

## PRODUCTION, BLEACHING, AND CHARACTERIZATION OF PULP FROM *Stipa tenacissima*

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*Alfa grass pulping was successfully performed in hydro-organic acid medium under mild conditions (107°C, atmospheric pressure, cooking time: 3 h). Use of an acetic acid/formic acid/water mixture as pulping liquor was perfectly suitable for selective isolation of pulp, lignin, and hemicelluloses. The unbleached pulp obtained in good yield was first delignified by peroxyacids in organic acid medium and then bleached with hydrogen peroxide in a basic medium to give pulp offering good physico-chemical and mechanical characteristics.*

**Keywords:** *Stipa tenacissima*, alfa, delignification, bleaching.

In North Africa the pulp and papermaking industry is based on an annual plant, *Stipa tenacissima*, also called alfa, which occupies about seven million ha. Cellulose fibers are obtained from this plant by soda cooking, which leads to high-quality pulp, but lignin and hemicelluloses are employed in low-added-value applications such as producing process energy. Moreover, the silicon derivatives initially present in alfa grass complicates considerably the recycling of the chemicals involved [1].

Organic processes based on the use of organic solvents such as methanol, ethanol, and acetic acid as cooking liquor resulted in extensive removal of both lignin and hemicelluloses under mild conditions without significant cellulose degradation as well as the retention of a large part of silicon derivatives in the unbleached pulp [2–4]. The CIMV process based on acetic acid/formic acid/water as the cooking liquor is easily adapted to unbleached pulp production from different annual plants and presents the advantage of conserving the environment by solvent recycling [5–8]. Recently we have reported some preliminary results on the use of the CIMV process for alfa grass refining [9]. Then we report in this article the production of crude pulp by treating this vegetable matter at low temperature under atmospheric pressure in acetic acid/formic acid/water media according to the CIMV process and then the application of a delignification and bleaching sequence using organic peracids and alkali hydrogen peroxide with regard to the properties of the ensuing material.

A series of experiments were carried out to determine the optimal cooking or refining conditions for the delignification rate and chemical characteristics of the pulp. The parameters scanned in this study included the acetic acid/formic acid ratio in the cooking solution, the reaction time, the liquor/dry matter ratio, as well as the percentage of water and the impregnation step while temperature and pressure were kept constant.

The presence of both acetic acid and formic acid in the medium improved simultaneously the pulping yield and the Kappa number. Acetic acid alone was not a good delignification agent since the absence of formic acid in the medium did not allow the delignification of the vegetable matter and only rejects were recuperated. When using formic acid in the absence of acetic acid, the pulping of alfa grass took place and the rejects were reduced to 0.4%, but the resultant pulp was obtained with low yield (39%) and presented a low DP<sub>v</sub> (576) with an approximately low residual lignin content (Kappa number = 17.8).

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TABLE 1. Physico-Chemical and Mechanical Properties of Alfa Pulps

| Property                           | Pulp       |             |          |
|------------------------------------|------------|-------------|----------|
|                                    | unbleached | delignified | bleached |
| Yield, % of dry matter             | 49.06      | 45.20       | 43.03    |
| Kappa number                       | 28.5       | 15          | 3.7      |
| Viscosity (cm <sup>3</sup> /g)/DPv | 617/909    | 602/884     | 556/811  |
| Slowness (°SR)                     | 52         | 53          | 41       |
| Grammage (g/m <sup>2</sup> )       | 58.5       | 58          | 57       |
| Breaking length (m)                | 4710       | 5560        | 5940     |
| Tear index (mNm <sup>2</sup> /g)   | 4.17       | 4.30        | 4.48     |
| Brightness index                   | 33.8       | 44          | 78       |

This behavior, which was similar to that reported for other vegetable matters [5, 7], could be attributed to two separate reasons, (i) formic acid is a strong delignification agent, which plays the role of the proton donor [10], (ii) acetic acid is a very good solvent of lignin and hemicellulose fragments [11]. The best results corresponded to a cooking liquor composition of 30% formic acid and 50% acetic acid, which produced pulp with good unbleached pulp yield (46%) and viscosity (580 cm<sup>3</sup>/g).

Cooking time varied between 2 to 8 h, showing that pulp yield and viscosity reached a maximum level between 3 and 4 h and decreased slowly thereafter. The Kappa number decreased little after 3 h, probably due to the competition between delignification and precipitation of dissolved lignin on the fiber surface [6].

Increasing the L–M ratio from 8:1 to 15:1 resulted in a considerable reduction in the Kappa number (from 38 to 26) and rejects. Cooking with a high L/M ratio contributed alfa hydrolyzed products in the form of soluble hemicelluloses and lignin fragments but implied important energy consumption for recycling the acids, increasing consequently the cost of the transformation of alfa into paper pulp. A L–M ratio of 10:1 would be suitable to perform alfa cooking based on these laboratory tests.

The water content in the cooking medium was also an important parameter in the pulping of *Alfa* because of its effect on organic acid dissociation and hydrolysis of hemicelluloses, but it was a very bad solvent for lignin. The best results in both yield (47%) and Kappa number (29.5) were obtained when using formic acid–acetic acid–water in 30:50:20 (% v/v) composition.

The delignification was improved (yield: 49%; Kappa number: 28.5) when alfa grass was first impregnated by formic acid–acetic acid–water (30:50:20) mixture during 1 h at 60°C. This impregnation step allowed uniform penetration and diffusion of the cooking liquor chemical [6].

The best conditions related to destructuring alfa grass by the CIMV process carried out at 107°C under atmospheric pressure can be summarized as follows: L–M ratio 10:1; cooking liquor formic acid–acetic acid–water (30:50:20: v/v/v); impregnation 1 h at 60°C, reaction time 3 h.

In order to make the bleaching of alfa pulp easier, it was of interest to improve, in the first stage, the delignification of unbleached pulp with peroxyacids synthesized by adding hydrogen peroxide to the acetic acid/formic acid mixture [12]. This medium has the advantage of being compatible with the pulping process used. The delignification stage was carried out in various conditions aimed at optimizing the yield and the characteristics of the pulp. Based on earlier studies [8, 12], the effects of three factors were examined: formic acid–acetic acid ratio (00:100, 25:75, 50:50, 75:25, and 100:00 v/v), delignification time (0.5, 1, 2, 3, and 4 h), and reaction temperature (50, 60, 70, and 90°C). The best results (yield: 45.2%, DPv: 884, Kappa number: 15) were obtained when using formic acid–acetic acid in 25:75 v/v ratio at 60°C during 1 h. Figure 1 shows the evolution of pulp characteristics in term of both degree of polymerization (DPv) and Kappa number during the delignification step development.

During degradation of lignin by peroxyacids in the first step, conjugated compounds, responsible for the delignified pulp color, were inevitably produced, as shown by its relatively low brightness index value (44). The elimination of these undesirable chromophores was achieved, in a second step, by oxidative reaction with perhydroxyl anion HOO<sup>-</sup> produced by using hydrogen peroxide in a basic medium. This bleaching reagent is very efficient at producing bleached pulp from annual plants [8, 13] and was well adapted to alfa unbleached pulp previously delignified by organic peroxyacids since the brightness index increased from 44 to higher values according to the number of steps (after one step: 70; after two steps: 78).

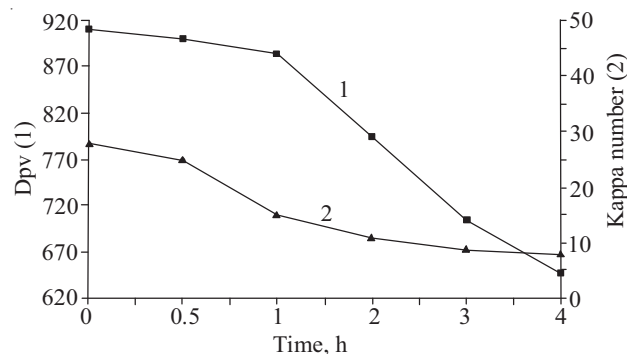


Fig. 1. Evolution of DPv and Kappa number of pulp in delignification stage. Delignification conditions: weight of unbleached pulp: 10 g; formic acid/acetic acid ratio: 25:75 (v/v); volume of liquor: 80 mL; weight of H<sub>2</sub>O<sub>2</sub>: 1.8g; temperature: 60°C.

A comparison of some physico-chemical and mechanical characteristics of unbleached, delignified, and bleached pulps is presented in Table 1. The results given show that these characteristics were improved by treating the pulp successively with peroxyacids and hydrogen peroxide in a basic medium: at the end of the treatments the alfa pulp was obtained in good yield (43.03) with a low Kappa number (3.7), a satisfactory DPv (811), and a good brightness index (78); in comparison with unbleached pulp, there was an increase in breaking length (from 4710 to 5940) and tear index (from 4.17 to 4.48).

The increase in mechanical properties, which was similar to that reported for other annual plant pulps, resulted in a better cohesion of fibers after pulp treatments, which could be attributed to an increase in OH functions, which enhances the number of hydrogen bonds between the cellulose fibers [8].

## EXPERIMENTAL

**Material.** Alfa grass came from the middle west of Tunisia. This vegetable matter, analyzed by the method of Van Soest and Wine (method NDF-ADF), contained 55% cellulose, 9% lignin, 31% hemicelluloses, 1.84% minerals, and 3.16% water. The acetic acid (99 to 100%), formic acid (99 to 100%), and hydrogen peroxide (30% by mass) used were commercial products (Merck).

**Cooking.** Cooking was carried out in a 1-liter glass reactor at atmospheric pressure. The alfa (30 g), cut into fragments of average length 3 cm, was first impregnated with the cooking liquor at 60°C for 1 h and then heated at 107°C under various conditions as discussed later. The pulp thus obtained was first filtered, pressed, and washed twice with acetic acid solution, then with water. The fibers were then screened on 65 and 100 mesh sieves using pressurized water. The undercooked pulp (rejects) was collected on a 65-mesh sieve, while that on the 100-mesh sieve was collected as the accepted fiber, and both were dried and analyzed.

The acid media was recycled in each assay by simple evaporation. The addition of water to the residue obtained after evaporation of the acids led to the precipitation of the lignin, which was filtered, washed until neutral pH with distilled water, and then dried. The water-soluble sugars were obtained in the form of syrup after concentration.

**Bleaching Process.** The process used involved two steps: (i) delignification by peroxyacids generated in situ by adding hydrogen peroxide in organic acidic medium and (ii) bleaching by hydrogen peroxide in alkaline medium [8].

**Delignification Stage.** The crude pulp (10 g) obtained by alfa grass organic refining was introduced into a reactor at atmospheric pressure, and the formic acid/acetic acid mixture (80 mL) and hydrogen peroxide (9%) were added. The reaction medium is heated under various conditions as discussed later and then filtered to separate the delignified pulp, which was pressed, washed with distilled water, and dried.

**Bleaching Stage.** The delignified pulp (10 g) was introduced into 100 mL of sodium hydroxide solution (0.4 g) containing (0.6 g) hydrogen peroxide, and the mixture (pH 11) was heated for 1 h at 90°C. The pulp thus bleached was first filtered, washed several times with distilled water, and then pressed.

**Pulp Analysis: Physico-Chemical and Mechanical Properties.** Pulp was first refined according to AFNOR standards NF Q50-002 (Rapid-Kothen method) to test its mechanical properties. Physico-chemical and mechanical characteristics are measured in accordance with the following standards: kappa number (AFNOR NF T 12-018 and T 12-019), DP<sub>v</sub> (degree of polymerization 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, Q03-001, Q 50-003).

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