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Organic Acid Pulping of Rice Straw. I: Cooking

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Abstract: Acetic acid or formic acid treatment of rice straw with the variation of reaction variables, namely acid concentration, catalyst (HCl or H_2SO_4) concentration, reaction time, temperature and liquor ratio, was investigated to ascertain effects on the dissolution of hemicellulose, which facilitates the dissolution of lignin during alkaline extraction or peroxyacid treatment and improved the drainability of straw pulp. Maximum pentosan dissolution was observed in 80% acetic acid with 0.6% H_2SO_4 catalyst at 80 °C for 120 min. Acetic acid dissolved pentosan more slowly than formic acid. The catalytic activity of H_2SO_4 was higher than that of HCl with respect to pentosan dissolution from rice straw. The optimum pulp yields with the lowest kappa number and the highest pulp yield with the optimum kappa number were obtained with formic acid/peroxyformic acid and acetic acid/peroxyacetic acid pulping, respectively. Acetic or formic acid treated pulp did not produce a lower kappa number in alkaline extraction. Acetic acid/peroxyacetic acid pulping produces better pulp from rice straw.

Key Words: Rice straw, formic acid pulping, acetic acid pulping, peroxy acid, alkaline extraction, pentosan

Introduction

The main aim of any pulping procedure consists of a selective extraction of lignin from lignocellulosics like wood and nonwood materials without degradation of cellulose. The principle drawback of any conventional pulping process of lignocellulosics is that it is not possible to separate lignin and hemicelluloses without alteration of their chemical structure. Therefore, the by-products are unable to be utilized as the raw material of chemicals. They are used as process fuels with low heat value added for the recovery of pulping reagents in alkaline pulping processes, and in general are discarded together with waste liquors in the sulfite process, causing severe environmental problems. Therefore, the demand for environmentally sound chemical pulping industries has increased interest in alternative pulping processes. During the last few years many attempts have been made to develop organosolv processes based on the application of alcohol (Lora and Aziz, 1985; Lonnberg et al., 1987) and organic acid (Young and Davis, 1986; Parajo et al., 1993). The main objectives of these processes were the reduction of sulfur emission as well as the total utilization of lignocellulosics.

Wood could not be delignified with aqueous acetic acid at 107 °C but the addition of 1%-2% HCl made it possible (Schutz and Knackstedt, 1942). Aqueous acetic acid could delignify aspen and spruce in 30-60 min at 175-220 °C. Stronger conditions were needed for softwood (Young et al., 1985). Davis (1987) reported that acetic acid pulping trials gave the lowest kappa number (10-16), highest pulp yield and best strength properties when cooking at high temperature for less than 60 min using high acetic acid concentration (87.7%). The best pulp had excellent tensile strength, marginal burst strength and a low tear index as compared to kraft pulp.

Beech and poplar pulping with aqueous acetic acid at 155 °C for 4 h produced a pulp yield of 50.0% and 48.3%, respectively, and the strength properties of the 2 pulps were better than those of the corresponding sulfite pulps. When the spent pulping liquor was reused for pulping with the addition of 33% fresh acetic acid, no significant change in pulp properties were observed over the 10 pulping cycles (Simkhovich et al., 1987). Sano et al. (1990) reported that birch could be pulped in aqueous acetic acid with H_2SO_4 at atmospheric pressure; the pulp

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yield was 51%-54% with significant delignification. Beech wood pulping in HCl-catalyzed aqueous solution of acetic acid produced a pulp yield of 45.8% to 50.0% (Vila et al., 2000). The pulp compositions were 5.8% to 7.5% Klason lignin (kappa number 25 to 33), 77.2% to 81.4% cellulose and 3.3% to 6.1% xylan with good viscosity (723 to 814 ml g-1). Nimz et al. (1993) showed that the addition of 10% formic acid to the aqueous acetic acid reduced the kappa number from 15.6 to 3.6, while the yield was reduced by 2.2%. At the same time DP value was increased.

Both softwoods and hardwoods produced pulps with low kappa numbers in high yields by peroxyformic or peroxyacetic acid (Poppius et al., 1986). Single stage peroxyacid required a high percentage of hydrogen peroxide (30%-60% on wood) for a high degree of delignification. Hydrogen peroxide was reduced with the introduction of 2- to 3-stage peroxyacid pulping (Poppius et al., 1987).

Traditionally nonwood raw materials are cooked using alkaline processes. The pulp yield and properties are good but the main drawback is the dissolution of silica in the black liquor, which causes problems during recovery of the cooking reagents. However, in solvent pulping, the major portion of silica remains on the fiber (Lora et al., 1995; Seisto and Poppius, 1997).

Rice straw will be one of the most important raw materials in the future for the pulp and paper industry in Asian countries. The major problem in rice straw pulping is silica, which inhibits the recovery of black liquor in alkali pulping processes. Another drawback of rice straw is the high amounts of hemicelluloses, which cause drainage problems.

The objective of the present investigation was to study rice straw pulping by acetic or formic acid with HCl or H_2SO_4 catalyst at temperatures below 100 °C in the first stage followed by alkaline extraction or peroxy acid treatment in the second stage.

Experimental

Acetic acid (AA) or formic acid (FA) treatment

The first stage involved treating rice straw with acetic acid in a polyethylene bag under the following conditions:

- Acetic acid concentration: 50%, 60%, 70%, 80% and 90% (w/v)

- Catalyst (H_2SO_4 or HCl) concentration: 0.3%, 0.6%, 0.9%, 1.2% and 1.5% (v/v)

- Temperature 60, 70, 80 and 90 °C

- Reaction time: 60, 90, 120, 150 and 180 min

- Liquor to straw ratio: 5/1, 10/1 and 15/1

The reaction was carried out in a thermostatic water bath. Another set of experiments was performed using formic acid instead of acetic acid and the other by HCl instead of H_2SO_4 as catalyst.

After completion of the pulping, the pulp obtained was filtered off and washed with the fresh corresponding organic acid without mineral acid, and finally with water. Pulp yield was determined on the basis of oven dried (o.d.) raw materials. Kappa number (T236 om 85), pentosan (T223 cm 84), Klason lignin (T222 om-98) and ash (T211 om 93) in rice straw and pulp were determined according to Tappi standard methods.

Alkaline extraction (AE)

Acetic acid pulp had better properties prepared by 80% CH_3COOH with 0.6% H_2SO_4 at 80 °C for 120 min extracted with 4%-12% NaOH for a fixed time.

- Alkali concentration: 4%, 6%, 8%, 10% and 12% of pulp

- Temperature: 70, 80 and 90 °C

- Time: 120, 150 and 180 min

- Consistency: 10%

After alkali extraction the pH of the filtrate separated from the pulp was measured. The pulp was washed with water, and then subjected to the determination of yield, kappa number and pentosan content.

Peroxy acid treatment

Acetic or formic acid pulp was further delignified with peroxyformic (PFA) and peroxyacetic acid (PAA) at 80 °C for 120 min. The H_2O_2 was 3%, 5% and 7% of o.d. rice straw pulp. One set of experiments was carried out under the same conditions without washing after the acetic or formic acid treatment. Fresh formic or acetic acid and H_2O_2 was added to the pulp after removal of liquors.

Physical properties

AA/PAA, FA/PFA, AA/AE and FA/AE pulps were beaten in a PFI mill to about 40°SR and handsheets were made for determine tear index (T414 om-98), tensile index (T404 cm-92), burst index (T403 om-97) and folding endurance (T511 om-96).

Results and Discussion

In this investigation low temperature (below 100 °C) acid treatment was used to dissolve hemicellulose in order to increase lignin dissolution in the subsequent delignification stage.

Acetic acid treatment (AA)

The results obtained from the acetic acid treatment of rice straw under different conditions are shown in Table 1. The yield, kappa number, pentosan yield and Klason lignin of pulp decreased with increasing acetic acid concentration. The pentosan content was greatly decreased from 13.1% to 7.1% with the increase in acetic acid concentration from 70% to 80% (trial no. 3 and 4). When acid concentration increased from 80% to 90% dissolution of pentosan did not increase significantly.

The effects of catalyst (H_2SO_4) concentration on pulp yield, kappa number, pentosan yield and Klason lignin are also given in Table 1. The pulp yield, kappa number, pentosan yield and Klason lignin decreased rapidly with increasing H_2SO_4 concentration. The pentosan yield decreased from 15.1% to 7.1% with the increase in H_2SO_4 from 0.3% to 0.6% (trial no. 4 and 6). Parajo et al. (1993) observed similar results during pine fractionation with catalyzed acetic acid. Pan and Sano (2005) showed that 60% of wheat straw xylose was removed during acetic acid pulping in the presence of H_2SO_4 catalyst.

Pulp yield, kappa number and Klason lignin were decreased through the entire range of reaction time as shown in Table 1. However, pentosan yield decreased with the increase in reaction time up to 150 min (trial no. 11). With the increase in liquor ratio pulp yield, kappa

Table 1. Effect of process variables on the acetolysis of rice straw (RS).

Run No.	Acetic acid conc.%	H_2SO_4 /HCl conc. %	Time min	Liquor to straw ratio	Temp °C	Pulp yield, %	Pentosan yield, % on RS	Kappa number	Klason lignin, %
1	50	0.6	120	10	80	71.0 ± 3.3	14.0 ± 1.0	40.7 ± 2.0	12.8 ± 0.9
2	60	0.6	120	10	80	67.9 ± 3.1	12.8 ± 1.0	38.3 ± 1.9	12.4 ± 1.0
3	70	0.6	120	10	80	67.7 ± 3.2	13.1 ± 0.9	38.0 ± 2.0	12.3 ± 0.8
4	80	0.6	120	10	80	59.4 ± 3.0	7.1 ± 1.0	37.0 ± 1.8	11.9 ± 0.8
5	90	0.6	120	10	80	55.3 ± 2.6	6.9 ± 0.7	35.4 ± 1.7	11.0 ± 0.7
6	80	0.3	120	10	80	74.4 ± 3.5	15.1 ± 1.2	46.2 ± 1.9	14.2 ± 0.9
7	80	0.9	120	10	80	51.5 ± 2.5	7.0 ± 1.0	34.1 ± 1.7	10.6 ± 0.7
8	80	1.2	120	10	80	48.2 ± 2.3	6.0 ± 0.5	34.0 ± 1.8	10.2 ± 0.7
9	80	0.6	60	10	80	62.5 ± 2.8	9.0 ± 0.9	43.1 ± 2.0	13.5 ± 1.1
10	80	0.6	90	10	80	61.8 ± 2.8	7.8 ± 0.8	41.9 ± 2.0	12.7 ± 0.9
11	80	0.6	150	10	80	55.6 ± 2.1	6.8 ± 0.7	36.7 ± 1.7	10.5 ± 0.7
12	80	0.6	180	10	80	53.6 ± 2.2	8.4 ± 0.9	32.8 ± 1.8	9.5 ± 0.6
13	80	0.6	120	5	80	69.0 ± 2.7	12.5 ± 1.1	45.8 ± 2.1	13.6 ± 1.1
14	80	0.6	120	15	80	58.9 ± 2.3	7.0 ± 0.7	36.3 ± 1.7	10.6 ± 1.0
15	80	0.6	120	10	60	87.7 ± 3.6	17.8 ± 1.3	58.1 ± 2.1	16.0 ± 1.2
16	80	0.6	120	10	70	77.4 ± 3.8	16.2 ± 1.3	47.2 ± 2.0	14.0 ± 1.1
17	80	0.6	120	10	90	57.9 ± 3.1	7.2 ± 0.8	36.9 ± 1.7	9.8 ± 0.8
18	80	0.3*	120	10	80	84.7 ± 3.8	15.6 ± 1.3	54.9 ± 2.2	15.1 ± 1.2
19	80	0.6*	120	10	80	67.8 ± 3.2	10.9 ± 1.1	43.7 ± 2.0	13.3 ± 1.1
20	80	0.9*	120	10	80	56.0 ± 2.5	7.1 ± 0.8	37.2 ± 1.8	10.7 ± 0.8
21	80	1.2*	120	10	80	51.9 ± 2.1	6.7 ± 0.7	33.7 ± 1.5	9.4 ± 0.7
22	80	1.5*	120	10	80	51.0 ± 1.9	6.4 ± 0.7	31.6 ± 1.4	8.9 ± 0.6

*HCl

Percentage of pentosan was based on original RS; Kappa number and Klason lignin were based on pulp

number, pentosan yield and Klason lignin decreased. Similar effects of the liquor ratio were found by Vezquez et al. (1992). Delmas et al. (2003) observed that the kappa number was progressively reduced with an increasing liquor to material ratio during formic acid pulping of rice straw. At 60 °C (trial no. 15) no change in fiber liberation from rice straw was observed. Pulp yield, kappa umber and Klason lignin decreased progressively with increasing temperature. Pentosan yield was increased at 90 °C. This may be a result of redeposition of hemicellulose on the fiber.

The effects of HCl catalyst were also studied at 80 °C for 120 min in 80% acetic acid concentration. The liquor to straw ratio was 10. With increasing HCl catalyst concentration, pulp yield, kappa number, pentosan yield and Klason lignin decreased. Compared to H_2SO_4, HCl produced a higher pentosan yield and lower kappa number and Klason lignin (Figure 1). Kin (1990) also observed lower pentosan in H_2SO_4 catalyzed acetic acid pulp of beech as compared to HCl catalyzed pulp. However, reverse results was observed in acetic acid pulping of maize stalks (Mondal et al., 2004).

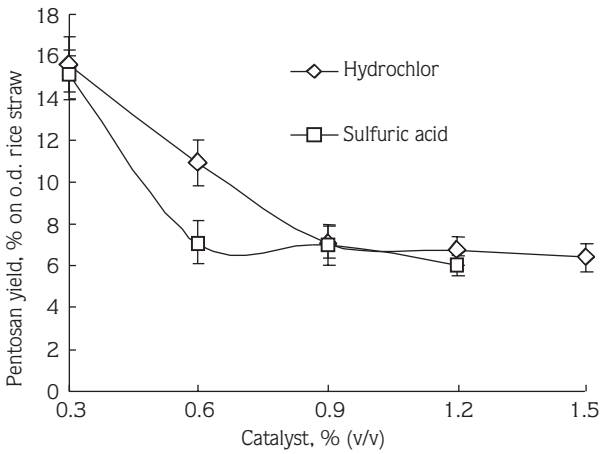

Figure 1. Effect of inorganic acid catalyst in the pentosan dissolution of rice straw.

Formic acid treatment (FA)

One set of experiments was performed using formic acid instead of acetic acid. All conditions remained constant, 0% or 0.6% H_2SO_4, liquor to straw ratio 10 and 120 min at 80 °C. The formic acid concentration was varied. The pulp yield, kappa number, pentosan yield and Klason lignin decreased with increasing formic acid concentration (Table 2). Formic acid dissolved pentosan more rapidly than acetic acid (Figure 2). All pulp properties were lower than those of the acetic acid treatment. These results are in accordance with previous studies of organic acid pulping of wheat straw (Jimenez et al., 1998). Formic acid is a good delignifying agent as well as a solubilization solvent for hemicellulose. The higher formic acid concentration speeds up the delignification and pentosan hydrolysis (Mire et al., 2005). Pulp yield was increased if H_2SO_4 was not used in FA treatment but the kappa number and pentosan yield were higher. This behavior was also observed for formic acid/peroxyformic acid pulping of pine (Poppius et al., 1986).

Table 2. Effect of formic acid and catalyst (H_2SO_4) concentration on the formolysis of rice straw

Run number number	Formic acid acid conc. %	H_2SO_4 conc. %	Time min at 80 °C	Liquor to straw ratio	Pulp yield, %	Pentosan yield, % on o.d. RS	Kappa number	Klason lignin %
23	50	0.6	120	10	53.3 ± 2.1	10.4 ± 0.7	32.6 ± 1.9	9.8 ± 0.9
24	60	0.6	120	10	49.2 ± 2.0	7.8 ± 0.6	31.9 ± 1.8	9.2 ± 1.0
25	70	0.6	120	10	46.7 ± 1.9	7.2 ± 0.6	31.0 ± 1.8	8.9 ± 0.9
26	80	0.6	120	10	45.5 ± 1.7	6.0 ± 0.4	28.1 ± 1.7	8.0 ± 0.8
27	85	0.6	120	10	42.1 ± 1.5	6.2 ± 0.5	28.0 ± 1.6	7.7 ± 0.7
28	50	0	120	10	69.7 ± 2.3	14.0 ± 0.9	43.8 ± 2.2	13.0 ± 0.9
29	60	0	120	10	63.0 ± 2.2	11.6 ± 1.0	34.8 ± 1.9	10.1 ± 0.9
30	70	0	120	10	55.9 ± 2.1	9.0 ± 0.8	33.5 ± 1.8	9.7 ± 0.8
31	80	0	120	10	54.2 ± 2.0	7.3 ± 0.7	32.3 ± 1.8	8.9 ± 0.7
32	85	0	120	10	50.4 ± 1.9	6.6 ± 0.6	30.7 ± 1.6	8.2 ± 0.7

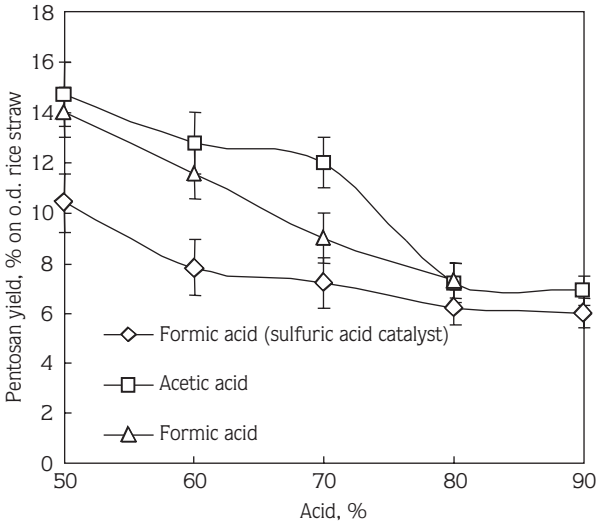

Figure 2. Effect of organic acid on the pentosan dissolution of rice straw.

Alkaline Extraction (AE)

It is known that organic acid pulping gives rigid and brittle fibers and this pulp has lower strength properties. Therefore, in this investigation an effort was made to improve the strength properties of organic acid treated pulp by alkali. The pulp of kappa number 37.0 was extracted by alkaline solution using varying conditions, which are shown in Table 3. With the increase in temperature from 70 to 90 °C for 120 min in 10% alkali, the kappa number dropped from 32.7 to 29.4 with the loss of 2.95% in yield. At 90 °C, the pulp was treated with 4%, 6%, 8%, 10% and 12% alkali for 120 min. The kappa number was reduced from 35.1 to 29.1 with increasing alkali concentration from 4% to 12%, while pulp yield was reduced to 39.5% from 48.7%. The effect of extraction time in 10% alkali at 90 °C on the delignification of AA pulp is also shown in Table 3. The kappa number decreased from 29.4 to 27.8 with increasing time from 120 to 180 min. Figure 3 shows that there is no significant change in the kappa number as extraction time increased from 120 to 180 min.

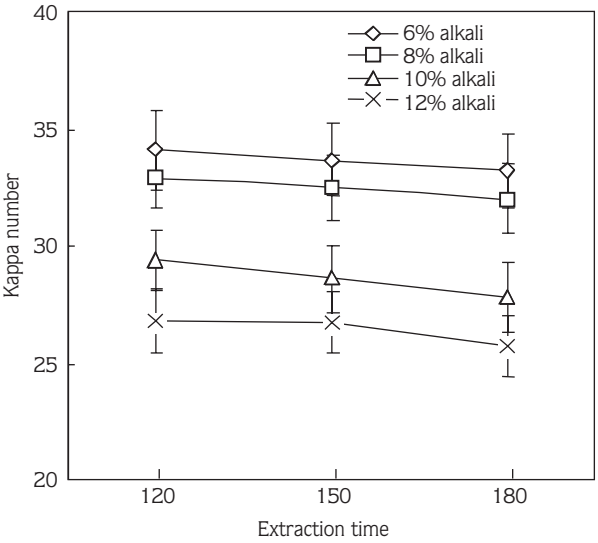

Figure 3. Effect of extraction time and alkali concentration on the delignification of acetic acid (AA) pulps.

Table 3. Effects of extraction time, temperature and alkali concentration (consistency 10%) on yield, kappa number and pentosan content of organic acid treated pulp, RS- Rice straw

Temp. °C	Alkali, % on o.d. RS	Extraction time, min	Pulp yield % on o.d. RS	Kappa number	Pentosan %	pH of the spent liquor
70	10	120	42.85 ± 1.5	32.7 ± 1.7	18.73 ± 1.3	11.1 ± 1.1
80	10	120	40.35 ± 1.3	32.1 ± 1.6	18.69 ± 1.4	10.9 ± 1.0
90	10	120	39.9 ± 1.2	29.4 ± 1.3	17.8 ± 1.3	10.7 ± 1.0
90	4	120	48.7 ± 2.1	35.1 ± 1.9	17.0 ± 1.2	9.5 ± 0.9
90	6	120	41.4 ± 1.6	34.1 ± 1.7	18.0 ± 1.3	10.3 ± 0.9
90	8	120	41.2 ± 1.5	32.9 ± 1.6	17.8 ± 1.2	10.4 ± 0.8
90	12	120	39.5 ± 1.4	29.1 ± 1.4	17.3 ± 1.3	10.7 ± 0.8
90	10	150	39.5 ± 1.3	28.6 ± 1.4	17.7 ± 1.3	10.6 ± 1.0
90	10	180	38.9 ± 1.3	27.8 ± 1.5	17.8 ± 1.2	10.5 ± 0.9
90	8*	120	36.3 ± 1.4	27.1 ± 1.4	12.7 ± 1.0	10.4 ± 0.9
90	10*	120	34.6 ± 1.3	24.8 ± 1.2	12.4 ± 0.9	10.6 ± 0.9
90	12*	120	32.1 ± 1.4	24.2 ± 1.3	11.8 ± 0.7	10.7 ± 1.0

*Formic acid treated pulp

However, a remarkable effect on the kappa number was observed with increasing alkali concentration. It decreased from about 35 to 27 with the increase in alkali concentration from 6% to 12%.

Figure 4 shows the effect of alkali concentration and temperature on the kappa number. No remarkable change in the kappa number was observed with temperature in 6% and 8% alkali. The kappa number fell to 29.4 from 32.7 with the rise in temperature from 70 to 90 °C in 10% alkali (Table 3). It is known that the following 3 reactions take place with alkali treatment: 1) solubilization of residual lignin in pulp, 2) deacetylation or deformylation of pulp, and 3) solubilization of residual silica in pulp. Higher temperature and alkali increased the solubilization of residual lignin in pulp. Pentosan content was almost constant with the variation of extraction variables (Table 3). The pH of all spent liquor decreased with temperature and extraction time. The yield was lowered during alkaline extraction from 60% to about 40% due to the dissolution of silica (ash), which was retained on the fiber during acetic acid treatment.

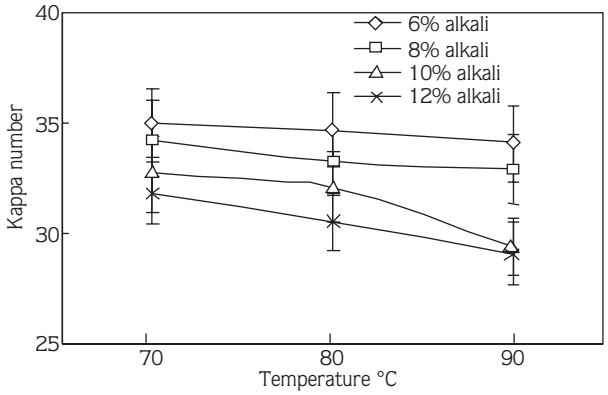

Figure 4. Effect of temperature and alkali concentration on delignification of acetic acid pulps (Time, 120 min)

Formic acid (FA) treated pulp had a 29.1 kappa number when extracted with alkali solution at 90 °C for 120 min. It is seen from the Table 3 that the kappa number was reduced to 24.2 with a huge loss of pulp yield by using 12% alkali. Severe pentosan loss was observed during alkaline extraction. The lower pulp yield may be due to the dissolution of hemicellulose and silica during alkaline extraction. The ash content of pulp after alkali extraction decreased to 3% from 14% in the formic acid treated pulp (Figure 5).

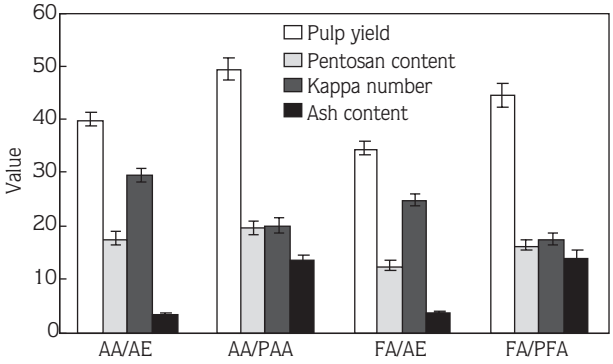

Figure 5. Comparison of acetic acid/ alkaline extraction (AA/AE), acetic acid/ peroxy acetic acid (AA/PAA), formic acid/alkaline extraction (FA/AE) and formic acid/ peroxy formic acid (FA/PFA) pulps.

Peroxyformic acid (PFA) treatment

Partially delignified washed acetic acid treated pulp was delignified with peroxyformic acid and the results are shown in Table 4. The kappa number decreased to 25.9 from 37.0 at the hydrogen peroxide concentration of 7% on o.d RS. At this peroxide concentration, pulp yield was 42.1%. These results were better than those with alkaline extraction (Table 3). Higher pulp yield and lower kappa number were observed if pulp was not washed with water after the acetic acid treatment in the first stage. By using 5% hydrogen peroxide, the rice straw produced a 45.5% pulp yield with kappa number 20.1. The lower delignification in washed pulp is due to lower formic acid concentration in the peroxyformic acid (2nd stage). The high water content of washed pulp did not permit the use of formic acid more than 67%. The delignification increased significantly in peroxyformic acid pulping with the increase in formic acid concentration as shown by Poppius et al. (1987).

Table 4. Effect of peroxy formic acid delignification of partially delignified acetic acid treated pulp.

H_2O_2 % on o.d. Rice straw	Pulp yield, %	Kappa number
3	43.8 ± 2.1	29.1 ± 1.8
5	42.8 ± 1.8	27.1 ± 1.7
7	42.1 ± 1.8	25.9 ± 1.5
5*	45.5 ± 1.9	20.1 ± 1.3

*Without washing

Peroxy acid pulping

Peroxy acid pulping was carried out on rice straw using 80% acetic acid or formic acid with 0.6% H_2SO_4 at 80 °C for 120 min (liquor ratio 10) in the first stage followed by removal of liquor. In the second stage, partially delignified rice straw was treated with 80% acetic acid or formic acid and hydrogen peroxide (3, 5 and 7) at 80 °C for 120 min. The results are shown in Table 5. With the increase in hydrogen peroxide, the kappa number fell remarkably in both peroxyacids. With a 5% peroxide charge, PFA produced 44.5% pulp yield with kappa number 17.7 and PAA produced 51.8% pulp yield with kappa number 25.3. However, an increase in peroxide from 5% to 7% reduced the kappa number to 20.1 without significant change of yield. When H_2SO_4 was added to a FA solution with 5% H_2O_2, the pulp yield decreased remarkably from 44.5% to 35.7% without a significant reduction in the kappa number (17.7 to 17.1). PAA produced higher pulp yield than PFA. This is may be due to the higher retention of hemicellulose in PAA (Figure 5). Kham et al. (2005) reduced the kappa number of 'rice straw organic acid pulp' from 50.4 to 23.2 by peroxyacid treatment.

Physical properties

Table 6 presents the physical properties of rice straw pulps from different processes at about 40°SR. In order to obtain better physical properties, acid treated pulp was further delignified by alkaline treatment, but it is observed that AA/AE pulp did not show a better tensile index. AA/PAA pulp showed the highest tensile index, followed by FA/AE. FA/AE pulp showed the highest burst index, tear index and folding endurance. A detailed study of bleaching and strength properties has been published in another article (Jahan et al., 2005).

Table 6. Physical properties of organic acid pulp (AA/PAA - Acetic acid/Peroxyacetic acid, FA/PFA- Formic Acid/Peroxyformic acid, AA/AE- Acetic acid/alkaline extraction, FA/AE- Formic acid/alkaline extraction)

Type of pulp	Tensile index, N mg^{-1}	Burst index, kPa m^2 g^{-1}	Tear index, mN m^2 g^{-1}	Folding Endurance
AA/PAA*	49.1 ± 5.2	2.3 ± 0.4	5.1 ± 1.0	50 ± 10
FA/PFA**	40.0 ± 5.0	2.8 ± 0.5	8.2 ± 1.3	52 ± 12
AA/AE***	40.1 ± 4.8	2.9 ± 0.5	6.3 ± 1.1	53 ± 12
FA/AE****	48.8 ± 5.4	3.3 ± 0.6	9.1 ± 1.3	57 ± 15

Pulping condition

*Acetic acid/ Peroxyacetic acid: 1st stage AA 80%, Temp. 80 °C, Time 120 min and liquor to straw ratio 10/1; 2nd stage AA 80% & H_2O_2 5%, Temp. 80 °C, Time 120 min and consistency 10%

** Formic Acid/ Peroxyformic acid: 1st stage FA 80%, Temp. 80 °C, Time 120 min and liquor to straw ratio 10/1; 2nd stage FA 80% & H_2O_2 5%, Temp. 80 °C, Time 120 min and consistency 10%

*** Acetic acid/ alkaline extraction: 1st stage AA 80%, Temp. 80 °C, Time 120 min and liquor to straw ratio 10/1; 2nd stage NaOH 10%, Temp. 90 °C, Time 120 min and consistency 10%

**** Formic acid/ alkaline extraction: 1st stage FA 80%, Temp. 80 °C, Time 120 min and liquor to straw ratio 10/1; 2nd stage NaOH 10%, Temp. 90 °C, Time 120 min and consistency 10%

Table 5. Peroxy acid treatment of rice straw pulp.

Name of the process	H_2O_2 % on RS	Pulp yield, %	Kappa number	Pentosan content %
Formic Acid/ Peroxyformic acid	3	45.9 ± 1.7	20.7 ± 1.2	17.1 ± 0.9
	5	44.6 ± 2.3	17.7 ± 1.1	16.3 ± 1.0
	7	43.4 ± 1.9	15.5 ± 0.9	15.1 ± 0.9
	5*	35.4 ± 1.5	17.1 ± 1.1	12.5 ± 0.8
Acetic acid/ Peroxyacetic acid	3	52.4 ± 2.4	28.5 ± 1.6	19.3 ± 1.4
	5	51.8 ± 1.9	25.3 ± 1.6	20.1 ± 1.5
	7	49.4 ± 2.0	20.1 ± 1.3	19.7 ± 1.3

* 0.6% H_2SO_4 was used as catalyst

Comparison

Figure 5 shows the comparison of AA/PAA, FA/PFA, AA/AE and FA/AE pulps. Among these, AA/PAA produced the highest (49.4%) and FA/AE the lowest pulp yield (34.6%). The higher pulp yield in the AA/PAA process agrees well with Poppius et al. (1991). FA/PFA showed optimum results with respect to pulp yield. However, FA/PFA produced the lowest (17.7) and AA/PAA an intermediate kappa number (20.1). The higher kappa number in alkaline extracted pulp may be due to the improper washing of acid treated pulp. The highest pentosan content was observed in AA/PAA pulp and the lowest in FA/AE pulp (Figure 5). Ash content was reduced in alkaline extraction.

Lignin vs. kappa number

The Klason lignin content of the organic acid pulp from rice straw was higher with respect to kappa number. If Klason lignin content is plotted against kappa number the factor is 0.2644 for converting lignin from kappa number (Figure 6). However, in kraft pulp factors of 0.15-0.17 are used for converting kappa number to the respective lignin content. A higher kappa factor for converting kappa number to Klason lignin in organic acid pulp was also seen elsewhere (Poppius et al., 1987).

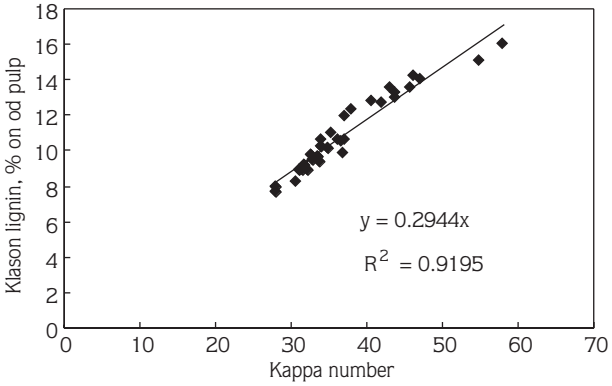

Figure 6. Relationship between Kappa number and Klason lignin of organic acid pulps.

Conclusions

The following conclusions may be drawn from this study:

- Pentosan dissolution from rice straw increased with the increase in acetic acid concentration, catalyst concentration, liquor to straw ratio, time and temperature. Formic acid dissolved pentosan from rice straw more rapidly than acetic acid.
- Alkaline extraction of the pulp delignified with acetic acid or formic acid did not reduce the kappa number significantly but reduced pulp yield and ash rapidly due to silica removal. The kappa number was reduced more rapidly when peroxyformic acid was used for delignification instead of alkaline extraction.
- Acetic acid or formic acid treatment (80 °C for 120 min) in the first stage followed by removal of liquor and then peroxyacid treatment produced high pulp yield and a low kappa number.
- Peroxyacid pulp contains high amounts of ash but after alkaline extraction of organic acid treated pulp reduces ash in pulp.

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