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## Bleaching of Rice Straw Pulps with Hydrogen Peroxide

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**Abstract:** In this study, 9 one-stage hydrogen peroxide bleaching trials were carried out to obtain high brightness levels in oxide added soda-oxygen-anthraquinone rice straw pulps of 52.4% (Elrepho) initial brightness. The results indicated that optimum oxide added soda-oxygen-anthraquinone rice straw pulp bleaching conditions were as follows: Hydrogen peroxide ( $H_2O_2$ ) ratio on oven dry (o.d) pulp: 2-4%, Alkali (NaOH) charge on o.d pulp: 1.5-3%,  $Na_2SiO_3$  ratio on o.d pulp: 3%,  $MgSO_4$  ratio on o.d pulp: 0.5%, EDTA ratio on o.d pulp: 0.5%, reaction temperature: 70°C, reaction time: 70 min. and concentration: 16%. Brightness, breaking length, burst and tear index of rice straw pulps bleached with  $H_2O_2$  were found to be 23.32, 8.05, 10.97 and 23.69%, respectively, higher than those of unbleached rice straw pulps. Yellowness decreased from 314.85 to 218.48‰ elrepho.

**Key words:** Bleaching, rice straw, pulp, hydrogen peroxide

### INTRODUCTION

Rice straw can be used to prepare a variety of paper-grade pulps. The pulps are characterized by high ash content, which is mostly silica, and fibers are short but narrow giving a high slenderness ratio. The presence of parenchyma and epithelial cells as well as other fine debris results in relatively low pulp yields<sup>[1,2]</sup>. The high silica content together with the fines results in papers with good ink receptivity and high opacity<sup>[3,4]</sup> but presents problems in equipment wear and chemical recovery<sup>[5]</sup>.

Due to environmental pressure there is increasing use of hydrogen peroxide as a total or partial substitute for chlorine-based bleaching agents with elemental chlorine-free totally chlorine-free bleaching sequences<sup>[6]</sup>.

The pulp and pulp bleaching industry is a large and growing portion of the world's economy. Pulp and paper production from cereal straw has increased globally, and will continue to increase in the near future. However, the industry is very capital-intensive with small profit margins, which tends to limit experimentation, development and incorporation of new technologies into the mills. The pulp-paper and bleaching industries are also under constant pressure to reduce and modify environmental emissions to air and water<sup>[6,7]</sup>.

Today, bleaching technology is possibly developing faster than ever. Hydrogen peroxide is one of the most important bleaching chemicals. It is a strong oxidising agent, which has variety of different applications in all

kinds of pulp produced in the pulp and paper industry. On of the biggest advantage of hydrogen peroxide is that it is environmentally friendly throughout its whole life cycle, from the raw materials used in production to the disposal of the product<sup>[5]</sup>.

In chemical pulp bleaching, hydrogen peroxide is most important future bleaching chemical. It replaces chlorine and chlorine dioxide. Bleaching of chemical pulp has been dominant application hydrogen peroxide. Hydrogen peroxide bleaching improves pulp quality making it possible to use more chemical pulp in the higher grades of paper<sup>[8]</sup>.

The perhydroxyl anion ( $HOO^-$ ) is generally accepted as being the principal active species in peroxide bleaching. This anion is a strong nucleophile which, during bleaching, converts electron-rich chromophores typified by  $\alpha$ - $\beta$ -unsaturated aldehydes and ketones, and phenolic ring-conjugated ethylenic or carbonyl groups to their non-chromophoric counterparts. The reactions of lignin with peroxide are not reversible and lead to the permanent removal of most of the chromophoric groups present in the lignin molecule<sup>[9]</sup>.

In the bleaching of beech NSSC pulps with  $H_2O_2$ , brightness increased from 39 to 71.6% elrepho and kappa number decreased from 89.7 to 39.4<sup>[10]</sup>. In a study conducted by Allison<sup>[11]</sup> on pine TMP and CMP bleaching, brightness of TMP rises to 76% ISO and that of CTMP to 78.5% ISO under the conditions of 3% sodium silicate, 20% concentration, 60°C temperature, 120 min reaction time and 4%  $H_2O_2$ .

Usta *et al.*<sup>[8]</sup> indicated that when CTMP having 47% elrepho brightness was bleached under the conditions of 3.5% H<sub>2</sub>O<sub>2</sub>, 3% NaOH, 3% Na<sub>2</sub>SiO<sub>3</sub>, 0.5% MgSO<sub>4</sub>, 0.5% EDTA and 70°C temperature and 100 min reaction time, brightness value was determined to be 74.20% elrepho and yellowness decreased from 321 to 193.8% elrepho.

In this study, 9 trials were performed with using H<sub>2</sub>O<sub>2</sub> as bleaching chemical agent. Physical and optical properties of bleached oxide added soda-oxygen-anthraquinone rice straw pulps results were expressed.

## MATERIALS AND METHODS

Oxide added Soda-oxygen anthraquinase (SOAQ) rice straw pulps used in this study were produced in the laboratory conditions. Pulping conditions of rice straw were as follows:

Alkali charge on oven dry (o.d) raw material: 15%, anthraquinone (AQ) charge (on o.d raw material): 0.1%, Al<sub>2</sub>O<sub>3</sub> charge (on o.d raw material): 1.5%, temperature: 130°C, time at max. temperature: 45 min oxygen pressure: 6 kg cm<sup>-2</sup> and liquor to straw ratio: 5/1.

The yield, brightness, yellowness, breaking length, burst index and tear index of these pulps were 49.14%, 52.40% elrepho, 314.85% elrepho, 5.94 km, 4.14 kPa m<sup>2</sup>g<sup>-1</sup> and 3.80 mN m<sup>2</sup>g<sup>-1</sup>, respectively.

In order to determine optimum hydrogen peroxide bleaching conditions of rice straw pulp, 9 bleaching experiments were carried out in this study. In these trials, different parameters of bleaching were varied at the level indicated below:

H<sub>2</sub>O<sub>2</sub> : 2, 3 and 4%  
NaOH : 1.50, 2.25 and 3.0%  
Reaction time: 60, 70 and 80 min.

On the other hand, ratio of Na<sub>2</sub>SiO<sub>3</sub>, MgSO<sub>4</sub> and EDTA, reaction temperature and concentration were kept constant at the levels 3, 0.5 and 0.5%, 70°C and 16%, respectively.

The bleaching liquor was added pre-treated pulp. Immediately after mixing the liquor and the pulp, initial pH was measured. They were placed in polyethylene bags. Then, the mixtures were put in a circulation water bath and the temperature was controlled by a thermostat. The pulps were remixed manually at 20 min intervals to achieve a proper liquor-pulp homogenization.

At the end of the bleaching time, liquor samples were taken to determine final pH and residuals in according to CPPA standard J.16P<sup>[12]</sup>. The pulps were diluted to 1% consistency and then neutralized with sodium metabisulfite in order to decompose the residual H<sub>2</sub>O<sub>2</sub> and stabilize the brightness. Then bleached pulp was pressed up to 15-20% dryness. Later on, moisture content of pulps

regulated to 20-25% and placed in polyethylene bags and moisture content determinations were realized. All pulps were beaten in a valley beater to 40±2 and 50±2 SR° freeness levels and hand sheet were made on a Rapid Kothen machine. In 40±2 SR° optical and in 50±2 SR° physical properties of hand sheets were performed according to TAPPI test methods<sup>[13]</sup>, but viscosity values according to SCAN C 16:88<sup>[14]</sup>.

## RESULTS AND DISCUSSION

Results of the 9 trials (Table 1) reported that, peroxide consumption decreased with the increased of the reaction time. The bleaching yield, kappa number and pulp viscosity decreased with increased reaction time, which corresponds to other H<sub>2</sub>O<sub>2</sub> pulp bleaching<sup>[5]</sup>. When all other conditions were kept constant, bleaching yield decreased with increasing hydrogen peroxide ratio (Table 1). For example, while bleaching yield was 94.78% with 2% peroxide, the same value was found to be 94.05% with using 4% peroxide. In these trials reaction temperature, MgSO<sub>4</sub>%, EDTA%, Na<sub>2</sub>SiO<sub>3</sub>% and concentration were constant at the levels of 70°C, 0.5, 0.5 and 16%, respectively.

Pulp brightness is reached to maximum value at 70 min reaction time and decreases of pulp brightness at increasing times. For instance, at 60 min reaction time, the brightness was 62.70% elrepho, whereas, at 70 and 80 min reaction times, the brightness was found to be as 68.34 and 67.12% elrepho, respectively. Yellowness of the bleached pulps decreased with increased % peroxide rate and the pulp brightness.

The results of present study revealed that oxide added SOAQ pulps can be bleached to 68.34% elrepho brightness with one stage bleaching using H<sub>2</sub>O<sub>2</sub> as chemical agent. At the bleaching of oxide added SOAQ pulps brightness of pulp increased from 52.40 to 68.34% elrepho and yellowness of pulp with bleaching decreased from 314.85 to 218.48% elrepho.

When increased reaction time to 60, 70 and 80 min while keeping other bleaching condition constant has slightly decreased pulp opacity.

The effect of reaction time and peroxide rate on strength properties of hand sheets illustrated in Table 1. The bleached oxide added SOAQ pulps were beaten to 50±2 SR° freeness levels. Regular slightly increase of breaking length with the increase of the time from 6.12 to 6.37 and to 6.28 km (trials no: 1.2 and 3; Table 1).

Generally, breaking length increases with increasing the of H<sub>2</sub>O<sub>2</sub> rate<sup>[15]</sup>. At 2, 3 and 4% H<sub>2</sub>O<sub>2</sub> rate, breaking length were 6.12, 6.20 and 6.32 km, respectively (Table 1). In addition, increasing reaction time from

Table 1: Experimental design and some chemical, optical and physical properties of H<sub>2</sub>O<sub>2</sub> bleached oxide added SOAQ rice straw pulps

Trial no.	H <sub>2</sub> O <sub>2</sub> rate (%)	NaOH rate (%)	Reaction time (min)	White liquor pH	Black liquor pH	H <sub>2</sub> O <sub>2</sub> consumption (%)	Bleaching yield (%)	Kappa number	Pulp viscosity (cm <sup>3</sup> g <sup>-1</sup> )	Brightness (% Elrepho)	Yellowness (% Elrepho)	Opacity (%)	Breaking length (km)	Tear index (mN m <sup>2</sup> g <sup>-1</sup> )	Burst index (kPa m <sup>2</sup> g <sup>-1</sup> )
1	2	1.5	60	11.08	10.10	97.10	94.78	17.02	574	59.17	269.19	90.10	6.12	4.30	3.32
2	2	1.5	70	11.08	9.95	95.17	93.42	15.54	568	65.28	248.10	89.24	6.37	4.90	3.94
6	2	1.5	80	11.08	9.80	91.86	92.17	14.77	559	64.10	254.75	88.17	6.28	4.83	3.87
4	3	2.25	60	11.67	10.45	97.25	94.29	16.43	570	62.70	259.20	91.68	6.20	4.42	3.50
5	3	2.25	70	11.67	10.30	94.13	93.11	14.15	562	68.34	218.48	90.18	6.46	4.98	4.65
6	3	2.25	80	11.67	10.14	90.40	92.00	14.05	550	67.12	225.21	89.40	6.38	4.85	3.91
7	4	3	60	11.75	10.50	96.12	94.05	16.35	561	61.45	261.11	89.00	6.32	4.54	3.64
8	4	3	70	11.75	10.34	93.70	92.65	14.00	555	67.60	223.05	87.84	6.54	5.10	4.15
9	4	3	80	11.75	10.20	90.15	91.04	13.94	543	66.85	234.27	86.65	6.47	4.91	3.99

Note: For all trials EDTA, MgSO<sub>4</sub>, reaction temperature and concentration were taken constant as 0.5%, 0.5%, 70°C and 16%, respectively.

60 to 80 min and peroxide rate from 2 to 4% caused increase in tear and burst index.

The following results were obtained in laboratory-scale peroxide bleach tests using oxide added SOAQ pulps:

- Brightness increased up to 68.34% elrepho was possible in one peroxide stage.
- Kappa number and viscosity of bleached pulp could be reduced by 13.94 and 543 cm<sup>3</sup> g<sup>-1</sup>, respectively.
- Physical and optical properties were improved during H<sub>2</sub>O<sub>2</sub> bleaching.
- Printing and aspect properties of bleached oxide added SOAQ rice straw pulps are improved with brightness increase and yellowness decrease.
- The aging tendency of bleaching oxide added SOAQ rice straw pulp decreases with single sequences using H<sub>2</sub>O<sub>2</sub>.
- Hydrogen peroxide bleaching will reduce effluent colour.

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