A new non-wood pulping process for high silicon content raw materials. Application to rice straw

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SUMMARY

The cooking of rice straw is carried out at atmospheric pressure using a mixture of formic acid/acetic acid/water. The chemical and mechanical properties of the pulp obtained are similar to pulp obtained with a mixture of caustic soda/anthraquinone. The majority of the silica derivatives are retained in the pulp because of the acid cooking conditions. However the cooking chemicals are easily recyclable, because of the absence of mineral reagents, without the need for combustion of the black liquor.

Keywords
Formic acid, acetic acid, delignification, non-wood pulp, rice straw

Cereal straw is readily available but is only reluctantly used as a raw material in the pulp and paper industry because of processing problems experienced due to the high silicon content. During cooking the silicon compounds are largely transformed into soluble silicates, which transfer to the black liquor and cause major problems in the recovery circuit.

The production of non-wood pulp from cereal straw, of which the worldwide annual production is around 1 billion tonnes, should allow for the simultaneous use of a large part of the excess straw and supply potentially valuable raw material to meet the growing demand for paper.

Recently Pan et al. (*1*,*2*) showed interesting results using an acidic cooking method. This cooking method, in comparison with the more traditional methods, produced pulp with satisfactory mechanical properties as well as retention of a large part (75%) of the silica derivatives in the unbleached pulp. However, the presence of sulfuric acid in the black liquor complicates the recycling of the cooking chemicals.

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The cooking process used in this study is an extension of the study by Avignon and Delmas (*3*) of the treatment of rice straw with a mixture of formic acid/acetic acid/water (fa/aa/water) where rice straw delignification can occur at atmospheric pressure and the cooking chemicals can be recycled.

EXPERIMENTAL

Pulping raw material

The raw material used was rice straw from Vietnam (*O. Sativa*). This straw had a moisture content of 9% and chemical composition: 37.0% cellulose, 18.3% lignin, 22.0% pentosans, 14.6% ash and 7.0% silica (based on dry straw).

Cooking

Different rice straw cooking methods were carried out with a mixture of formic acid/acetic acid/water. Cooking was performed in a 1-L glass reactor at atmospheric pressure using 40 g o.d. samples. The rice straw was cut into 3 cm long pieces, soaked in the cooking liquor at 50°C for 30 min then heated to temperature (30 min) and held for the prescribed cooking time.

The pulp thus obtained was filtered, pressed and washed twice with a mixture of formic acid/acetic acid/water of the same composition as the cooking liquor, then with water. Finally, it was dried and analysed.

The acids used were recycled by simple distillation. Lignin was precipitated by adding water to the residue obtained after evaporation of the acids and collected by filtration, washed several times with distilled water and dried. The water-soluble sugars were obtained as syrup after concentration.

Analysis of pulp chemical and mechanical properties

The chemical and mechanical properties of the pulp were determined in accordance with the following methods: Kappa number (AFNOR NF T 12-018), viscosity (cm^3/g) (AFNOR NF T 12-005), mechanical properties (AFNOR NF Q 03-004, Q 03-053, Q 03-001), whiteness index (AFNOR NF T 12-030), ash and silicon content (Chinese Standard G.B 2677.3-81).

Chemical analysis of straw and unbleached pulp ashes was by scanning electron microscopy and X-ray diffraction.

RESULTS AND DISCUSSION

Different rice straw cooking methods were carried out with a mixture of formic acid/acetic acid/water to study the effect of:

- formic acid concentration,
- cooking time,
- liquor/dry straw ratio (L/M) and fa/aa/water ratio on the pulp characteristics.

Influence of formic acid concentration

Formic acid is a strong delignification agent but it also readily hydrolyses polysaccharides (*4*), thus its concentration was limited to between 0% and 30% of cooking liquor volume (Table 1).

Table 1 shows that under mild conditions of pressure and temperature acetic acid alone was not a good delignification agent. However, addition of protons (acid), as expected (*5*), greatly improved delignification.

Addition of formic acid improved both delignification rate and pentosan removal. Its selectivity was higher than that of sulfuric acid. At the same yield (~53%), pulp obtained with fa/aa/water had a lower Kappa and higher viscosity than pulp cooked with aa/sa/water.

The pulp viscosity reached a maximum at a cooking liquor composition of 20 to 30% formic acid producing pulp with:

- high unbleached pulp yield,
- good pentosan content and high viscosity, and
- acceptable Kappa number.

Moreover, when the formic acid concentration was near 20%, separating and recycling the acids was easier (*6*,*7*). For these reasons this concentration was used in subsequent experiments.

Effect of cooking time

Cooking time was varied between 1 to 4 hours to evaluate the effect on pulp quality.

Table 1.
Effect of formic acid concentration on pulp chemical characteristics.

Fa/aa/water ratio* (% v/v)	Yield (%)	Kappa No.	Pentosans (%)	Viscosity (cm^3/g)	DPv
0/80/20	87.0	–	–	–	–
10/70/20	57.8	59.0	25.3	762	1113
20/60/20	52.9	45.8	18.6	820	1206
30/50/20	47.5	34.6	15.1	817	1202
aa/sa/water**	53.6	56.0	20.7	758	1107

* Cooking conditions: temperature, 107°C; time, 2 h; L/M (liquor to straw) ratio, 12/1. Water included straw moisture content.
** Cooking with acetic acid/sulfuric acid/water. Cooking conditions: aa/water ratio, 80/20 (per cent by volume); temperature, 115°C; time, 2 h; L/M ratio, 12/1; sulfuric acid, 6% on o.d. straw.

Table 2.
Effect of L/M ratio and fa/aa/water ratio on pulp yield and Kappa number (results in brackets). Cooking conditions were: time, 3 h and temperature, 107°C.

Fa/aa/water ratio (% v/v/v)	L/M ratio			
	7/1	10/1	12/1	15/1
20/75/5	62.2 (60.5)	56.6 (57.8)	54.8 (52.4)	50.8 (46.2)
20/70/10	54.7 (50.9)	52.8 (45.4)	51.0 (43.8)	50.3 (40.8)
20/60/20	50.8 (44.3)	48.8 (41.9)	48.7 (39.8)	48.1 (36.6)
20/50/30	49.5 (45.9)	49.2 (42.5)	48.3 (43.0)	48.0 (37.9)
20/40/40	51.0 (53.9)	48.3 (46.7)	47.5 (44.8)	45.3 (40.5)

Table 3.
Effect of the L/M ratio on pulp chemical properties. Cooking conditions were: time, 3 h; temperature, 107°C; fa/aa/water, 20/60/20 (per cent by volume).

L/M ratio	Yield (%)	Kappa No.	Pentosans (%)	Viscosity (cm^3/g)	DPv
7/1	50.8	44.3	18.8	821	120
10/1	48.8	41.9	18.4	835	1231
12/1	48.7	39.8	17.4	840	1240
15/1	48.1	36.6	17.0	863	1277

Table 4.
Effect of fa/aa/water ratio on pulp chemical characteristics. Cooking conditions were: L/M ratio, 12/1; temperature, 107°C; time, 3 h.

Fa/aa/water ratio (% v/v/v)	Yield (%)	Kappa No.	Pentosans (%)	Viscosity (cm^3/g)	DPv
20/75/5	54.8	52.8	20.3	662	984
20/70/10	51.0	43.8	18.0	787	1153
20/60/20	48.7	39.8	17.4	840	1240
20/50/30	48.3	43.0	16.6	832	1227
20/40/40	47.5	44.8	16.3	803	1179

Figure 1 shows that increasing the cooking time reduced pulp yield, Kappa number and pulp pentosan content. Kappa number reduced little after 3 h, probably due to the competition between delignification and precipitation of dissolved lignins.

Pulp viscosity reached a maximum level after 3 hours and decreased slowly thereafter. Overall a cooking time of 3 h appears optimal.

Effect of the L/M ratio and fa/aa/water ratio on pulp quality

The main objective of these tests (Table 2) was to determine the 'best' L/M ratio for this cooking process and to study the role of water in cooking with fa/aa/water (formic acid was fixed at 20%).

Table 2 shows that whatever the fa/aa/water mixture, increasing the L/M ratio progressively reduced Kappa number and pulp yield. This effect of L/M ratio on rice straw delignification with fa/aa/water was because:

- a L/M ratio higher than the straw saturation L/M ratio is required to give homogeneous impregnation, and
- a high L/M ratio improves transport of straw hydrolysis products to the cooking liquor and the production of soluble hemicelluloses and lignins fragments. These results are in agreement with those obtained by Pan et al. (*1*) for rice straw cooking with aa/sa/water.

Pulp pentosan content decreased with an increase in L/M ratio (Table 3), whereas viscosity increased.

Cooking with a high L/M ratio would require higher energy consumption for recycling the acids, consequently increasing pulping costs. An L/M ratio of 10/1 to 12/1 would be suitable to perform rice straw cooking based on these laboratory tests.

Tables 2 and 4 show the effect of water content in the cooking mixture on pulp chemical properties as follows:

- At a water content of 20% (20/60/20) delignification increased at all L/M ratios (Table 2). Beyond this water content delignification decreased (i.e. Kappa number increased, see Table 4). Accurate control of water quantity is therefore important to obtain maximal delignification.
- Pulp pentosans content decreased progressively with increase of water content in the cooking mixture (Table 4).
- Viscosity reached a maximum level when cooking was performed with 20% water (20/60/20) (Table 4).

Based on these results, the 'best' experimental conditions to obtain good rice straw delignification are:

- cooking time: 3 hours,
- liquid/dry straw ratio: 12/1,
- fa/aa/water ratio: 20/60/20, and
- cooking temperature: 107°C.

Pulp mechanical properties

Table 5 shows the mechanical properties of pulps obtained under different cooking conditions.

Table 5 clearly shows that:

- Pulp mechanical properties obtained by fa/aa/water cooking are better than these obtained using the aa/sa/water process.
- Increasing water concentration in fa/aa/water cooking, at constant cooking time, reduced breaking length and slightly improved pulp tear and burst index.

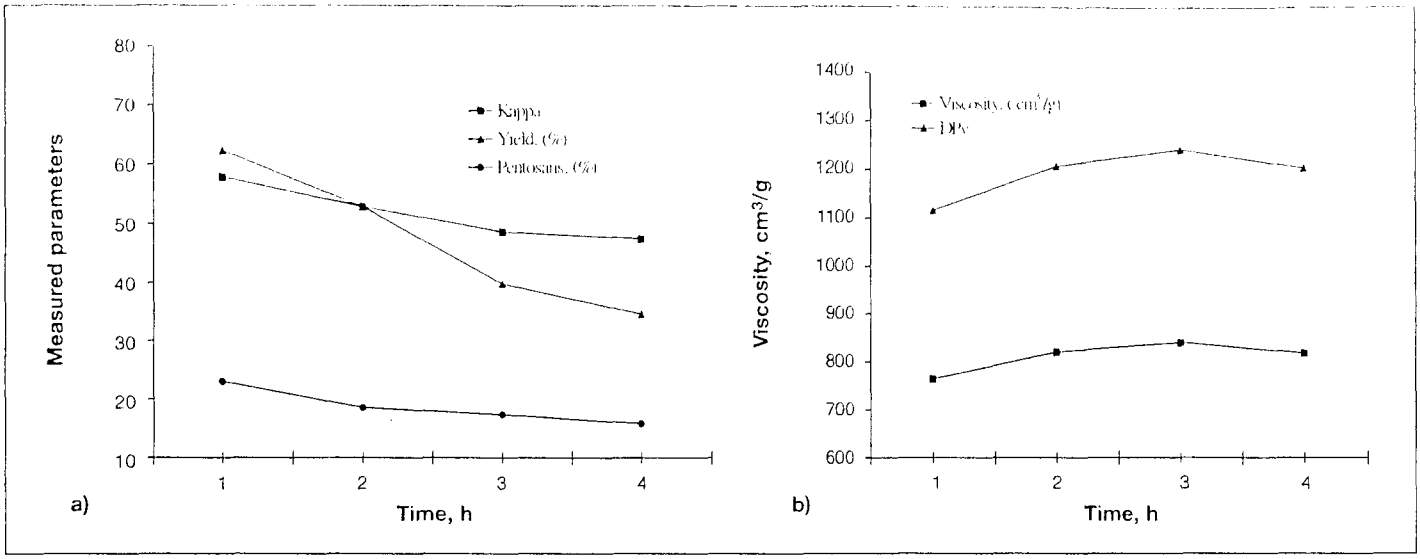

Fig. 1 Effect of cooking time on a) pulp yield, pentosan content and Kappa number, and b) the viscosity of rice straw pulp produced using the fa/aa/water process. Cooking conditions were: temperature, 107°C; L/M ratio, 12/1; fa/aa/water, 20/60/20 (per cent by volume).

- Increasing cooking time from 2 to 3 h, with fa/aa/water cooking at a ratio of 20/60/20, had the same effect as water concentration on pulp mechanical properties (breaking length decreased, and tear index and burst index increased slightly).
- Compared with soda-AQ pulping, the fa/aa/water process (20/60/20) gave higher breaking length but lower burst and tear values.

This lower burst and tearing resistance of pulp obtained using organic acid, compared with using caustic soda/anthraquinone, was presumably due to the esterification reaction between organic acid, cellulose and hemicellulose (2,5), equation 1:

$$R_1\text{–}CH_2OH + R_2\text{–}COOH \rightleftharpoons R_1\text{–}\underset{H}{\overset{H}{C}}\text{–}O\text{–}\overset{O}{C}\text{–}R_2 + H_2O \quad [1]$$

(R_1 = Polysaccharide, R_2 = H, CH_3)

The esterification of polysaccharide alcohol groups reduces pulp mechanical properties because it reduces the number of hydrogen bonds, which inhibits swelling and reduces fibrillation during refining. This process should be reversible such that pulp strength can be improved.

Table 5.
Effect of fa/aa/water cooking conditions on pulp mechanical properties.

Fa/aa/water* (% v/v/v)	Time (h)	Breaking length (m)	Tear index (mNm^2/g)	Burst index ($kPam^2/g$)
20/70/10	2	5530	4.00	2.18
20/60/20	2	5527	4.22	2.27
20/60/20	3	5314	4.38	2.52
20/50/30	2	5500	4.28	2.35
20/40/40	2	5320	4.32	2.40
aa/sa/water**	2	4542	3.15	2.00
NaOH/AQ	1	5028	5.10	3.20

* Cooking conditions for fa/aa/water: temperature, 107°C; L/M ratio, 12/1.
** Cooking conditions: aa/water, 80/20 (per cent by volume); temperature, 115°C; L/M ratio, 12/1; sulfuric acid concentration, 6% on o.d. straw.

Table 6.
Mechanical properties of pulp obtained using the fa/aa/water process followed by alkaline extraction.

Pulp property	Fa/aa/water pulp		NaOH-AQ pulp**
	Before treatment	After treatment*	
Grammage, (g/m^2)	66.3	65.8	66.0
Slowness, °SR	45	43	42
Breaking length, (m)	5314	5625	5028
Tear index, (mN m^2/g)	4.38	5.06	5.10
Burst index, (kPa m^2/g)	2.52	3.02	3.20

* NaOH concentration, 4% (by mass on o.d. pulp); L/M ratio, 20/1; temperature, 80°C; time, 2 h.
** Soda-AQ cooking conditions: soda concentration, 12% (by mass on o.d. straw); temperature, 160°C; L/M ratio, 6/1; time, 1 h.

Effect of alkaline extraction of unbleached pulp obtained using organic acid on their mechanical properties

Table 6 shows the effect of an alkaline treatment (caustic soda-water) on unbleached fa/aa/water pulp mechanical properties. Cooking conditions were: fa/aa/water, 20/60/20; time, 3 hours; temperature, 107°C; L/M ratio, 12/1.

The results given in Table 6 show alkaline extraction of fa/aa/water pulp improved their mechanical properties to a level comparable to those obtained using a caustic soda/anthraquinone mixture.

Distribution of silica derivatives during rice straw cooking in organic acid, and pulp ash content

Unbleached pulp and initial straw were analysed to study the silica derivatives behaviour during fa/aa/water cooking (Table 7).

Table 7 shows that:

- Silica derivatives were almost completely retained by the pulp (92.9%). They were almost inert during organic acid cooking and represented the major part of the pulp ash (6.5 g silica derivatives in 6.8 g pulp ash).
- The other inorganic compounds in the straw ash (53.4%) were made

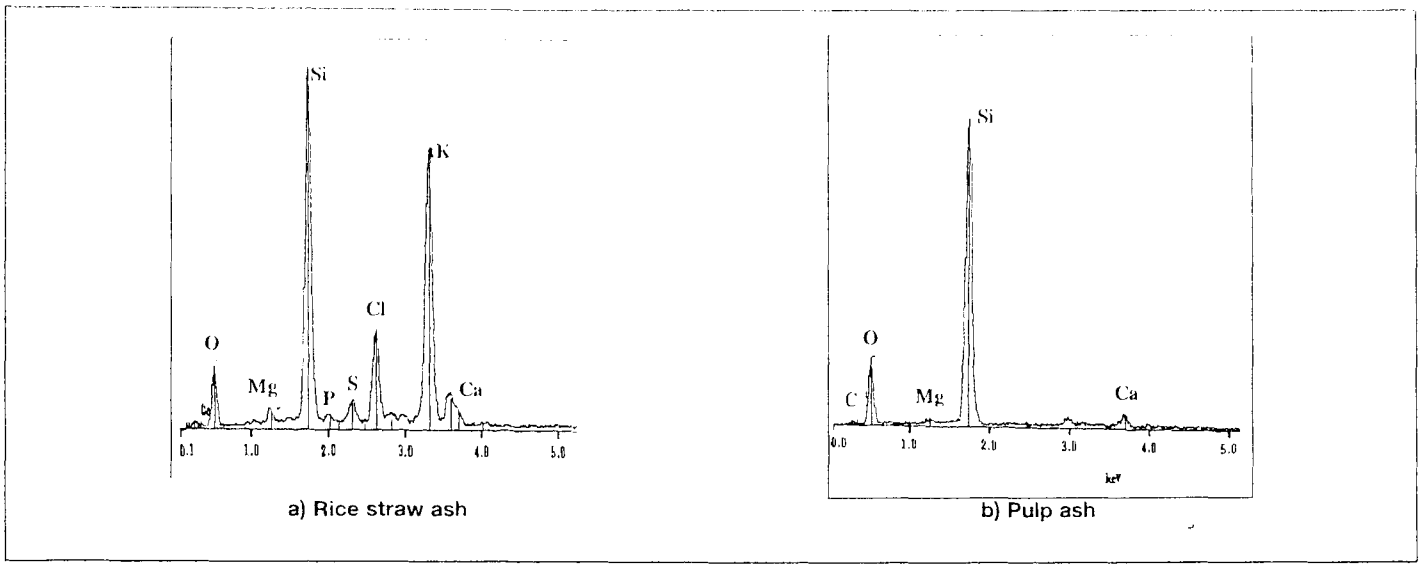

Fig. 2 Analysis of the chemicals present in rice straw and unbleached pulp ash using scanning electron microscopy and X-ray diffraction.

Table 7.
Straw and pulp silica and ash content.

Measured parameter	Straw	Pulp*
Dry matter, (g)	100	48.7
Ash weight, (g)	14.6	6.8
Ash yield, (%)	–	46.6
Silica weight, (g)	7.0	6.5
Silica derivatives retained by pulp, (%)	–	92.9

* Cooking conditions: time, 3 h; temperature, 107°C; fa/aa/water, 20/60/20 (per cent by volume); L/M ratio, 12/1.

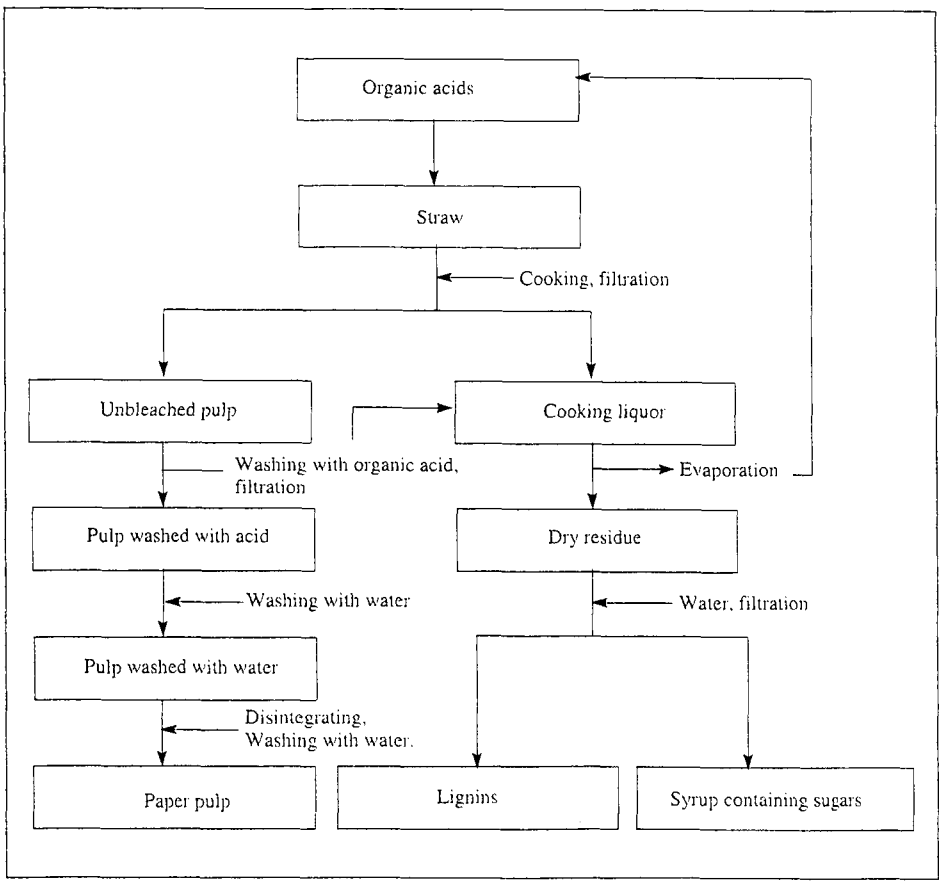

Fig. 3 Schematic diagram of the rice straw pulping process.

soluble during cooking and were removed in the spent cooking liquor. Figure 2 shows that the potassium, chlorine, sulfur, magnesium, etc. derivatives initially present in rice straw ash (Fig. 2a) were almost completely removed from the pulp (Fig. 2b).

- Low silica content in the spent pulping liquor should minimise problems in chemical recovery operations.

Description of the rice straw pulping process

The rice straw pulping process is shown schematically in Figure 3. Rice straw and an adequate fa/aa/water mixture are introduced into a reactor. After cooking at atmospheric pressure under conditions outlined above the liquid and solid phases are separated by filtration and treated independently.

The pulp is washed with an organic acid solution to extract lignin surrounding the cellulose fibres, then with water. The pulp is then treated with NaOH solution (4%) to improve its mechanical properties and to eliminate excess organic acid.

The spent cooking acid mixture is evaporated and the recovered acids distilled and recycled. Lignin is precipitated by adding water, filtered, washed several times with water and dried if necessary. The water-soluble sugar residue is concentrated by evaporation. The water recovered from unbleached pulp washing and sugar concentration contains organic acids and requires treatment before recycling.

The recovered lignin can be burnt to recover energy or sold for other uses. Similarly the sugar solution can be fermented or sold for other uses.

CONCLUSIONS

This new non-wood pulping process:

- Produces unbleached pulp with good chemical and mechanical properties, due to the very high selective separation of vegetable matter components (cellulose, hemicelluloses, lignin).
- Facilitates simple recovery of the cooking chemicals because of the absence of silica derivates in the black liquor.
- Requires only low water consumption.
- Has a low effluent emission with low inorganics concentrations.

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