Formic acid/acetic acid pulping of banana stem (*Musa Cavendish*)

MARCELLE-ASTRID MIRE[*], BOUCHRA BENJELLOUN MLAYAH[*], MICHEL DELMAS[*†] AND RENE BRAVO[‡]

SUMMARY

The separation of lignin from lignocellulosic biomass by organic solvents can be considered as a very effective approach. In this study, the pulping process using formic acid/acetic acid/water to selectively separate cellulose, hemicellulose and lignin from banana stem at atmospheric pressure was optimised. Different pulping variables were studied, especially formic acid percentage, liquor-to-fibre ratio and pulping time. The pulps obtained had good physico-chemical characteristics, superior to those of kraft or sulfite banana pulp.

Keywords
Acetic acid, formic acid, pulping, banana stem, *Musa Cavendish*

Growing worldwide importance of the utilisation of various non-wood plant fibres, as an alternative to wood pulp, in the manufacture of pulp, paper and paperboard is now well established (*1*).

Many non-wood fibres, such as bamboo, jute, straw, rice, abaca and bagasse, are currently used in small commercial pulping operations (*2*). Other agricultural residues such as banana stem possess characteristics suitable for papermaking (*3,4*). Banana is one of the important fruit and vegetable crop plants and belongs to the genus Musa. Other well-known species are abaca (*Musa Textilis*) and other wild banana plants used as a source of fibres for the paper and cordage industries (*5,6*).

Musa Cavendish is extensively cultivated in French West Indies Islands for export. After harvesting the fruit, the plant is cut down and thrown away, mostly as waste.

Banana stem pulping has been the subject of conflicting reports that showed pulping agents like caustic soda, caustic soda and sodium sulfite, or calcium bisulfite don't produce an easily bleachable pulp 7.

Despite low lignin content, the delignification of banana stems appears difficult. However some authors think banana stem can give a high quality specialty fibre with high yield if the preparation of the material is adequate. Heikal et al. compared the kraft (*8*) and nitric acid (*9*) pulping of retted and unretted banana chips. They reported that pulping of retted samples gave pulps with better chemical and strength properties than that from unretted samples.

Fernandes (*10*) removed the gummy material by acid extraction before kraft pulping. Both the unbleached and bleached pulps (by CEH sequence) possessed satisfactory strength properties, suitable for writing and printing paper.

Our results (*11,12,13*) revealed that separation of lignin from lignocellulosic biomass by organic solvents can be considered now as a very effective approach. This paper presents a simple procedure for destructuring the banana stem at atmospheric pressure by the catalyst/solvent system: formic acid/acetic acid/water. The pulp obtained was bleached by a hydrogen peroxide sequence.

MATERIALS AND METHODS

Vegetable matter

The raw material used was banana stem from Martinique Island (*Musa Cavendish*). The freshly cut banana stem (92% moisture) was squeezed to remove the juice and cut into 3.0 cm lengths. Chips were air-dried to about 8% moisture. The chemical composition of a representative sample is shown in Table 1.

Pulping

Pulping was conducted using a 2-litre glass reaction vessel under mechanical shaking at atmospheric pressure. Each pulping trial was carried out on 50 g of banana stem. A mixture of formic acid/acetic acid/water was used as cooking liquor. The pulping consisted of two stages. The first one was on vegetable matter impregnation for 1 hour at 60°C; cooking at 105°C (temperature near the boiling point of formic acid/water azeotrope) was performed under the conditions described for each test. The resulting pulp was filtered, pressed, washed twice with acetic acid, once with hot water and once again with cold water. The pulp was processed in a defibrator to separate the fibres, and screened on 65 and 100 mesh sieves. The rejects were retained on 65 mesh sieves. The pulp was collected on the 100 mesh sieves, then dried and analysed.

Table 1
Chemical composition of banana stem.

	% (on dry material)
Cellulose	43.6
Lignin	11
Pentosans	14
Solubilities**:	
- Cold water	19
- Hot water	23
- 1% NaOH	48
- ethanol-toluene	14.5
Ash**	7.1

** In accordance with the TAPPI Tests Methods

Analysis of the chemical and mechanical characteristics of the pulp

Each pulp was characterised by the yield, Kappa number and viscosity limit index (cm^3/g).

The pulp was refined in a Lampen mill then transformed into handsheets using a Frank apparatus, according to AFNOR Standard NF Q50-0019-2 (Rapid-Köthen method).

The various chemical and the mechanical characteristics of the pulp were determined in accordance with the following methods: Kappa index: AFNOR NF T 12-018, viscosity limit index (cm^3/g): AFNOR NF T 12-005, mechanical characteristics: breaking length AFNOR NF Q 03-004, burst index: AFNOR NF Q 03-113, tear index: AFNOR NF Q 03-011, pulp slowness: AFNOR NF Q 50-003.

---

[*] Institut National Polytechnique,Ecole Nationale Supérieure des Ingenieurs en Arts Chimiques et Technologiques, Laboratoire de Catalyse, Chimie fine et Polymères, 118 Route de Narbonne, 31077 Toulouse Cedex 04, France.

[†] Corresponding author.

[‡] Université des Antilles et de la Guyane, Département scientique interfacultaire, Laboratoire COVACHIM,Campus de Schoelcher,97233 Martinique.

RESULTS AND DISCUSSION

Pulp delignification

Delignification of the chopped banana stem was varied according to independent parameters. The independent variables included the reaction time, cooking mixture formic acid/acetic acid/water ratio and the liquor-to-dry-matter ratio were studied separately. Each factor was studied in relation to pulp yield (%), residual lignin content (Kappa number) and viscosity (cm^3/g).

The pulping trials were carried out first with an impregnation stage of 1 hour at 60°C in fa/aa/water media. Various ratios were studied as shown in Table 2. For ratios of 30/50/20, 40/40/20 and 50/30/20, the resultant pulps presented high amounts of rejects (respectively 40, 20, and 12%) and a low delignification rate (high Kappa number: 54 to 40). However, increasing formic acid concentration in the medium improved the delignification rate. The Kappa number values and pulp yield improved simultaneously. When the formic acid concentration increased, the Kappa number of the pulp obtained decreased, the rejects rate decreased and the pulp yield increased. But despite the improved delignification obtained, the reject rate was still high. The impregnation stage is important because it allows uniform penetration and diffusion of the cooking liquor chemical.

The results given in Table 2 show that the delignification of banana stem can be improved. The rejects were reduced to zero when the impregnation liquor was based on formic acid. Acetic acid is a very good lignin solvent, it is assumed to promote the solvation of lignin fragments but at the same time, reduces swelling of the predominantly carbohydrate fibres (*14*).

An impregnation stage in a formic acid medium improved the delignification of the banana stem. When the impregnation liquor was made by means of formic acid (100%), the Kappa number decreased 10 units. However, the formic acid attacked cellulose and the increase of this acid in the medium leads to a decrease of pulp viscosity.

The effect of cooking time on the delignification and chemical properties of pulp are reported in Table 3. It seems that an increase in the cooking time from 4 to 6 h improved the destructuring of the vegetable matter when the cooking was made with fa/aa/water (30/50/20) media. A long cooking time reduced the Kappa number for 46 to 39. However, in the case of a fa/aa/water ratio of 50/30/20, a maximum delignification (Kappa= 30) was observed for 3 hours. For all reactions, the pulp yield and viscosity systematically decreased as the cooking time increased. The pulp pentosan content was gradually reduced by increasing the cooking time, while viscosity decreased when the formic acid concentration and the cooking time increased.

The cooking time has an important effect on pulp yield and chemical properties. When the formic acid amount in the media is low, a longer reaction time is required to obtain good matter breakdown. When the fa/aa/water ratio is 30/50/20, prolonged cooking reduced the pulp yield and improved the delignification; the pulp Kappa number was reduced from 46 to 39 when the cooking time increased from 4 to 6 hours. However, when the fa/aa/water

Table 2

Effect of the impregnation stage and the fa/aa/water ratio on the chemical characteristics of the unbleached pulp of banana stem chips.

Cooking liquor(FA/AA/W)	Impregnation liquor (FA/AA/W)	Yield (%)	Rejects (%)	Kappa	Viscosity (cm^3/g)
30/50/20	30/50/20	38	40	54	1099
	100/0/0	47	15	45	1090
40/40/20	40/40/20	47	20	50	1062
	50/50/0	44	<10	50	863
	60/0/40	50	-	46	850
	100/0/0	40	-	40	852
50/30/20	50/30/20	53	12	40	903
	65/0/35	38	-	38	828
	100/0/0	55	-	30	841
60/20/20	70/0/30	38	-	40	752
	100/0/0	30	-	40	757

Impregnation: 1 hour at 60°C, Cooking: 4 hours at 105°C.

Table 3

The effect of cooking time on crude pulp chemical properties.

fa/aa/water (%v/v)	Time (h)	Yield (%)	Kappa	Pentosans (%)	Viscosity (cm^3/g)
50/30/20	2	43	41	11.2	852
	3	41	30	10.9	836
	4	38	38	10.5	828
30/50/20	4	50	46	11	954
	5	48	41	10.4	960
	6	46	39	9.7	955

Table 4

Effect of water content in the cooking medium on the delignification and pentosans hydrolysis.

fa/aa/w (%)	Pulp yield	Kappa	Pentosans (%)	Viscosity (cm^3/g)
50/40/10	44	41	7.5	718
60/30/10	44	34	7.2	696
50/30/20	38	38	10.5	828
60/20/20	38	40	10	752
50/20/30	47	46	11.3	851

*Impregnation: 1 hour at 60°C in fa/water, cooking: 4 hours at 105°C.

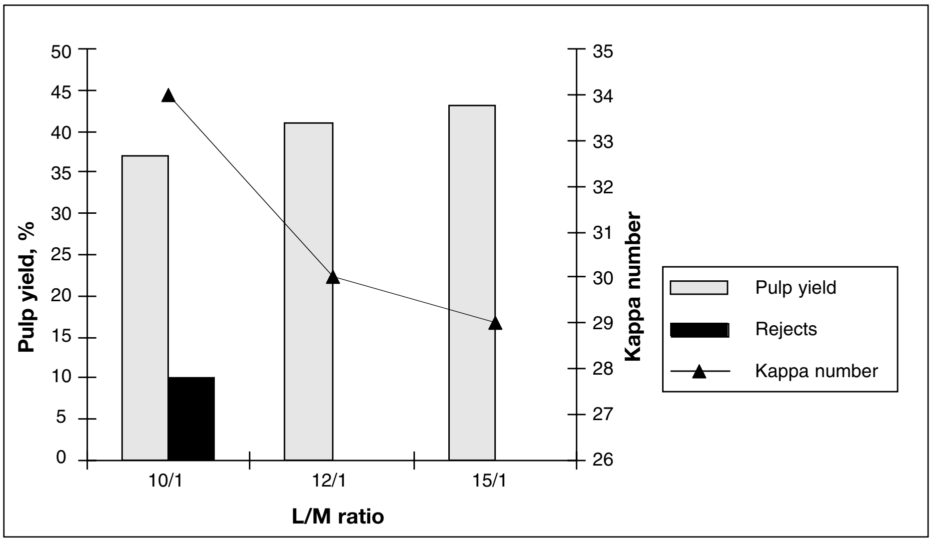

Fig. 1 Effect of L/M ratio on pulp yield and Kappa number.

ratio was 50/30/20, a maximum delignification was observed after 3 hours. Beyond 3 hours, the increase in Kappa number can be explained by the low lignin solubility in formic acid or the precipitation of the dissolved lignin fragments onto the cellulose fibres (*15*). The higher formic acid concentration sped up the delignification of the vegetable matter and the pentosan hydrolysis.

Because of the bulky nature of the banana stem, it is necessary to maintain the liquor/matter ratio for uniform chip impregnation and solubilisation of the dissolved matter (lignin and hydrolysed hemicelluloses fragments). So the higher cooking liquor content allowed improving simultaneously the pulping and the yield of the pulp. Figure 1 shows that an L/M ratio above 10/1 was required for cooking without rejects.

Impregnation: 1 hour at 60°C in 65/0/35 (%v/v); cooking: 50/30/20 (%v/v); 3 hours at 105°C.

Another parameter studied was the water content in the cooking medium. The water has an effect on organic acid dissociation. It also participates in the hydrolysis of the hemicelluloses, but it is a very bad solvent for lignin. Table 4 shows that the pulp obtained by banana stem cooking in fa/aa/water of 50/20/30 has a high Kappa number (Kappa=46).

All the pulps had a brown colour and rough texture.

According to the different results reported on Tables 2, 3 and 4, the banana stem pulp, which presented the best physico-chemical properties, was obtained with the following conditions:

Impregnation: 1 h in fa/water,
FA/AA/water ratio: 50/30/20,
L/M ratio: 15/1,
Cooking time: 3 h

Physico-chemical and mechanical characteristics of the pulp obtained by the organic acid process (Table 5) show that unbleached banana stem pulp had some mechanical properties similar to those generally observed in the pulp and paper industry for a softwood chemithermomechanical pulp (CTMP). The low porosity value and the high beating degree (pulp slowness = 81°SR, ~81 CSF) indicate that the crude pulp had a slow drainage rate. The breaking length and burst index of banana stem pulp were comparable to those of a CTMP softwood pulp. The drainage problem was probably due to the large amount of parenchymatous tissue present in this vegetable matter. The strength properties of the organic acid pulp obtained were compared with those of pulps obtained by the kraft and sulfite cooking of banana stems (*8*), with similar beating treatment. The results reported in Table 5 show that the strength properties of organic acid pulp are superior to those of the alkaline pulp obtained from the same species of banana (*8*), except for tearing resistance.

Table 5

Properties of crude pulp obtained by organic acid under optimal chemical conditions and alkaline (*8*) cooking of banana stem (*Musa Cavendish*).

Process	Af/aa/water*	Kraft	Sulfite
Kappa number (% lignin)	34.7 (5.55)	(10.5)	(10)
Viscosity, (cm^3/g)	836	-	-
Grammage (g/m^2)	59.7	60	60
Breaking length (m)	3889	2338	2067
Burst factor	78.2	24.6	24.4
Tear factor	12.4	43.9	29.5

Cooking condition: Af/aa/water: 50/30/20; L/M: 15/1; 3 hours at 105°C
Kraft: NaOH (4%); Na_2S (6%); L/M: 10/1; 15 min at 100°C
Sulfite: NaOH (4%); Na_2SO_3 (6%); L/M: 10/1; 15 min at 100°C

The strength properties depend on the pulp slowness (°SR 81). The beating and the tensile strength vary in the same direction. The pulp contains a fraction of much smaller material, called the fine fraction. Refining of the pulp increases the fines amount. A negative feature of fines is decreasing dewatering capacity of the pulp with increased amount of fines. The results show that the banana stem pulps studied have moderate strength. Beating increased the tensile strength of the pulp but also increased the drainage time very considerably.

CONCLUSIONS

Crude banana stem can be delignified by the formic acid / acetic acid system at low temperature (105°C). Cooking time varied with the acid proportion in the cooking medium. A high formic acid amount is important for effective delignification, but the acetic acid amount needs to be sufficient for good solubilisation of lignin fragments. The pulp obtained with the best conditions (fa/aa/w: 50/30/20 %v/v) possessed a low Kappa number and moderate strength properties; these characteristics are however superior to those of kraft and sulfite banana pulp.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from Conseil Général de la Martinique (French Caraibean Island) and the CIMV Company (Paris, France).

They also thank M. Bongrand, Papeteries de Gascogne (Mimizan, France) for the mechanical analysis of pulps.

REFERENCES

(*1*) Atchison, J.E. and McGovern, J. N. – History of paper and the importance of non-wood plant fibers, In Kocurek, M.J. (ed.) **Pulp and Paper Manufacture, Vol. 3**: Secondary fibers and non-wood pulping, TAPPI PRESS (1993).

(*2*) Hurter, A.M. – Utilization of annual plants agricultural residues for the production of pulp and paper, *Proc. TAPPI Pulping Conference*, p.139 (1988).

(*3*) Darkwa, N.A. – Pulping characteristics of plantain (*Musa Paradisiaca L.*) pseudostems, *Proc. International Non-wood Fiber Pulp and Paper Congress*, p.973 (1988).

(*4*) Escolano, J.O.V. and Ballon, C. H. – The pulping characteristics of some *Musa sp.* fibers other than Abaca (Musa Textilis nee.), *Proc. International Non-wood Fiber Pulp and Paper Congress*, p.197 (1988).

(*5*) Franco, P.T., et al. – Abaca pulp and paper industry in the Philippines, *Proc. TAPPI Pulping Conference*, p.133 (1981).

(*6*) Saikia, D.C., et al. – Wild banana plants (Musa species) as source of fiber for paper and cordage industries, *J. Sci. Ind. Res.* **56**(7):408 (1997).

(*7*) Kane, J.G. and Marathe, G.K. – Preparation of pulp from banana stalk, *Journal of the Indian Chemical Society, Industrial and News Edition* **12**:113 (1949).

(*8*) Heikal, S.O. and Fadl, M.H. - Mild pulping of banana stem, *Research and Industry* **22**(4):222 (1977).

(*9*) Heikal, S.O. – Nitric acid paper pulps from banana stems, Indian Pulp and Paper **31**(3):5 (1976).

(*10*) Fernandes, J.D.U., Meshramkar, P. M., Jaspal, N. S. and Didwania, H. P. – Pulping and papermaking of banana (*Musa Cavendish*) plant, *Nonwood Plant Fiber Pulping* **11**:73 (1981).

(*11*) Lam H.Q., Le Bigot, Y., Delmas, M. and Avignon, G. – 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, *Industrial Crops and Products* **14**:139 (2001).

(*12*) Lam, H.Q., Le Bigot, Y., Delmas, M. and Avignon, G. – Formic acid pulping of rice straw, *Industrial Crops and Products* 14:65 (2001).

(*13*) Lam, H.Q., Le Bigot, Y., Delmas, M. and Avignon, G. – Production of paper grade pulp from bagasse by a novel pulping process, *Appita J.* **57**(1):26 (2004).

(*14*) Young, R.A.D. – Organic acid pulping of wood. Part II: acetic acid pulping of aspen. *Holzforschung* **40**(2):99 (1986).

(*15*) Shimada, K., Hosoya, S. and Ikeda, T. – Condensation reactions of softwood lignin model compounds under organic acid cooking conditions, *J. Wood Chem. Technol* **17**(1-2):57 (1997).

Revised manuscript received for publication 8.9.04.