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# A new procedure for the destructuring of vegetable matter at atmospheric pressure by a catalyst/solvent system of formic acid/acetic acid.Applied to the pulping of triticale straw

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## Abstract

The selective separation of cellulose, hemicelluloses and lignin of triticale straw is achieved, at atmospheric pressure, using a mixture of formic acid/acetic acid/water. The chemical and mechanical characteristics of the obtained pulp are good. The majority of the silica derivatives are retained in the pulp because of the acidic cooking conditions. The cooking agents are easily recyclable without combustion of the cooking liquor. The lignin and sugars are also isolated. This method of cooking the vegetable matter provides paper pulp which is very well suited to a TCF bleaching sequence. Use of this sequence produces bleached pulps of very satisfactory chemical and optical characteristics.

*Keywords:* Formic acid; Acetic acid; Pulp; Lignin; Sugars; Triticale straw

## 1. Introduction

Obtaining cellulose fibres from vegetable matter, using traditional paper producing procedures, consists of degrading a large amount of lignin and hemicelluloses and making them soluble in the aqueous medium. After concentration of the black liquor, these lignins and hemicelluloses fragments are soluble in the cooking liquor and in general serve as fuel with regards to recycling the chemical used.

In the case of cereal straw, its transformation into paper pulp in accordance with traditional processes is faced with technological challenges which are difficult to overcome because the majority of silicon derivatives are transformed into soluble silicates in the black liquor. Their presence interferes considerably with the recycling of the chemicals involved.

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The production of paper pulp from cereal straw, of which the worldwide annual production is considerable, should allow for the simultaneous use of a large part of the excess straw and therefore supply an indispensable primary material to meet the growing demand for paper.

In this context, the development of a new technology for the production of paper pulp from cereal straw with the best use of agricultural resources, seems to be the only efficient way out the present situation. It poses, however, a significant economic and ecological challenge.

It was only quite recently (Pan et al., 1998, 1999) that a study was carried out on the delignification of rice straw in an acetic acid/water medium using sulphuric acid as a catalyst. This cooking method in comparison to the more traditional methods results in satisfactory mechanical characteristics of the pulp as well as the retention of a large part (75%) of the silicon derivatives in the unbleached pulp. However, the presence of a mineral acid in the cooking liquor complicates the recycling of the reaction reagents.

We present in this article a new procedure for separating the chemical components of vegetable matter (Delmas and Avignon, 1997; Lam et al., 2000) which we have adapted to triticale straw. It uses a mixture of formic acid/acetic acid/water (fa/aa/water) as the cooking liquor, and is carried out at atmospheric pressure and slightly raised temperature: 107°C (boiling point of azeotrope formic acid/water).

## 2. Materials and methods

### 2.1. Vegetable matter

The vegetable matter used was triticale straw (hybrid of rye and wheat) from south of France. This straw contains 86.8% dry matter, of which 48.5% is ADF (Acid Detergent Fibre), 3.5% is ash and 2.2% are silicon derivatives.

### 2.2. Cooking

The cooking was carried out in a 1-l glass reactor at atmospheric pressure. The triticale straw, cut into pieces with an average length of 3.0 cm, is first saturated by the cooking liquor at 50°C for 30 min, the ratio liquor/dry matter being 12/1. The rise in temperature is fixed at 114°C/h. A total of 40 g of straw was used for each test. The cooking temperature is 107°C. The cooking liquor is a mix: formic acid/acetic acid/water in a ratio by volume of 20/60/20 or 30/50/20%.

After saturation, the cooking is carried out under the conditions specified for each trial.

The pulp thus obtained is filtered, pressed and washed twice with a mixture of formic acid/acetic acid/water of identical composition to that of the cooking liquor, then with water. Finally, it is dried and analysed. The remaining formic/acetic acid in the pulp is close to 1% with respect to the dry pulp.

The acids used are recycled by simple distillation. The addition of water to the residue obtained after evaporation of the acids leads to the precipitation of the lignin. These were filtered, then washed until neutral pH with distilled water and dried. The soluble sugars in the water were obtained in the form of a syrup after concentration.

### 2.3. Bleaching

The unbleached pulp obtained by the cooking of the triticale straw in a formic acid/acetic acid/water medium is bleached by means of a PaZEP sequence. The operating conditions were as follow:

Pa: Bleaching in a formic acid/acetic acid medium, ratio liquor/dry matter: 8/1, ratio fa/aa: 30/70 (% v/v), quantity of hydrogen peroxide: 0.46% by weight in comparison to the bleaching liquor, quantity of sodium pyrophosphate: 0.5% with respect to the dry pulp, temperature: 90°C, time: 1 h. The addition of hydrogen peroxide to the fa/aa mixture is carried out at room temperature 24 h before a treatment in order to allow the conversion of 70% of hydrogen peroxide in corresponding peracids.

Z: Amount of ozone: 1% with respect to the dry pulp, temperature: 25°C, consistency: 35%.

EP: Quantity of NaOH: 4% with respect to the pulp, quantity of hydrogen peroxide: 1% with respect to the pulp, consistency: 10%, temperature: 90°C, time: 1 h.

### 2.4. Analysis of the chemical and mechanical characteristics of the pulp

Pulp was first refined in a Valley beater then transformed into sheets using a Frank apparatus with two dryers, according to AFNOR standards NF Q50-002 (Rapid-Köthen method) to test its mechanical properties.

The chemical and mechanical characteristics of the pulp are determined in accordance with the following norms:

| | |
|---|---|
| Kappa index: | AFNOR NF T 12-018, |
| Viscosity limit index expressed in $cm^3/g$: | AFNOR NF T 12-005 |
| Mechanical characteristics: | AFNOR NF Q 03-004<br>AFNOR NF Q 03-053<br>AFNOR NF Q 03-001 |
| Whiteness index: | AFNOR NF T 12-030 |
| Content in ashes and silicon: | Chinese norm G.B 2677.3-81 |

### 2.5. Characterisation of the lignin

The infrared spectra were recorded with a Perkin Elmer 1600 using KBr discs and unrefined lignin.

The proton NMR spectra were registered at 200 MHz in DMSO d6 using acetylated lignin and a Brucker AC 200 spectrometer.

Acetylation of the lignin: 0.6 g of the lignin was dissolved in 9 ml of a mixture pyridine/acetic anhydride 1:1 for 24 h at 50°C in a 200 ml round bottom flask. The acetylated lignins were precipitated with cold distilled water, then filtered and dried.

Each experiment have been duplicate.

## 3. Results and discussion

### 3.1. Delignification and chemical characteristics of the unbleached pulp

The effects of the cooking time and of the fa/aa/water ratio on the chemical characteristics of the unbleached pulp are reported in Table 1.

These results show that a composition of formic acid/acetic acid/water of 30/50/20 is superior in delignification of the triticale straw with limited degradation of the cellulose. This can be concluded from the relatively high viscosities for those pulps

Under those cooking conditions:

- the formic acid essentially plays the role of a proton donor. This has the effect of hydrolysing the lignins and hemicelluloses. The absence of this acid in the medium (Lam, 2000)

Table 1
Effects of the cooking time and the fa/aa/water ratio on the chemical characteristics of the pulp

| fa/aa/water (% v/v) | Time (h) | Yield (%) | Kappa | Pentosanes (%) | Viscosity ($cm^3/g$) | DPv |
|---|---|---|---|---|---|---|
| 20/60/20[a] | 2 | 54.1 | 63.2 | 19.4 | 1022 | 1540 |
| | 3 | 51.3 | 50.6 | 18.7 | 1087 | 1648 |
| | 4 | 51.1 | 45.9 | 16.7 | 1148 | 1750 |
| | 5 | 50.3 | 48.1 | 14.5 | 1100 | 1670 |
| 30/50/20 | 2 | 50.9 | 42.6 | 15.5 | 1167 | 1782 |
| | 3 | 48.5 | 33.8 | 14.3 | 1181 | 1806 |
| | 4 | 46.7 | 27.9 | 13.9 | 1160 | 1770 |
| | 5 | 43.8 | 30.1 | 10.6 | 1055 | 1595 |

[a] Values shown are the best of those adapted from the cooking of rice straw (Delmas and Avignon, 1997; Lam et al., 2000).

does not allow, with these temperature and pressure conditions, the delignification of the vegetable matter;

- the acetic acid serves as, in accordance with the observation of Young and Davis (1986), the solvent of the lignin and hemicellulose fragments;
- the water intervenes at the level of the dissociation of the organic acids. It also participates in the hydrolysis of the hemicelluloses.

It may also be seen from Table 1 that an increase in the cooking time from 2 to 4 h accelerates the destructuring of the vegetable matter, expressed by the progressive decrease in the yield, the Kappa index and the pentosanes content in the pulp. Beyond a cooking time of 4 h we observe:

- a decrease in the value of the viscosity limit index which shows a slight degradation of the cellulose when the cooking time is too long;
- an increase of the Kappa index of the pulps. In this respect, Shimada et al. (1997) showed that dissolved lignin fragments may aggregate in an organic acid medium. This was demonstrated by the precipitation of these macromolecules onto the cellulose fibres.

It was concluded that the following conditions:

| | |
|---|---|
| Ratio fa/aa/water: | 30/50/20 |
| Cooking time: | 3 h |
| Temperature of bath: | 107°C |
| Ratio L/M: | 12/1 |

were the optimal conditions for the production of paper pulp from triticale straw. In effect, they allow a pulp to be obtained that has a satisfactory Kappa index, a high viscosity and a suitable pentosanes content. The usefulness of this procedure was confirmed by the measurement of the mechanical characteristics of this pulp.

### 3.2. Mechanical characteristics of the pulp

Mechanical characteristics of the unbleached pulp are reported in Table 2. It may be seen from the results that the mechanical properties of the unbleached pulp are such that further bleaching procedures may be carried out.

Table 2
Mechanical characteristics of the triticale straw pulp prepared in a fa/aa/water medium

| Measured parameters | Obtained values |
|---|---|
| SR | 42 |
| Grammage (g/m$^2$) | 66.5 |
| Breaking length (m) | 7415 |
| Tear index (mN m$^2$/g) | 5.42 |
| Burst index (Kpa m$^2$/g) | 3.83 |

### 3.3. Bleaching of the pulp

The bleaching of the pulp was carried out in a sequence involving an organic peracid step and an ozone step. It was then treated with hydrogen peroxide in a basic medium (PaZEP). This sequence was chosen because of the acidic pH of the unbleached pulp. The use of either the organic peracids or the ozone does not require a sharp change in the pH of the medium. It has also been observed that the combination of the action of the peracids and the ozone in the bleaching sequence is more selective than that of using only the ozone (Lam, 2000).

The experimental results are reported in Table 3.

It may be seen from the table that the triticale straw pulp is very well bleached by the TCF: PaZEP sequence. After undergoing this sequence, the pulp exhibits a raised viscosity and a very satisfactory whiteness that is completely stable. It may therefore be used for the production of quality paper.

Table 3
Chemical and optical characteristics of the bleached triticale straw pulp

| Characteristics | Measured values |
|---|---|
| Yield (% of dry straw) | 42.5 |
| Silica content (% of dry pulp) | 4.7 |
| Silica yield (%) | 80.0 |
| Kappa | <1 |
| Viscosity (cm$^3$/g) | 856 |
| DPv | 1266 |
| Whiteness index (% photovolt) | 83.0 |
| Whiteness stability (%) | 95.6 |

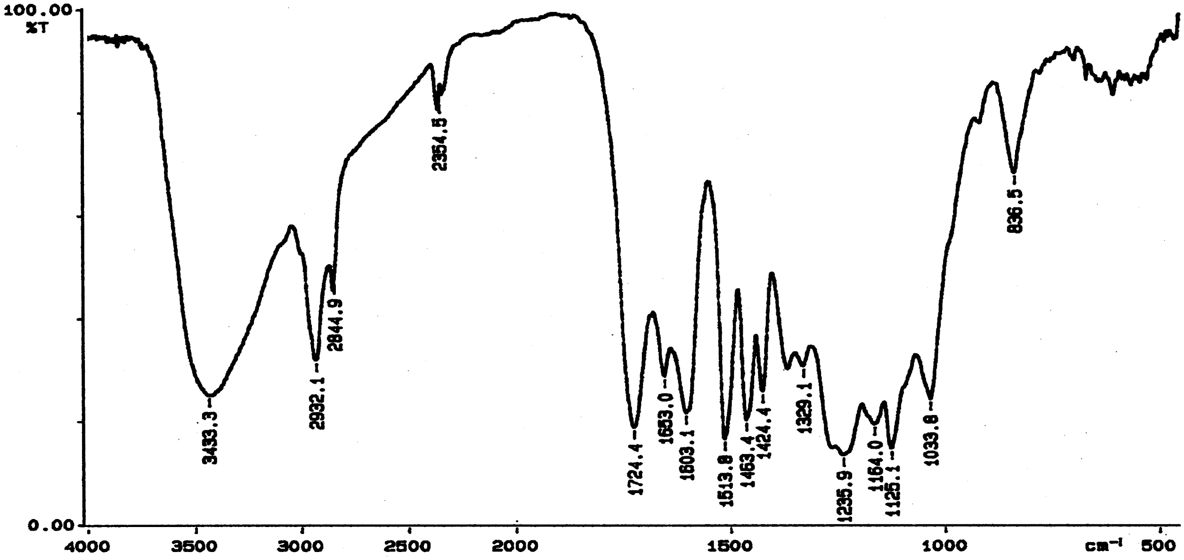

Fig. 1. Infrared spectrum of lignin extracted from the cooking of triticale straw in an organic acid medium.

It has also been observed that the silicon derivatives are retained for the most part in the pulp. Their presence in the cooking liquor is therefore weak and this low silicon content facilitates the recycling of the chemicals used during the course of the cooking and bleaching.

### *3.4. Characterisation of the lignin obtained from the fractioning of the triticale straw in a formic acid/acetic acid/water medium*

The infrared spectrum (Fig. 1) of the lignin extracted from the cooking of triticale straw in a fa/aa/water medium shows that they demonstrate the characteristic bands of gramineous lignins. These lignins are made up of three types of phenylpropane units: p-hydroxyphenylpropane (H), guaiacylpropane (G) and syringylpropane (S).

Thus, the absorption band at 836.5 cm$^{-1}$ is attributed to $\nu_{C-H}$ vibrations of the p-hydroxyphenylpropane (H) units, and the one at 1125 cm$^{-1}$ is characteristic of the G and S units. The band at 1164 cm$^{-1}$, characteristic of the three types of units H, G and S of the lignin, indicate the presence of carbonyl groups in a conjugated ester structure (Seisto and Poppius-Levlin, 1997). The band at 1033.8 cm$^{-1}$ is characteristic of non condensed guaiacyl nuclei (Baeza et al., 1990). The two bands at 1603.1 and 1513.8 cm$^{-1}$ correspond to $\nu_{C-C}$ vibrations of aromatic nuclei. The band at 1653 cm$^{-1}$ observed for the lignin of triticale straw is attributed to carbonyl grouping in the amide groups {–NH(C=O)} (Hortling et al., 1997) the presence of which is due to protein contaminants. The presence of nitrogen atoms is confirmed by the results of an elemental analysis of the lignin.

A strong absorption band around 1724.4 cm$^{-1}$ indicates the presence of carbonyl functional groups. The relatively strong intensity of this band is unexpected because the lignin in general contains very little of these groups. Its presence however is due to the esterification of certain alcohol and phenol functions of the lignin by the cooking agents (formic and/or acetic acid).

An examination of the proton spectrum of acetylated lignin confirms this by the presence of a singulet signal at 8 ppm which is attributed to the resonance of formiate protons H–C(=O)O–. This spectrum also shows the presence of signals that are attributed to:

- aromatic protons, guaiacyl (6.7–7.6 ppm) and syringyl (6.3–6.7 ppm);

- methoxy protons (3.5–4.0 ppm); and
- protons of phenol (2.0–2.5 ppm) and alcohol (1.8–2.0 ppm) acetyls.

The essential point which comes from the characterisation of triticale straw lignins is that the hydroxyl groups of these lignins have been partially esterified and that this reaction can alter their depolymerisation process (Hortling et al., 1991).

## 4. Conclusion

The cooking of tritical straw in a formic acid/acetic acid/water medium is very well suited for separating the principal chemical components. However, the parameters such as: L/M ratio, fa /aa/water ratio and the cooking time must be selected with care.

This method of cooking permits: (1) the production of unbleached pulp (cellulose fibres) which exhibits remarkable chemical and mechanical characteristics; (2) the elimination of difficulties linked to the solubility of the silicon derivatives in the cooking liquor; (3) the easy recycling of chemical used; and (4) the isolation of the lignin and hemicelluloses.

The unbleached pulp obtained in this manner may be bleached in a very satisfactory fashion using a series of steps involving organic peracids, ozone and hydrogen peroxide in a basic medium.

The bleaching by the TCF: PaZEP sequence permits, in comparison to the ECF: $OD_1EPD_2P$ (Pan et al., 1999), a simplification of the process. It also significantly reduces the consumption of water and NaOH solution during the course of the bleaching process.

In effect, this is a procedure which does not generate charged effluents but which produces bleached pulp that exhibits excellent chemical and optical characteristics.

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