



Delignification of wheat straw using a mixture of carboxylic acids and peroxyacids

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Abstract

Wheat straw was pulping by an Organosolv process using a mixture of acetic acid/formic acid/water (AA/FA/water). In order to make easier the bleaching step, it was possible to improve the delignification in an efficient and selective manner by using peroxyacids in acidic organic medium. First a solution of peroxyacids was synthesized by adding hydrogen peroxide in a mixture of acetic acid/formic acid, without any inorganic acids as catalyst. Then this mixture was added to the unbleached pulp. Several parameters (temperature, extraction alkaline, reaction time . . .) were investigated.

This simple and innovative way to use peroxyacids allows to overcome problem due to the control of their stability in aqueous medium and proves to be perfectly complementary to the cooking method in a carboxylic acid medium. Low kappa numbers and high viscosity were obtained. Strength properties of the pulp after the peroxyacids step were improved.

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1. Introduction

Manufacturing of paper pulp from cereal straw has always proven to be a delicate process to carry out in traditional paper mills. In fact, the presence of silicon derivatives in these raw materials renders recycling of the chemical agents contained in the black liquors difficult.

Organosolves pulping in acidic medium seem to be able to solve this problem (Pan et al., 1999, Seisto

and Poppius-Levlin, 1997; Nimz and Schöne, 1993). Among them, the Avidel process (Delmas and Avignon, 1997) makes it possible to obtain good-quality, unbleached paper pulp using non-wood fibres, such as triticale straw or rice straw (Lam et al., 2001a,b), as well as to retain virtually the silicon derivatives in the pulp. This result is obtained using an original type of cooking carried out at atmospheric pressure, at relatively low temperature (110 °C), and using a mixture of acetic acid, formic acid and water (AA/FA/water).

From now on, it is worthwhile to perfect a delignification procedure in order to make the bleaching step easier. This process must be adapted to the acidic

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nature of the chemical medium obtained after cooking, while at the same time conserving the environment.

Out of the three main delignification agents generally used for a totally chlorine free (TCF) bleaching process—that is, ozone, oxygen and hydrogen peroxide—none seems to be able to solve this problem. In fact, bleaching through the use of hydrogen peroxide or oxygen is done in an alkaline medium. In addition, these reagents do not have a sufficient delignifying action to obtain pulp with a high brightness (Desprez et al., 1994; Jääskeläinen et al., 2000). As for ozone, although its delignifying action takes place in an acid medium, its possible decomposition into free radicals can cause deterioration of the carbohydrates as well as depolymerization of the cellulose chains, which results in a decrease in the mechanical properties of the pulp (Liebergott, 1996a). We were therefore interested in another type of oxidizing agent: the peroxyacids.

Various recent works cover their action at the level of Kraft pulp bleaching (Liebergott, 1996b; Poppius et al., 1986). The results obtained during these various studies demonstrate the higher bleaching capacity of peroxyacids as compared to hydrogen peroxide, as well as the better delignifying action and higher selectivity. Peroxyacids such as per(oxo)acetic acid (PAA), per(oxo)formic acid (PFA) or peroxymonosulphuric acid can also be easily synthesized using hydrogen peroxide and the corresponding acid.

It is nevertheless worthwhile to point out that pulp delignification/bleaching through the use of peroxyacids is generally carried out in an aqueous medium, after addition of sodium carbonate to buffer the medium and chelating agents to prevent production of free radicals that are highly reactive with regard to cellulose chains (Desprez et al., 1994). These conditions, which use large quantities of water, prevent neither condensation of the residual lignin between the cellulose fibres, nor hydrolysis reactions of the peroxyacids (Poppius-Levlin et al., 2000).

However, these problems which make the use of peroxyacids complicated and expensive should be resolved easily in the Avidel process. In fact, the cooking and washing step in acidic organic medium allow to remove the metallic cations responsible of the formation of free radicals (Lam et al., 2003). Moreover, working in this medium improve the stability of the peroxyacids and the delignification of the pulp. We re-

port also here the new and innovative results obtained by this process (Delmas and Avignon, 2000).

2. Experimental

2.1. Pulping raw material

Wheat straw (*Triticum Turgidum*) comes from the south of France. It contains cellulose: 39.4%; lignin: 11.2%; and hemicelluloses: 24.0%; water: 8.0%. The analysis was realized by the method of Van Soest and Wine (method NDF-ADF).

2.2. Material

The acetic acid (99–100%), formic acid (98–100%) and hydrogen peroxide (–50% by mass) are commercial products (Merck Eurolab).

2.3. Analysis of pulp: chemical, mechanical, and optical properties

Chemical and mechanical characteristics are 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), mechanical properties (AFNOR NF Q 03-004, Q 03-053, Q 03-001, Q 50-003), brightness index (AFNOR NF T12-030).

2.4. Cooking

Wheat straw is cooked in accordance with the Avidel process (Delmas and Avignon, 1997).

Wheat straw, cut into pieces of approximately 3 cm, are placed in a 1 l reactor heated in an oil bath. The cooking liquor is made of a mixture of AA/FA/water, in the proportions 60–20–20 in volume, with the liquor/dry material ratio being 15:1.

After impregnation of the wheat straw for 30 min at 50 °C, the reactional medium is brought up to 107 °C at a rate of 2 °C/min. This temperature is held for 1 h 30 min. The cooking liquor is then extracted in order to simulate a continuous reactor and replaced by the same volume of fresh liquor in relation to the AA/FA

ratio, but without adding water. The purpose of this procedure is not only to improve delignification, but also to dissolve the lignin. Cooking is then continued for 1 h 30 min.

The mixture is then filtered and the pulp pressed to recover the essential part of the cooking liquor. The raw pulp obtained is washed two more times with acetic acid (98–100%) in order to eliminate the residual lignin. The unbleached pulp obtained in this manner can then be directly treated by peroxyacids, without washing it with water before and/or without intermediate neutralization.

2.5. Synthesis of the solution of peroxyacids

The solution of peroxyacids is prepared using a mixture initially made of varying proportions of AA/FA. The quantity of hydrogen peroxide introduced is 2% in relation to the total volume, i.e. 1.18 g for every 100 ml of acid mixture.

Composition of the various media is followed using the Greenspan and MacKeller method, which makes it possible in order to measure both the quantity of the hydrogen peroxide remaining and the peroxyacids. However, we cannot differentiate peroxyacetic and peroxyformic acids.

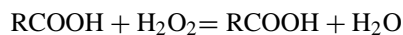
2.6. Treatment of unbleached pulp by peroxyacids

This treatment use synthesized peroxyacids solutions. The liquor/material ratio is 8:1, the bleaching temperature is between 50 and 90 °C inclusive, and bleaching lasts 2 or 3 h. The initial peroxide charge is 9.36% to one part pulp. This step is carried out in an anhydrous medium, after simple washing with acetic acid and pressing of the pulp.

3. Results and discussions

3.1. Synthesis of peroxyacids

Peroxyacids are generally synthesized through a reaction between a carboxylic acid and the hydrogen peroxide, in accordance with the following reaction:



This reversible reaction is slow (it takes several days) when there is no strong mineral acid catalyst.

The role of the strong acid is to supply the protons required for synthesis of peroxyacids.

Nevertheless, sulphuric acid, which is generally used as catalyst for this reaction, is not suitable in our case, since it would lead to deterioration of the pulp, which would result in a decrease in its mechanical properties (Poppius et al., 1986).

In our former work (Lam et al., 2001b), we demonstrated that the vegetable matter could be destructured in an acetic acid medium in the presence of formic acid, which would serve as proton donor.

It was also pointed out that the formation of PFA through the reaction of the hydrogen peroxide with the formic acid does not require the addition of a strong mineral acid, since the reaction can be autocatalyzed (Swern, 1970).

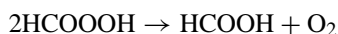
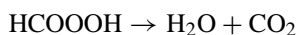
So as to reduce the deterioration of the pulp, we tried to synthesize peroxyacids by replacing the sulphuric acid with formic acid as proton donor in the peroxyacids formation reaction.

3.2. Preliminary tests on peroxyacids formation

The formation of peroxyacids at 27 °C, from a mixture initially made up of 25 ml of FA, 75 ml of AA, and 2 ml of H₂O₂ (at 50% concentration), is followed by a continuous dosage, in accordance with the Greenspan and Mac Keller (1948) method. The quantity of FA used is limited in order to prevent hydrolysis of the cellulose chains (Lam et al., 2003). The results obtained are shown in Fig. 1.

Close examination of this figure shows that the FA effectively serves as proton donor for the reaction. A conversion rate of 75% is then reached for the transformation of hydrogen peroxide into peroxyacids after 8 h of agitation at 27 °C.

A rise in temperature makes it possible to balance the reaction more quickly (Fig. 1). In this way, at 60 °C, a 70% conversion rate is reached after only one hour of reaction. The decrease in the quantity of peroxyacids after 2 h of reaction is linked to the breakdown of the peroxyacids at this temperature. In fact, the PFA is particularly unstable (Swern, 1970) and breaks down in accordance with the following reactions:



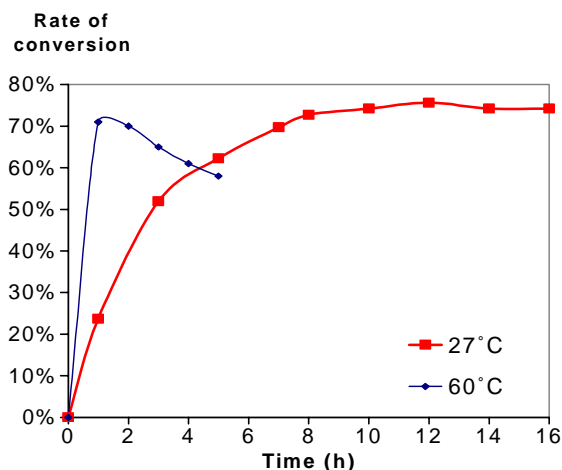
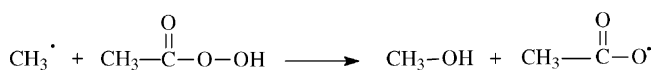
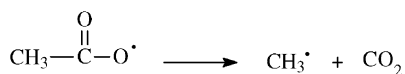
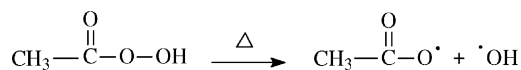


Fig. 1. Rate of conversion of H₂O₂ in peroxyacids at 27 and 60 °C. Conditions—acid volume: 100 ml; AA/FA: 75/25. Hydrogen peroxide volume: 2 ml.

As for the peroxyacetic acid, it can be decomposed by a radical process, according to the reactions (Swern, 1970).



This breakdown is particularly harmful for the pulp, since it generates OH[•] free radicals that are highly reactive toward the cellulose. The temperature must also be chosen carefully to limit the loss of peroxyacids.

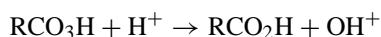
3.3. Delignification of an unbleached pulp using peroxyacids solution

Such a mixture of AA, FA, hydrogen peroxide and peroxyacids proves to be efficient (Table 1) for delignifying the unbleached pulp through the combined action of the peroxyacids as oxidizing agent and of the acetic acid as solvent for the lignin.

This preliminary test shows that this oxidizing medium in fact proves to be suitable for delignification of the unbleached pulp, since the following can be observed:

- significant decrease in the kappa number;
- high selectivity of the reaction, since the variation in the DP_v is relatively low;
- slight gain in brightness index.

These interesting results can be explained by the action of the hydroxonium ion OH⁺ formed during the peroxyacids stage in acidic medium:



In fact, OH⁺ ion is a strong electrophilic agent which can react with lignins (Gierer, 1982) as:

- ring hydroxylation;
- oxidative ring opening;
- substitution of side chains;
- cleavage of β-aryl ether;
- epoxidation.

By contrast, it does not react with hydroxyl groups of carbohydrates in pulp (Poppius et al., 1986).

It is worthwhile to point out that peroxyacids, under acidic medium, act as delignifying and activating agents and not as bleaching agent.

Table 1
Delignification of the unbleached pulp using peroxyacids

	Yield (%)	Kappa number	DP _v	Brightness index
Unbleached pulp	43.0	50.4	1553	36.5
Pulp treated by the peroxyacids solution	39.3	23.2	1458	39

Test conditions—preparation of peroxyacids: temperature, 60 °C; reaction time, 2 h; AA/FA, 75/25. Treatment by peroxyacids: Reaction time, 2 h; temperature: 60 °C; L/M ratio, 8/1; quantity of peroxide/pulp, 9.36%.

Table 2
Effect of an alkaline extraction (E)

	Kappa number	DPv	Brightness index
Unbleached pulp	50.4	1553	36.5
Pulp treated by the peroxyacids solution	23.2	1458	39
Pulp after the E stage	9.3	1376	45

Test conditions—preparation of peroxyacids: temperature, 60 °C; reaction time, 2 h; AA/FA, 75/25. Treatment by peroxyacids: reaction time, 2 h; temperature, 60 °C; L/M ratio, 8/1; quantity of peroxide/pulp, 9.36%. Alkaline extraction: % NaOH/pulp, 5%; L/M, 10; T, 90 °C; reaction time, 1 h.

It was possible to improve these results through a study of the influence of the various parameters, such as an alkaline extraction, reaction time, temperature, composition of the delignification liquor on the delignification of the unbleached pulp.

3.4. Influence of an alkaline extraction

Miscellaneous works emphasize the importance of an alkaline extraction step following the step using oxidizing agents (Desprez et al., 1994; Liebergott, 1996a). We therefore studied its effect on pulp delignification (Table 2).

The result obtained in fact demonstrates that an alkaline extraction carried out on a pulp obtained after the step with peroxyacids at 60 °C arises in a considerable decrease in the kappa number, since a single alkaline extraction make it possible to change its value from 23.2 to 9.3, without viscosity loss and with a gain of six points in brightness. In fact soda allows to dissolve the lignin fragments modified by the peroxyacids step. Moreover, the elimination of these fragments can decrease the consumption of chemical product for the next step.

From now on, an alkaline extraction step will be carried out after each test using peroxyacids.

3.5. Influence of the reaction time

To study the influence of the reaction time, some pulp was sampled each hour and analyzed (Fig. 2).

These results show:

- the most of the delignification take place in three hours. But after 3 h of reaction, the delignification seems to be stopped.

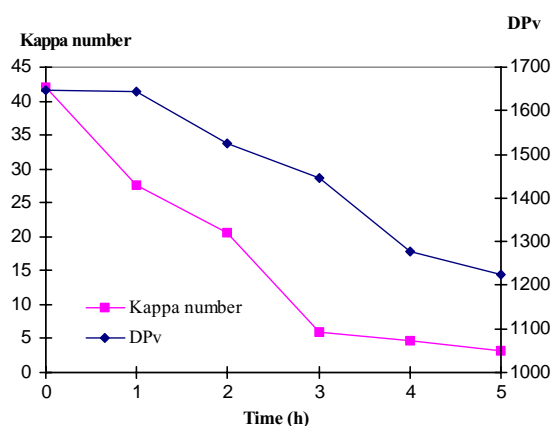


Fig. 2. Effect of the time reaction on delignification and viscosity of pulp. Test conditions—preparation of peroxyacids: temperature, 60 °C; reaction time, 2 h; AA/FA, 75/25. Treatment by peroxyacids: temperature, 60 °C; L/M ratio, 8/1; quantity of peroxide/pulp, 9.36%. Alkaline extraction: % NaOH/pulp, 5%; L/M, 10; T, 90 °C; reaction time: 1 h.

- a continuous loss of viscosity with the reaction time which proves that a too long one can degrade cellulose chain.

The reaction time is so an important parameter which control the delignification of the pulp and the selectivity. Here, we choose a reaction time of 3 h to obtain well-delignifying pulp without too much viscosity lost.

3.6. Influence of temperature

To study the influence of temperature, various delignification tests were run on our unbleached pulp at 50, 60, 80 and 90 °C (Table 3).

Table 3
Effect of temperature on delignifying action of peroxyacids

	Kappa number	DPv	Brightness index
Unbleached pulp	38.1	1297	36.7
50 °C	8.5	1140	47.4
60 °C	5.8	1022	52.5
70 °C	5.1	921	55.1
90 °C	4.4	843	55.3

Test conditions—preparation of peroxyacids: temperature, 60 °C; reaction time, 2 h; AA/FA, 75/25. Treatment by peroxyacids: reaction time, 2 h; L/M ratio, 8/1; composition of AA/FA mixture 75/25; quantity of peroxide/pulp, 9.36%. Alkaline extraction: % NaOH/pulp, 5%; L/M, 10; T, 90 °C; duration of 1 h.

The strong decrease in the kappa number emphasizes the importance of the temperature on the delignifying action of peroxyacids. Nevertheless, a too high temperature in the reactional medium results in a large decrease in the degree of polymerisation. The deterioration of the cellulose chains can be due to:

- acid hydrolysis of the cellulose;
- breakdown of peroxides (H_2O_2 and RCO_3H) into free radicals that are highly reactive with the various functions.

The first hypothesis is highly unlikely, since it has already been demonstrated that during cooking, this proportion of formic acid and acetic acid does not deteriorate cellulose, even at 107°C (Lam et al., 2001b). A treatment of the unbleached pulp in the same experimental conditions (AA/FA: 75/25; temperature: 90°C ; L/M: 15) but without adding hydrogen peroxide has shown that the viscosity was unchanged.

The decrease in DPv can also be explained by the thermal breakdown of peroxides (probably peroxyformic acid which become unstable at these temperatures) which leads to the formation of free radicals.

The delignification step using peroxyacids should therefore be carried out at a relatively low temperature in order to prevent deterioration of the cellulose fibres. Here, a temperature of 60°C will be adopted for the rest of our tests.

3.7. Influence of delignification liquor composition

Tests performed in the presence of variable proportions of acetic and formic acid (Table 4) show that this parameter has a none negligible influence in terms of delignification and bleaching of unbleached pulp.

Table 4
Influence of initial acid ratio on delignification

AA/FA	Kappa number	DPv	Brightness index
Unbleached pulp	42	1647	32
75/25	5.8	1534	52
50/50	5.7	1488	53
25/75	5.3	1319	53
0/100	5	1151	54

Test conditions—Preparation of peroxyacids: temperature, 60°C ; reaction time, 2 h. Delignification time: 3 h; temperature: 60°C ; quantity of peroxide/pulp: 9.36%; L/M: 8/1. Alkaline extraction: % NaOH/pulp, 5%; L/M, 10; T, 90°C for 1 h.

Table 5

Mechanicals properties of the pulp before and after the treatment by peroxyacids

	Unbleached pulp	Pulp treated by peroxyacids
Grammage (g/m^2)	59.6	59.5
Slowness (SR)	49	56
Breaking length (m)	4538	5851
Tear index ($\text{mN m}^2/\text{g}$)	3.27	3.45
Burst index ($\text{kPa m}^2/\text{g}$)	2.14	2.51

Pulps were beaten in a Lampen beater during 10,000 revolutions.

These results demonstrate a clear-cut decrease in the degree of polymerization. This is probably due to acid hydrolysis of the cellulose increasing by the quantity of FA introduced.

This decrease in the DPv as a function of the formic acid concentration is, furthermore, in agreement with the results obtained by Lam et al. (2003).

3.8. Pulp mechanical properties after treatment by peroxyacids

Pulp mechanical properties of the unbleached pulp and the pulp after treatment by peroxyacids were determined on sheet of $60 \text{ g}/\text{m}^2$ (Table 5).

The results given in Table 5 show that mechanical properties of the pulp treated by peroxyacids are improved. This can be explaining by a better hydration of the pulp treated by peroxyacids because of elimination of impurity around the fibres. Then fibrillation can take place more easily during the beating.

These results prove also that the treatment by peroxyacids in AA/FA medium, do not deteriorate the mechanical properties of the pulp.

4. Conclusion

Use of a PAA, PFA, AA, FA and hydrogen peroxide mixture is perfectly suitable for delignifying wheat straw pulp obtained through cooking in an AA/FA/water medium, and relatively simple to carry out. This delignification step, followed by alkaline extraction fully complements our method of cooking in a carboxylic acid medium, and makes it possible to obtain pulp offering good chemical characteristics. Moreover, mechanical properties of the pulp treated

by peroxyacids are improved. Pulp obtained by this process should also be bleached more easily.

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