | |
| 13 | | | | | 2 | | | |