Bleaching of solvent delignified wheat straw pulp

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SUMMARY

Hydrogen peroxide constitutes a bleaching agent well adapted to the treatment of pulp previously delignified by organic peroxyacids. Such bleached pulp presents, in an unexpected way, mechanical properties superior to those of unbleached (raw) pulp and to those of pulp treated by peroxyacids. This phenomenon is attributed to the effect of soda neutralisation of cellulosic fibres hydration, and hydrolysis of the ester functions formed during organic acid pulping. The regeneration of hydroxyl functions without cellulose chain degradation leads, by increasing the number of hydrogen bonds formed between the cellulose chains, to improved pulp mechanical properties and is of great interest for further industrial development.

Keywords

Bleaching, hydrogen peroxide, peroxyacids, mechanical properties, fibre hydration

The production of paper pulp from annual plants could resolve problems related to the increase of paper consumption notably in countries that do not possess forests. However, traditional non-wood pulping is difficult because of the high amount of silicates formed. To avoid this silicate formation, the delignification can be made with organic acids (*1-3*).

We showed previously that a mixture of formic and acetic acid and water is easily adapted to unbleached pulp production from different annual plants such as rice straw (*4-5*), the straw of triticale (*6*) and wheat straw (*7*).

We also showed that the delignification of unbleached pulp obtained from wheat straw could be achieved by peroxyacids in an acetic acid/formic acid/hydrogen peroxide media (*7*). This media presents the advantage of being compatible with the pulping method used. However, it produces no real improvement in pulp bleaching.

In this work, we propose an effective pulp bleaching process that produces good pulp mechanical properties.

MATERIALS AND METHODS

Raw material

Wheat straw (*Triticum turgidum*) came from the south of France. It contained 39.4% cellulose, 11.2% lignin, 24.0% hemicelluloses and 8.0% water as determined by the method of Van Soest and Wine (method NDF-ADF).

The acetic acid (99 to 100%), formic acid (98 to 100%) and hydrogen peroxide (~ 50% by mass) used were commercial products (Merck Eurolab).

Analytical methods

Chemical and mechanical characteristics were measured in accordance with the following standards: Kappa number (AFNOR NF T 12-018 and T 12-019), DPv (Degree of polymerisation of cellulose chain obtained by viscosity measure) (AFNOR NF T 12-005), bleaching index (AFNOR NF T 12-030), stability of whiteness (AFNOR NF Q 03-036), mechanical properties (AFNOR NF Q 03-004, Q 03-053, Q 03-001, Q 50-003).

Infrared spectra were obtained with a Bruker IFS45 spectrometer. The pulp samples were placed in a steam-heated room at 100°C for 24 hours to dry them.

Pulping and delignification by peroxyacids

Pulping of the wheat straw and the unbleached pulp delignification was made according to the operating protocol described previously (*7-8*).

Bleaching by hydrogen peroxide

The delignified pulp was mixed in a sodium hydroxide solution (4%) containing 1 to 2% hydrogen peroxide. The liquor/dry material ratio (L/M) was 10:1. The pulp was shaken regularly for 1 hour at 90°C, and the pH of the media was adjusted to pH 11 by adding additional NaOH. After treatment, the pulp was washed several times with distilled water and pressed. At the end of the sequence, the pulp samples were dispersed in a pulper before being filtered and dried under vacuum.

RESULTS AND DISCUSSIONS

Bleaching by hydrogen peroxide

Hydrogen peroxide in basic media was used to bleach the delignified pulp obtained after treatment by peroxyacids and neutralisation (*9*). The perhydroxyl anion HOO^- formed reacts with the quinones formed during lignin degradation by peroxyacids and this induces the elimination of the last conjugated compounds responsible for unbleached pulp colour.

The pulp bleaching by hydrogen peroxide (P) is carried out in several steps. However, to understand each step of the treatment, the chemical and optical characteristics of unbleached pulp and of pulp after treatment by organic acid and peroxyacids mixture were determined (Table 1).

Table 1
Chemical and optical characteristics of pulp during bleaching.

Sequences	Yield (%)	Kappa number	DPv	Brightness index	Brightness stability (%)
Unbleached pulp	43	50.4	1553	36	
Pulp treated by peroxyacids (PA) and neutralised (E)	33.2	9.3	1376	45	-
P_1	32.4	2.0	1276	73	96.2
P_1P_2	32.1	1.4	1148	81	97.9
$P_1P_2P_3$	31.9	< 1	1080	83	98.2

Test conditions: P_1: temperature, 90°C; reaction time, 1 hour; % NaOH/pulp, 4%; pH, 11 to 12; L/M, 10/1; %H_2O_2/pulp, 2%.

P_2, P_3: temperature, 90°C; reaction time, 1 hour; % NaOH/pulp, 4%; pH, 11 to 12; L/M, 10/1; H_2O_2/pulp, 1%.

PA: temperature, 60°C; reaction time, 3 hours; H_2O_2/pulp, 9.4%; L/M, 8/1; AA/AF, 75/25 (v/v).

E: temperature, 90°C; reaction time, 1 hour; % NaOH/pulp, 4%; pH 11 to 12.

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Table 2
Physico-chemical characteristics of pulp obtained at different stages of bleaching.

	Unbleached pulp *	Pulp treated by peroxyacids*	Bleached pulp
Slowness (SR)	49	56	44
Grammage (g/m^2)	59.6	59.5	58.5
Breaking length (m)	4538	5851	6123
Tear index (mNm^2/g)	3.27	3.45	3.59
Burst index (kPa.m^2/g)	2.14	2.51	3.56

Pulp beaten in Lampen mill for 10000 rev.
* Unbleached pulp and pulp treated by peroxyacids were neutralised
E: temperature, 90°, reaction time, 1 hour; % NaOH/dried pulp, 4%; pH, 11.

Table 1 shows the specifics of each step:

- the treatment by carboxylic acids allows the disintegration of the wheat straw. The unbleached pulp obtained is partially delignified (Kappa number 50.4); the degree of polymerisation of cellulose is high (DPv 1553)
- the treatment by hydrogen peroxide in organic acid media followed by an alkaline extraction leads to a delignified pulp (Kappa number 9.3) but with a relatively low brightness index (45)
- the action of hydrogen peroxide in basic media is effective in pulp bleaching. According to the number of steps, the value of brightness index is between 73 and 83 and the brightness stability is high (+96%).

At the end of the treatments the Kappa number is low and the DPv of pulp remains high.

Mechanical characteristics of the bleached pulp

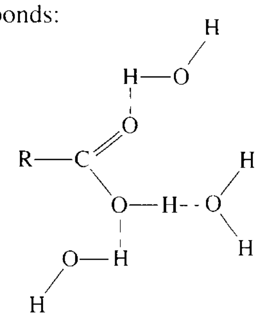
The mechanical characteristics of unbleached pulp, peroxyacids treated pulp and pulp bleached by the sequence P1P2P3 are reported in Table 2.

The results in Table 2 show an improvement in the mechanical characteristics of the bleached pulp, after refining, with regard to unbleached pulp and peroxyacids treated pulp. In comparison to unbleached pulp there was an increase in:

- breaking length (4538 to 6123 m)
- tear index (from 3.27 to 3.59 mNm^2/g)
- and burst index (from 2.14 to 3.56 kPa.m^2/g).

The pulp mechanical properties increased during bleaching. This could be a result of:

- better hydration of fibres during the bleaching stage
- stronger interactions between fibres
- *Effect of the fibre hydration on the mechanical characteristics of pulp:* During delignification the pulp was treated by a mixture of acetic acid/formic acid/water. In such strongly polar media, carboxylic acids are bonded to water molecules by hydrogen bonds:



The extraction of these acids at the end of treatment leads to fibre dehydration (Figure 1b). The fibre network becomes stiffer, more easily broken, and less flexible than when they are hydrated (Figure 1a); this induces a decrease in the mechanical properties of the pulp. A similar phenomenon was also observed by Neto et al. (10) after wood pulping in acetic acid/water or ethanol/water media.

The presence of NaOH molecules allows hydrogen bonds between hydroxide anions and hydroxyl functions of cellulose (*10*), which favours the hydration of fibres and their swelling. This confers better flexibility.

Effect of hydroxyl function esterification: The pulp's mechanical characteristics could also be explained by a better cohesion of fibres after pulp treatment in basic media.

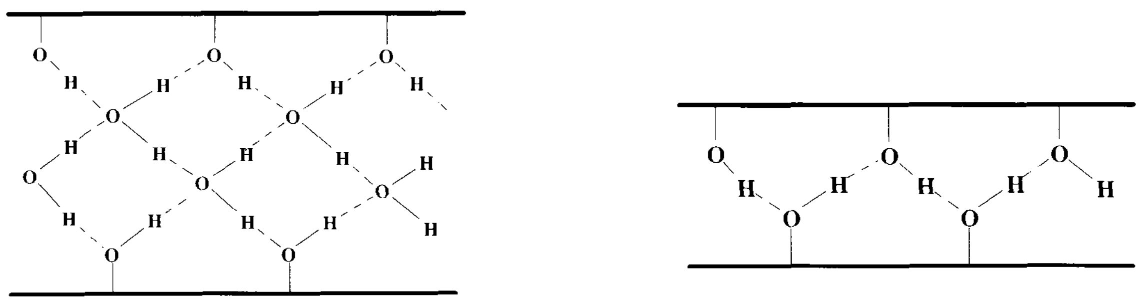
Indeed, during the various treatments of the vegetable material in organic acid media, some alcohols functions of polysaccharides are esterified. (see below)

This esterification influences the mechanical characteristics of pulp by decreasing the number of free hydroxyl groups; it reduces the number of hydrogen bonds between fibres and their cohesion.

The treatment of the pulp in basic media allows, during the stage of bleaching, the regeneration of hydroxyl functions (Fig. 2), and consequently an increase in hydrogen bonds between fibres.

$$R_1-CH_2OH + R_2-COOH \rightleftharpoons R_1-CH_2-O-C(=O)-R_2 + H_2O$$

(R_1= Polysaccharide, R_2= H, CH_3)



a. Hydrated fibre   b. Dehydrated fibre

Fig. 1 Hydrated and dehydrated cellulose fibres.

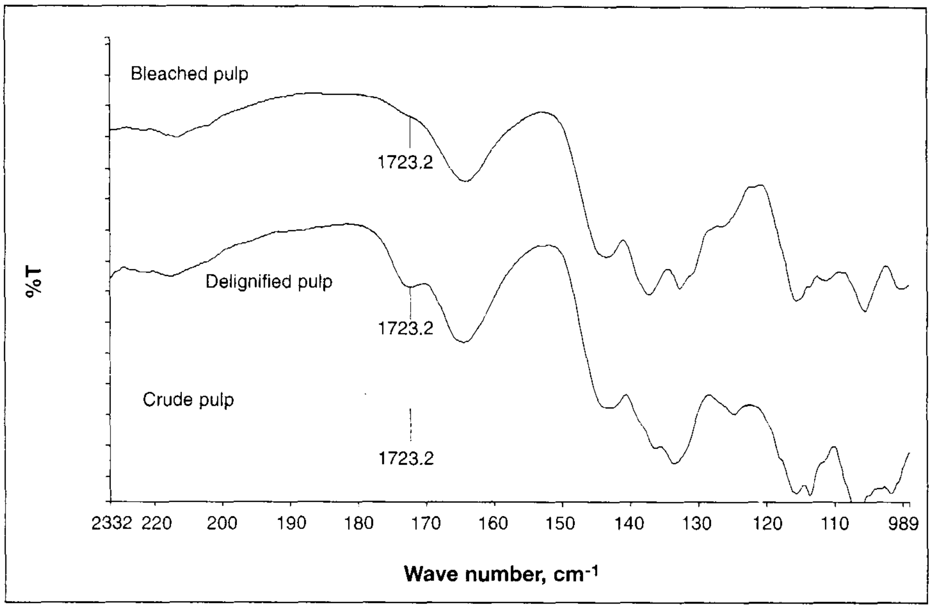


Fig. 2 Infrared spectra of the unbleached pulp, delignified pulp and bleached pulp.

Comparison of these three spectra shows the absence of an absorption band at 1725 cm^{-1} characteristic of ester function, only in the spectra of the bleached pulp.

The bleaching of delignified pulp by hydrogen peroxide in basic media thus favoured the regeneration of hydroxyl functions of the polysaccharides. This effect increases hydrogen bonds between fibres and consequently improves the mechanical properties of the pulp.

CONCLUSIONS

Hydrogen peroxide bleaching of pulp previously delignified by organic peroxyacids was particularly effective at producing bleached pulp from wheat straw. The operating conditions are relatively mild and the alkaline conditions (the hydroxide anions) give the final bleached pulp excellent mechanical properties.

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