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Formic acid pulping of rice straw

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Abstract

Rice straw pulping with formic acid was studied for different temperatures, cooking times and acid concentrations. Delignification percentage of approximately 85% with a pulp yield of 44.4% was obtained under relatively mild cooking conditions (temperature, 100°C; cooking time, 60 min; formic acid concentration, 90%). Pulp chemical and mechanical properties were comparable with those found for pulp obtained in basic environments. However, the advantage of this technique compared with cooking in basic environments is that most of the silicon derivatives remain in the pulp.

Keywords: Delignification; Formic acid; Paper-pulp; Rice straw

1. Introduction

Many cereal straws, particularly rice straw, have been used as raw materials for paper production. These raw materials were gradually replaced with wood products after World War II. However, straw is still a good source of raw material in areas where wood supplies are scarce.

The main reasons for the decreased use of straw in the paper industry are (Fineman et al., 1988; Kulkarni et al., 1989)

- using straw pulp in paper machines is harder than using wood pulp;
- the specific properties of the black liquors resulting from straw cooking in basic environments, makes them hard to use in industrial concentration/combustion/generation units.

These handicaps are primarily due to the presence of large amounts of pentosanes in the pulp and black liquors, which also contain silica. The need to add alkali to reduce or prevent silicate deposits or install a specific device to remove silica from the black liquors are factors currently limiting the use of rice or other cereal straws in paper mills, despite recent widespread progress in the field (Pedersen, 1989).

The development of new technologies for cereal straw pulping is the only solution to avoid the current industrial problems and to put to better use these generally undervalued agricultural resources.

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Table 1
Effect of different parameters on yield and kappa index (values in parentheses) of pulps obtained from rice straw in formic acid

Time (min)	Temperature (°C)	Acid concentration (% v/v)			
		70	80	90	98
30	90	69.8 (66.7)	56.9 (52.0)	46.2 (33.6)	46.9 (36.7)
	100	45.6 (54.3)	45.1 (38.0)	45.5 (29.5)	45.8 (29.5)
	110	44.7 (36.4)	43.7 (25.8)	41.4 (21.7)	40.2 (23.4)
	115	42.2 (27.9)	42.0 (24.4)	40.9 (17.6)	40.1 (19.9)
60	90	56.6 (50.6)	46.0 (37.4)	46.6 (31.9)	42.3 (34.3)
	100	46.6 (34.9)	46.4 (31.4)	44.4 (25.1)	41.2 (26.1)
	110	44.0 (34.0)	42.1 (23.6)	39.2 (19.6)	38.8 (19.6)
	115	42.3 (27.8)	38.5 (19.8)	38.2 (16.6)	40.2 (19.9)
90	90	49.6 (48.0)	46.7 (35.8)	42.0 (28.3)	41.8 (28.2)
	100	41.3 (36.3)	39.1 (25.8)	38.9 (23.4)	38.5 (23.3)
	110	40.0 (26.1)	38.3 (21.5)	36.0 (18.3)	38.8 (18.2)
	115	37.5 (20.8)	36.5 (17.6)	35.8 (16.3)	37.2 (17.5)
120	90	45.0 (46.8)	41.5 (32.0)	40.2 (19.3)	40.9 (20.5)
	100	40.5 (32.1)	37.2 (21.3)	39.3 (17.6)	39.9 (19.6)
	110	39.4 (21.6)	37.0 (18.5)	36.5 (15.2)	37.2 (17.6)
	115	33.0 (16.6)	32.1 (14.6)	34.2 (12.2)	37.0 (14.6)

In this article, we present processing techniques and pulp properties obtained through cooking rice straw with formic acid. This procedure makes it possible both to selectively separate the main chemical compounds of the plant material and to preserve most of the silicon derivatives in the cellulose fibers.

2. Material and methods

The raw material used was a rice straw from Vietnam (*Oryza sativa*). This straw has a water content of 9%. Its chemical composition is, 37.0% cellulose, 18.3% lignin, 22.0% pentosanes, 14.6% ash and 7.0% silica (based on dry straw).

Cooking was performed in a 1-l glass reactor at atmospheric pressure. Rice straw was cut into 0.3 cm long pieces then soaked in the cooking liquor at 50°C for 30 min. Heating took 20 min. The liquor/dry straw ratio (L/S) was 12/1. A 40 g of straw was used in each assay.

After soaking, cooking was performed under the conditions described for each assay.

The resulting pulp was filtered, pressed, washed twice in formic acid, then in hot water and finally again carefully in cold water (on a 200 mesh sieve), then dried and analyzed. The cooking liquor was evaporated to recycle the formic acid. Lignin was, then, precipitated by adding water, filtered, washed several times in water and dried. The water-soluble sugars were obtained as syrup.

Pulp was first refined in a Valley beater (°SR = 45), 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. Measurements of mechanical properties were performed using standard procedures.

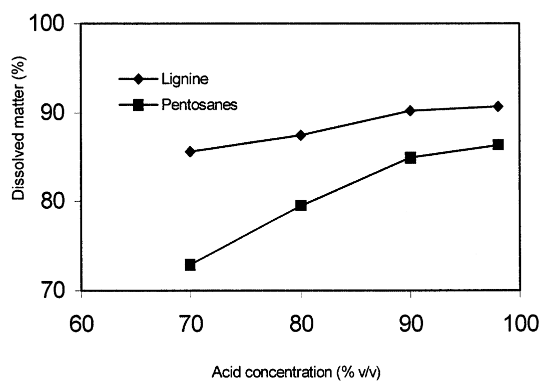

Fig. 1. Effect of formic acid concentration on dissolved matter concentration during rice straw cooking.

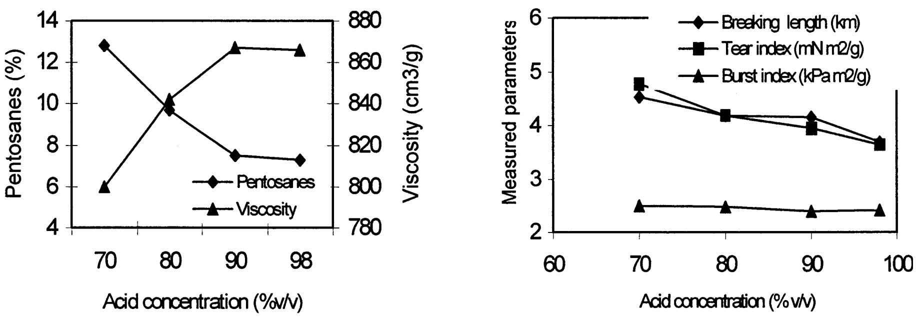

Fig. 2. Influence of acid concentration on pulp mechanical and chemical properties (cooking conditions: temperature, 100°C; time, 60 min).

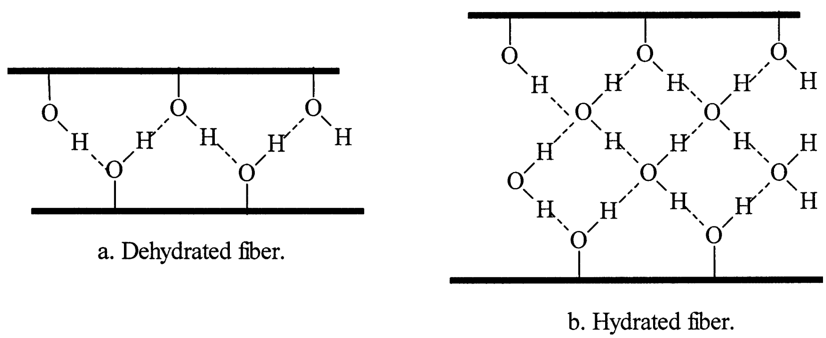

Fig. 3. Hydrogenous linkages between (a) dehydrated and (b) hydrated fibers (De Pascoal Neto, 1992).

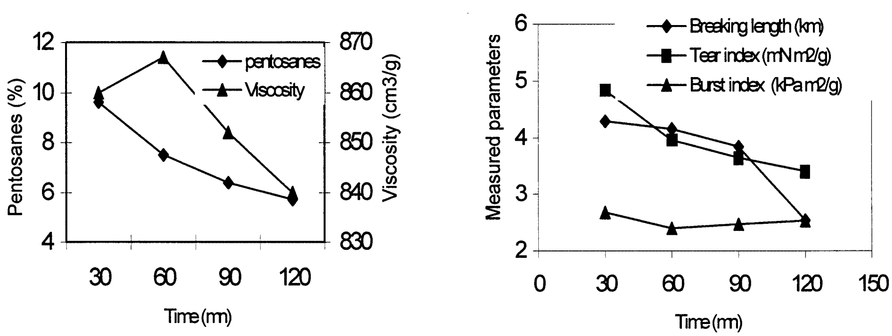

Fig. 4. Effect of cooking time on pulp chemical and mechanical properties (cooking conditions: temperature, 100°C; acid concentration, 90%).

Ash and silica percentages were obtained according to the Chinese standard GB 2677.3-81.

Unbleached pulps were first transformed into holocelluloses, using a sodium hypochlorite solution in a buffer (acetic acid and soda, pH 4.9), to measure viscosity. Holocelluloses viscosity was measured according to the NFT 12-005 standard.

Dissolved matter in the cooking solution was evaluated by calculating the difference between pulp and initial straw contents.

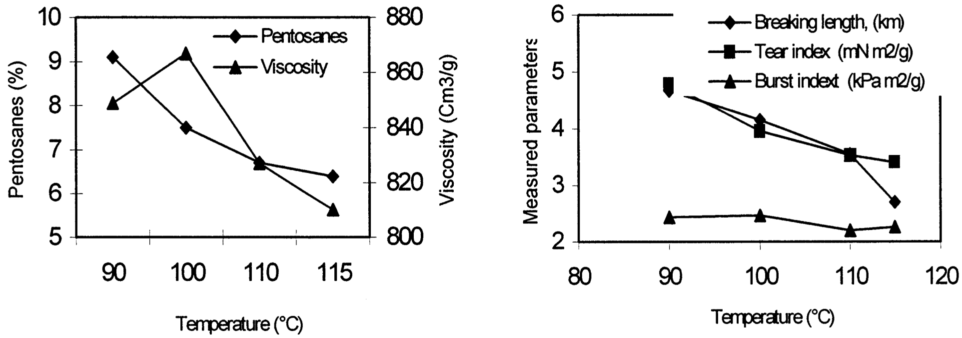

Fig. 5. Effect of cooking temperature on pulp chemical and mechanical properties (cooking conditions: acid concentration, 90%; time, 60 min).

Table 2
Acid and basic pulping characteristics

Medium	Yield (%)	Kappa number	Breaking length (m)	Tear index (mN m^2/g	Burst index (Kpa m^2/g
Acidic[a]	46.6	39.4	4524	4.78	2.49
Acidic[b]	44.4	25.1	3919	3.95	2.39
Basic[c]	59.4	12.1	3900	3.30	2.40

[a] Formic acid/water, 70/30 (% v/v); liquor dry matter ratio, 12/1; temperature (°C), 100; cooking time (min), 60.
[b] Formic acid/water, 90/10 (% v/v); liquor dry matter ratio, 12/1; temperature (°C), 100; cooking time (min), 60.
[c] NaOH (Patel et al., 1988), liquor/dry matter ratio, 6/1; temperature (°C), 140; cooking time (min), 90.

3. Results and discussion

3.1. Delignification

The effect of variables, such as temperature, acid concentration and cooking time on pulping and on the pulp's chemical and mechanical properties were studied (Table 1).

The results given in the table demonstrate that the delignification of rice straw can be successfully performed in formic acid. The kappa index values and pulp yields also progressed simultaneously. These values decreased, when the following increased.

- cooking time;
- oil bath temperature;
- acid concentration. The best values were obtained at a 90% acid concentration.

The formic acid concentration affects cooking quality as follows. Kappa index values indicate that rice straw pulping in formic acid reaches a

Table 3
Ash and silica distribution after cooking rice straw in formic acid[a]

Measured parameters	Straw	Pulp
Pulp yield (%)	100	44.4
Ash content (%)	14.6	16.4
Ash yield (%)	100	49.9
Silica content (% ratio to ash)	47.8	89.5
Silica yield (%)	100	93.4
Lignin alone		
Lignin content	18.3	15.2
Lignin yield (%)	100	83.1
Ash content (%)	–	3.0
Ash yield (%)	–	3.1
Water soluble substances		
Yield (%)		37.7
Ash content (%)	–	17.1
Ash yield (%)	–	44.2
Silica yield (%)	–	0.16

[a] Cooking conditions: acid concentration (%,v/v),90; cooking time (min), 60; temperature (°C), 100; liquor/dry matter ratio, 12/1).

maximum at a 90% acid concentration. A high acid concentration helps break down matter. This was further confirmed by the fact that the quantity of dissolved matter in formic acid (e.g. lignin and pentosanes) was higher during cooking at acid concentrations of 90%, than when cooking was performed at lower acid concentrations (Fig. 1).

These results differ from those obtained by Deineko and Kostyukevich (1989)during acetic acid pulping of wood. These authors found an optimal acetic acid concentration of 70% volume. This was due to the fact that the results obtained were naturally closely linked to experimental conditions, particularly acid and raw material structure used in cooking.

Cooking time affected pulping and pulp yields in the same way as cooking temperature. A lower cooking temperature required longer contact times to obtain good matter breakdown. For example, at 90% acid concentration, an increase of 30–120 min in cooking time at 90°C reduced the pulp kappa index by 14.3 U (from 33.6 to 19.3). The kappa index only decreased by 5.4 U, when cooking was performed at 115°C (from 17.6 to 12.2).

Temperature plays a vital role in rice straw cooking in formic acid. Increased cooking temperatures (from 90 to 115°C) always, considerably, sped up plant matter breakdown and, consequently, significantly reduced kappa index. Increasing cooking temperature also led to decreased pulp yield as complete pulping was achieved.

The severe effect temperature has on delignification and pulp yield during rice straw cooking in formic acid can be explained by the positive role of increased temperature on

- environment acidity (De Groote et al., 1993);
- availability of formic acid to active plant matter sites;
- reaction speeds leading to matter breakdown (primarily hemicellulose attack);
- lignin solubility in formic acid.

Temperature also has a stronger effect on pulp yield and kappa index, when cooking conditions are less efficient, particularly when cooking is performed at relatively low formic acid concentrations.

Table 1 illustrates that cooking temperature must be chosen carefully as

- too low a temperature means increased contact time;
- too high a temperature means reducing contact time to avoid carbohydrate degradation.

A 90% formic acid concentration was shown to be the most efficient.

3.2. Pulp chemical and mechanical properties

The chemical and mechanical properties of unbleached rice straw pulp obtained after cooking in formic acid were determined. Analytical results are shown in Fig. 2 and Figs. 4 and 5.

Increasing the formic acid concentration from 70 to 90% during cooking at 100°C for 60 min has the following effect on pulp chemistry (Fig. 2)

- a sharp reduction in pentosanes content;
- a gradual increase in viscosity.

These chemical characteristics remain constant, if the acid concentration is over 90%. This demonstrates that the cellulose macromolecules are not broken down, even when acid concentration is quite high. The selective separation of lignin, hemicelluloses and cellulose occurs, when acid concentration is high (the resulting pulp has high viscosity along with low pentosanes and lignin contents).

Pulp mechanical properties decrease, when formic acid concentration increases. These results can be surprising considering how stable cellulose is under these conditions. However, this phenomenon can be explained by the fact that the linkages between amorphous cellulose chains and water (H-bonds) are destroyed during cooking. When cooking is performed in highly concentrated formic acid, part of the formic acid molecules between the cellulose chains latch onto the water molecules during cooling, which produces direct H-bonds between cellulose macromolecule hydroxyl groups (Fig. 3a). Fibrous blocks are relatively uninflatable; the blocks are stiff, breakable, inflexible and easily cut during refining, as opposed to hydrated fibers (Fig. 3b).

Saake et al. (1995), as well as Seisto and Poppius-Levlin (1997a) proved that reducing pentosanes content was the main cause for the decrease in pulp mechanical properties, when pulp was obtained after cooking at extreme temperatures, cooking times and acid concentrations.

The mechanical properties of unbleached pulp obtained after cooking in 90–98% formic acid were lower than those found after cooking in 70% formic acid. These results are in agreement with those obtained later (Pan et al., 1998) during rice straw cooking in acetic acid, water and sulfuric acid.

The results shown in Fig. 4 demonstrate that increasing the cooking times gradually reduced pulp pentosanes content, while viscosity reached a maximum level (867 cm^3/g) after 60 min. Viscosity decreased beyond this threshold, indicating cellulose fiber breakdown. Break length and tear index of unbleached pulp decreased progressively along with increased cooking time, while the burst index remained relatively constant.

A similar reduction in pulp mechanical and chemical properties was observed, when temperature was increased (Fig. 5).

It should be noted that the chemical and mechanical properties of pulp obtained using formic acid were as good (Table 2) as those found in rice straw pulp obtained using alkali or alkaline/anthraquinone (Patel et al., 1988).

3.3. Ash and silica distribution in different fractions obtained after cooking

Ash and silicon contents were determined for each of the different fractions obtained, pulp, lignin water-soluble substances (Table 3).

These results indicate that

- ash content in pulp and water soluble substances was very high (16.4 and 17.1, respectively), while content in lignin was low (3.0%);
- silicon derivatives were the main components of rice straw ash and were primarily retained in pulp (93.4% compared with silicon derivative content in initial straw).

These results are very important, as they prove that cooking rice straw in formic acid helps retain most of the silicon derivatives in the pulp. This considerably simplifies cooking liquor treatment (Seisto and Poppius-Levlin, 1997b).

These results also demonstrate that the biomass recovery rate (pulp, lignin alone, water-soluble substances) during pulp making from rice straw using formic acid is very high (97.3%). Biomass loss is nearly null, but can occur when pulp is washed with water.

4. Conclusion

Rice straw pulping can be successfully performed in formic acid at atmospheric pressure.

The pulp obtained has

- a moderate degree of polymerization;
- a low lignin and pentosanes content;
- sufficient mechanical properties.

Temperature, acid concentration and contact time significantly affect pulping and hemicelluloses hydrolysis. Transforming pulp into paper requires mild conditions to maintain a reasonable pentosanes content in the pulp.

Most acid soluble substances dissolve during rice straw cooking in formic acid. Silicon derivatives remain primarily in pulp. Recycling formic acid can be achieved through simple distillation.

The numerous advantages of this procedure compared with using basic environment systems led us to focus on the following research directions

- localization of silicon derivatives in unbleached pulp and definition of their chemical structure;
- understanding the linkage types found between silicon derivatives, carbon and organic matter;
- examination of derivative behavior during refining and bleaching;
- characterization and utilization of lignins and sugars from the pulping processes.

The above themes are currently part of our research program. Results from our experiments will be presented shortly.

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