Formic Acid/Acetic Acid Pulping of Kash (*Saccharum Spontaneum*), Jute (*Chorcorus Capsularies*) and Dhaincha (*Sesbania Aculeata*)

M. Sarwar Jahan*, D. A. Nasima Chowdhury and M. Khalidul Islam

ABSTRACT

The cooking of kash (*Saccharum spontaneum*), jute (*chorcorus capsularies*) and dhaincha (*Sesbania aculeata*) was carried out at atmospheric pressure using a mixture of formic acid/ acetic acid/ water. Increasing formic acid concentration in the acid mixture improved the delignification rate. The unbleached pulp yield was higher than the conventional pulping process. In order to make easier and chlorine free bleaching, it was possible to improve the delignification in an efficient and selective manner by using peroxyacid in acidic organic medium. Low kappa number and high viscosity of pulp were obtained by treating formic acid/ acetic acid/ water pulp with peroxyacid. Alkaline peroxide bleaching gave pulp of above 80 % brightness. The acceptable strength properties were obtained. Bleaching improved the strength properties.

Keywords: Acetic acid, Formic acid, Pulping, Peroxy acid, *Saccharum spontaneum*, jute (*chorcorus capsularies*) and dhaincha (*Sesbania aculeata*)

INTRODUCTION

In order to achieve a complete and profitable utilization of lignocellulosic biomass, many efforts have been made all over the world to develop processes based on the utilization of organic solvents (1). Following the general idea of the "biomass fractionation" (2), these processes should improve the weak points of the kraft pulping technology, including: i) mitigation of the environmental impact, ii) generation of valuable by-products from hemicelluloses, iii) production of soluble, sulfur free lignin fragments useful for further processing, and iv) reduction of the investment needed for profitable operation.

Nonwood 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 and slow drainage of the resulting pulp. The silicon compounds are largely transformed into soluble silicates, which transfer to the black liquor and cause major problems in the recovery circuit during cooking. Recently, Pan and Sano (3) showed interesting results using acetic acid cooking methods, which produced pulp (cellulose) of acceptable mechanical properties as well as retention of a large part of silica derivatives in the unbleached pulp. However, the presence of sulfuric acid in the black liquor complicates the recycling of the cooking chemicals (4).

Pulp and Paper Research Division, BCSIR Laboratories, Dhaka, Dr. Qudrat-E-Khuda Road, Dhaka-1205, Bangladesh

Several approaches dealing with the fractionation in formic acid media have been reported, including operation in aqueous formic acid, acid catalyzed aqueous formic acid and formic acid peroxyformic acid (5-7).

The area of forestland in Bangladesh is only 10.2%. Therefore, it is hard to meet the raising fiber demand for paper and paper products from our forest resources. Alternatively, we have to consider nonwood for our pulp industry. In this article, we use kash (*Saccharum spontaneum*), jute (*chorcorus capsularies*) and dhaincha (*Sesbania aculeata*) as fibrous sources for pulping raw material.

A new procedure is presented in this article for delignifying nonwood. It uses a mixture of acetic acid/ formic acid/ water as the cooking liquor, and cooking is carried out at atmospheric pressure. Formic acid is used as proton supplier and acetic acid as lignin solvent.

EXPERIMENTAL

Materials

The nonwood used was jute, kash and dhaincha collected from Savar, Dhaka. The chemical compositions of kash (8) were 16.8% lignin, 24.0% pentosan, 42.8% l-cellulose and 75.4% hollocellulose, dhaincha stem had (9) 27.4% total lignin, 48.7% l-cellulose and 23.1% pentosan and jute fiber (10) were 66.0 % l-cellulose, 18.2 % hemicellulose and 13.7 % lignin.

Formic acid/ acetic acid/ water

The jute, dhaincha and kash were refluxed with formic acid/ acetic acid/ water mixture in a hotplate under the following different conditions:

- Formic acid/ acetic acid/ water ($FA/AA/H_2O$): 30/50/20, 40/40/20 and 50/30/20.

- Reaction time: 2, 3 and 4 h at boiling temperature.

- Liquor ratio 10.

After desired reaction time, pulp was filtered in a buckner funnel and washed with fresh formic acid/ acetic acid/ water followed by distilled water. Then the pulp yield was determined gravimetrically and kappa number (T 236 om 99) and viscosity (T230 om 99) was determined by Tappi Test Methods.

Peroxyformic acid treatment

FA/AA/water treated pulp was further delignified with peroxy acid at 80°C for 120 min. The reaction was carried out in a thermostatic water bath. The peroxy acid was prepared by adding 40/40/20 $FA/AA/H_2O$ acid mixture with 2% of H_2O_2 of o.d. jute, dhaincha and kash

Table 1. Effect of FA/AA/water ratios on the pulping of kash.

FA/AA/H_2O	Time, h	Pulp yield, %	Kappa number	Viscosity, m.Pa.s
30/50/20	2	61.9	75.0	18.7
30/50/20	3	59.3	64.9	16.1
30/50/20	4	58.5	64.0	15.3
40/40/20	2	59.2	58.8	18.8
40/40/20	3	56.6	58.1	17.7
40/40/20	4	56.2	57.2	17.3
50/30/20	2	54.2	55.2	18.5
50/30/20	3	53.9	53.5	17.4
50/30/20	4	53.5	52.4	16.9

Table 2. Effect of FA/AA/water ratios on the pulping of jute

FA/AA/H_2O	Time, h	Pulp yield, %	Kappa number	Viscosity, m.Pa.s
30/50/20	2	76.4	28.0	25.1
30/50/20	3	72.9	24.3	24.0
30/50/20	4	72.2	22.3	21.3
40/40/20	2	76.5	26.6	28.1
40/40/20	3	72.6	24.3	26.4
40/40/20	4	71.3	21.3	24.6
50/30/20	2	73.4	16.8	25.6
50/30/20	3	71.5	16.3	24.7
50/30/20	4	69.8	15.2	20.3

Table 3. Effect of FA/AA/water ratios on the pulping of dhaincha

FA/AA/H_2O	Time, h	Pulp yield, %	Kappa number	Viscosity, m.Pa.s
30/50/20	2	63.8	58.7	17.8
30/50/20	3	61.7	54.3	17.9
30/50/20	4	60.0	51.4	17.0
40/40/20	2	60.8	50.1	18.4
40/40/20	3	58.1	48.3	18.3
40/40/20	4	56.3	46.5	17.6
50/30/20	2	57.0	40.7	17.1
50/30/20	3	54.8	38.0	16.4
50/30/20	4	53.4	35.8	15.8

pulp. After completion of pulping, pulp was filtered off and washed with FA/AA/H_2O acid mixture, and finally with water. Then the pulp yield was determined gravimetrically and kappa number (T 236 om 99) and viscosity (T230 om 99) was determined by Tappi Test Methods.

Bleaching

Bleaching experiments were carried out with unbleached pulp (50g) at 10% pulp concentration. The pH was adjusted to 11 by adding NaOH. The hydrogen peroxide was 2 % on o.d pulp. The bleaching temperature was 80 °C for 1 h. Similar procedure was followed in the 2nd stage of peroxide bleaching.

Evaluation of formic acid pulp

FA/AA/H_2O pulp was beaten in a PFI mill to SR value of 40 and handsheets were prepared for tensile (T 494 om-96), tear (T 414 om-98) and burst (T 403 om-97). All properties were determined according to Tappi Standard Methods given in the parenthesis.

RESULTS AND DISCUSSION

Formic acid/ acetic acid/ water

Delignification of chopped dhaincha, jute and kash was varied with varying cooking parameters. The cooking variables included the cooking time and FA/AA/water ratio. Each factor was studied in relation to pulp yield (%), residual lignin (kappa number) and viscosity (mPa.s). The increase of formic acid proportion in the acid mixture decreased kappa number of all nonwood pulp at any period of cooking (Tables 1-3). Dhaincha and kash were not delignified sufficiently at any acid mixture. Pulping was not sufficient when the percentage of formic acid was limited to 20% in the acid mixture (data not shown). But jute was delignified to kappa number below 20 at 50% formic acid in the acid mixture. The pulp yield was exceptionally high especially in the case of jute fiber (>70%). The kappa number of kash pulp was decreased from 75.0 to 52.4 when cooking time and formic acid percentage increase from 2 h to 4 h and from 20 to 40% in the acid mixture respectively. In this condition yield was dropped from 61.9 to 53.5% and viscosity from 19.7 to 16.9 mPa.s. With similar increase of formic acid concentration in acid mixture and cooking time during dhaincha pulping decreased kappa number from 58.7 to 35.8. Earlier study (11) also showed that increasing formic acid concentration in the acid mixture improved delignification and decreased reject. It is clearly seen from Figures 1-3 that formic acid proportion in the acid mixture has a major effect on the delignification of all three types of nonwoods. We kept the water proportion constant (20%) in the acid mixture. A decrease in delignification was observed when water proportion in the acid mixture was very low. (12). A certain precise amount of water is therefore, necessary for optimal pulping. This is because of breakdown of plant matter in an organic acid environment, which favors the formation of solvated protons when water is added as follows:

$$RCOOH + H_2O \leftrightarrow RCOO^- + H_3O^+$$

In a concentrated organic acid solution, molecules are closely linked to each other by hydrogen bonds therefore, protons are not readily available. The addition of water is firstly used to break the links between the molecules of organic acid and then to favor the

Table 4. Effect of peroxy acid treatment and pre-alkaline extraction of kash jute and dhaincha pulp.

	Kappa number			Viscosity, mPa.s			Brightness, %		
	UB	Px	PE	UB	Px	PE	UB	Px	PE
Kash	58.1	27.8	29.9	17.7	17.4	16.2	24.5	38.1	36.6
Jute	24.3	18.1	19.8	26.4	25.1	24.7	34.5	48.6	48.0
Dhaincha	48.3	24.7	25.3	18.3	17.2	16.3	18.9	29.7	26.4

UB- Unbleached, Px-Peroxyacid, PE-Pre-alkaline extraction

Table 5. Strength properties bleached and unbleached pulp obtained from kash jute and dhaincha.

	Kash		Jute		Dhaincha	
	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
Tear index	8.9	9.3	9.1	8.3	5.4	5.6
Burst index	2.7	2.8	2.0	2.1	2.9	3.1
Breaking length, m	3587	3889	2514	2754	4977	5174
Brightness, %	24.5	83.1	34.5	85.2	18.9	80.3

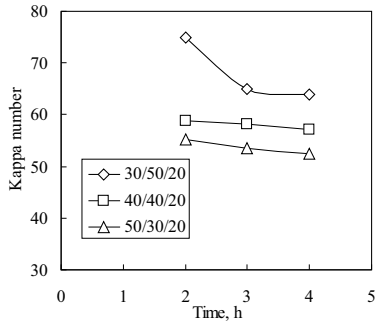

Fig. 1. Effect of acid mixture and cooking time on the delignification of kash

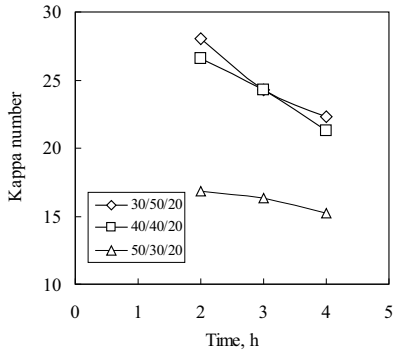

Fig. 2. Effect of acid mixture and cooking time on the delignification of jute.

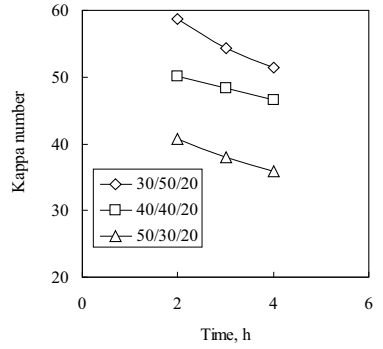

Fig. 3. Effect of acid mixture and cooking time on the delignification of dhaincha.

ionization and dissociation of these acids, which then supply the proton.

Peroxy acid treatment

Unbleached pulp obtained at the acid mixture of FA/AA/H_2O, 40/40/20 in 3 h of cooking was further delignified by peroxyacid or alkaline-extraction. Peroxyacid has proved an efficient delignifying agent for the unbleached pulp through the combined action of peroxyacid as oxidizing agent and acetic acid as solvent for the lignin. The peroxyacid delignified (reduction of kappa number) kash pulp by 52 %, jute pulp by 26 % and dhaincha by 49 %. The higher initial kappa number of kash pulp was the reason of higher delignification during peroxyacid treatment. But alkaline extraction, delignified at a lower rate than the peroxyacid treatment (Table 4). The brightness of kash pulp was improved by 13.6 % on peroxyacid and 12.1 % on alkaline extraction treatment, and 14.1 and 13.5 % and 10.8 and 7.5 % for jute and dhaincha pulp respectively. The viscosity dropped was marginal.

Physical properties

The papermaking properties of unbleached and bleached pulp were determined after beating in a PFI mill for 1000 revolution and shown in Table 5. Only 1000 PFI revolution increased the SR value to above 40. Similar result was reported elsewhere (13). The results show that bleaching of pulp improved physical properties. This can be explained by a better hydration of pulp during bleaching. Then fibrillation can take place more easily during beating. Dhaincha pulp showed better breaking length and burst index as compared to kash and jute pulp. All strength properties were inferior to conventional soda-AQ or kraft pulp (8, 14). The reason may be due to the damage of fibers during acidic pulping. Similar result was found in acetic acid pulping of wheat straw (3). Acetic acid is a very good solvent. It is assumed to promote the solvation of lignin fragments but at the same time, reduces swelling of the predominantly carbohydrate fibers (15), which may also be the cause of lower strength properties. Ash rich epidermal cells remaining in formic acid pulp can be considered as another reason of lower strength. These non-fiber cells were short and stiff. They have no contribution to the strength of the pulp, instead of obstructing bonding between fibers. The two stage alkaline peroxide bleaching responded very well. The final brightness of kash, jute and dhaincha was reached to 83.1, 85.2 and 80.3 %, respectively.

CONCLUSIONS

The following conclusions may be drawn from the results:

- The delignification was increased with increasing formic acid concentration in the FA/AA/water mixture or cooking time. The pulp yield was exceptionally high. The kash and dhaincha did not produce pulp of lower kappa number.

- The peroxyacid treatment of kash, jute and dhaincha pulp at 80 °C for 120 min reduced kappa number by 52, 26, and 49 % respectively. The pre alkaline extraction also reduced kappa number significantly. The brightness of peroxyacid treated or alkaline extracted pulp was improved for all three types of nonwoods.

- The alkaline peroxide bleaching of FA/AA/water kash, jute and dhaincha pulp reached the final brightness to above 80%. The bleached pulp had better strength properties than unbleached pulp. Acceptable strength properties were obtained for kash and dhaincha pulp, but jute fiber was detoriarated

tremendously during acidic pulping conditions.

REFERENCES

1. Johansson A., Altonen O., Ylinen P. *Biomass* 1987, 13: 45-65.

2. Myerly R.C., Nocholson M.D., Katzen R., Taylor J.M. The forestry refinery. *Chemical Technology* 1981, 11:186-92.

3. Pan, X., Sano, Y. *Bioresource Technology* 2005, 96: 1256-1263.

4. Muurinen, E. Organosolv pulping- A review and distillation study related to peroxyacid pulping. Ph.D dissertation 2000, Oulu University, Oulu, Finland.

5. Cordeiro, N., Belgacem, M.N., Tores, I.C., Moura, J.C. V.P. *Industrial Crops and Products* 2004,19 (2): 147-154.

6. Seisto, A., Poppius L. *Tappi J.* 1997, 80(9):215-221.

7. Jahan, M.S. Lee, Z.Z. and Y. Jin. *Cellulocse Chem. Technol* 2005, 39(1-2): 85-94.

8. Jahan, M.S. Moynul Hasan, A.J.M. Islam, M.K. and Nasima Chowdhury, D.A., *TAPPSA J.* May, 2002 p 21.

9. Jahan, M. S. Mun, S. P. and Rashid, M. *Ktappi J.* 2004, 36(5): 29.

10. Anon 1988. Task force report, a study on the utilization of jute cutting/ lower grade jute for papermaking. Ministry of jute, Govt. of the People's Republic of Bangladesh, Dhaka 132pp.

11. Mire, M. Mlayah, B.B. Delmas, M. Bravo, R. *Appita J.* 2005, 58(5): 393-396.

12. Lam H. Q., Bigot Y.L. Delmas, M. and Avignon G. *Appita J.* 2004, 57(1): 26-30.

13. Shatalov A.A. Pereira H. Arundo Donax L Reed: New perspectives for pulping and bleaching- organosolv delignification. Solution! for people, Process and Papers 2001, 84(11) Also available in www.tappi.org

14. Jahan, M.S. Evaluation of additive in soda pulping of jute. August, 2001, *Tappi* Also available in www.tappi.org

15. Young, R.A.D. *Holzforschung* 1986, 40 (2): 99.