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Formic Acid Pulping of Bagasse

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Abstract

Atmospheric formic acid pulping of bagasse was done with varying formic acid concentration and cooking time. Pulp yield and kappa number decreased with increasing formic acid concentration or cooking time. The optimal cooking conditions were 90 % formic acid and 90 min of cooking at 95^{O} C. The pulp yield at this condition was 44.4 % and kappa number 26.1. The strength properties were acceptable in formic acid pulping of bagasse. Addition of H_2SO_4 catalyst in formic acid degraded carbohydrate, resulting lower pulp yield and inferior strength properties. The strength properties were improved slightly after bleaching.

Introduction

The principle drawback of any conventional pulping process is that it is not possible to separate the lignin and hemicelluloses without alteration of their chemical structure. Therefore, the by-products remain unutilized as chemical intermediates. They are used as process fuels in recovery of pulping reagents. The conventional sulphur based processes impart severe environmental hazards, in addition poor utilization of the dissolved organics. Therefore, the demand for environmentally sound chemical pulp industries has increased interest to alternative pulping processes. During the last few years many attempts have been made to develop organosolv processes based on the application of alcohol and organic acid.[1-5] The main objectives of these processes were the reduction of sulphur emission as well as total utilization of lignicellulosics. Kin obtained 45.5 % pulp, 19.7-20.0 % lignin, and 2.5-5.5 % furfural from beech acidolysis.[6] Organic acid lignin is an optimal feedstock for many value added products due to its lower molecular weight and higher reactivity.[7,8]

Bagasse is one of the main fibrous raw materials in Bangladesh. About 0.7 million ton of bagasse is produced annually in Bangladesh. Only pulp mill in Bangladesh is based on bagasse, which is recently shutdown due to supply of fibrous raw materials. Bagasse is a by-product of sugar mills. Sugar mills in Bangladesh use bagasse as fuel for steam generation. Therefore, sugar mills consume almost all bagasse. Recently, Bangladesh government is connecting gas pipeline to the northern region, where almost all sugar mills are situated. If sugar mills use this gas for steam generation then bagasse can be used for pulp production, and Bangladesh can build more bagasse based pulp mill. Sugar mills are situated at the different region of Bangladesh. So, bagasse based pulp mills should be small in size and economically feasible. Pulp mills will not be feasible without chemical recovery system. On the other hand small pulp with recovery system is not economically viable due to high intensive capital investment in conventional pulping processes. Organic acid pulping process may solve this problems.[3]

In this article, an effort has been made to delignify bagasse by formic acid and to characterize the resulting pulp.

Materials and Methods

Pulping

Depithed bagasse obtained from Pakshi Paper Mills was used as raw material. The chemical compositions of bagasse are 32 - 44 % α-cellulose, 27-32 % pentosan, 19-24 % lignin and 1.5-5 % ash.[9] Cooking was performed in a thermostatic water bath at atmospheric pressure. Bagasse was soaked in the cooking liquor for 30 min at room temperature. The formic acid concentration was varied from 60-100 % (v/v), and cooking time was varied from 30 to 120 min at 95^{O} C. The liquor/ bagasse ratio was 10/1 (v/w). One experiment was done using 90 % formic acid with 0.2 % H_2SO_4 (on od bagasse basis) as catalyst in 90 min of cooking.

After completion of the pulping, the pulp was filtered off and washed with the fresh formic acid, and finally with water. Pulp yield was determined on the basis of oven dried (o.d.) bagasse. The kappa number (T236 om 85) of pulp and pentosan (T223cm 84), and ash (T211om 93) in bagasse were determined according to Tappi standard methods. For the determination of physical properties, pulps were beaten in a wearing blender and handsheets were made to determine tear (T414 om-98), tensile (T404 cm-92), burst (T403 om-97) and fold (511 om-96).

Peroxyformic acid treatment

Formic acid treated pulp was further delignified with peroxyformic acid (PFA) at 80^{O} C. The reaction was carried out in a thermostatic water bath. The peroxyformic was prepared by adding 90 % (v/v) formic acid with 4 % H_2O_2 (on od bagasse basis). After completion of the treatment the pulp was filtered off and washed with 80 % fresh formic acid and finally with water.

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^{O} C for 1 h. Similar procedure was followed in the 2nd stage of peroxide bleaching. The strength properties of the bleached pulp were determined as above. A pulp sheet was prepared in a buckner funnel for the determination of final brightness.

Results and Discussion

The formic acid pulping process is based on the action of concentrated formic acid for causing a variety of effects, including the hydrolysis of ether bonds of lignin, leading to fragments soluble in the organic media and the breakdown of hemicelluloses by hydrolysis of the glycosidic bonds, leading to sugar oligomers and monomers, both soluble in the liquid phase.[10,11] Table I shows the effect of formic acid concentration on yield and kappa number of bagasse pulp. It is clearly seen that the pulp yield and kappa number decreased with increasing formic acid concentration. At 60 % formic acid bagasse was not delignified sufficiently but with increasing formic acid concentration to 90 % bagasse was delignified to kappa number 26.1 (Table I). In this investigation the targeted kappa number was considered 26. Again an increase of formic acid concentration to 100 % did not reduce kappa number. This can be explained by the value of Hildebrand solubility parameter (δ) of 100 % formic acid, that was 10.1.[12] The solvent who have δ value approximately 11 was the best to dissolve lignin.[12] The pulp yield decreased from 48.4 to 44.4 % with the increase of formic acid concentration from 60 to 90 %. The behavior of formic acid concentration in the delignification is directly consistent with formic acid pulp of rice straw.[13]

Table II represents the effect of cooking time on pulp yield and kappa number in bagasse formalysis. The formic acid concentration was held constant at 90 %. Pulp yield and kappa number decreased with increasing cooking time. The desired kappa number was obtained in 90 min of cooking. The pulp yield decreased from 46.9 % to 44.4 % and kappa number from 30.8 to 26.1 with the increase of cooking time from 30 to 90 min. An addition of 0.2 % H_2SO_4 (V/V) in 90 % formic acid solution decreased kappa number to 24.0 in 90 min of cooking. At the same condition of formalysis without H_2SO_4, pulp showed 5.4 points higher kappa number. But pulp yield was significantly lost with using of H_2SO_4. Therefore, H_2SO_4 enhanced delignification and carbohydrate hydrolysis simultaneously.

Table I. Effect of Formic acid concentration on yield, kappa number and strength properties of bagasse pulp (Cooking time 90 min, liquor ratio 10)

Formic acid concentration % (v/v)	Pulp yield, %	Kappa number	Breaking length, Km	Burst index, kPa.m^2/g	Tear index, mN.m^2/g	Double fold number
60	48.4	33.9	4.3	2.1	6.3	9
70	47.1	32.1	4.4	2.5	6.8	10
80	45.7	29.1	4.6	2.9	7.2	11
90	44.4	26.1	4.7	3.2	7.8	11
100	43.8	26.2	4.7	2.9	7.6	10

Table II. Effect of cooking time on yield, kappa number and strength properties of bagasse pulp (Formic acid concentration 90 % (v/v), liquor ratio 10)

Cooking time, %	Pulp yield, %	Kappa number	Breaking length, Km	Burst index, $kPa.m^2/g$	Tear index, $mN.m^2/g$	Double fold number
30	46.9	30.8	4.3	2.2	5.6	10
60	45.8	29.4	4.5	2.7	6.1	11
90	44.4	26.1	4.7	3.2	7.8	11
120	43.9	25.6	4.8	3.1	7.4	12
90*	37.3	24.0	4.4	2.8	7.2	9

* 0.2 % H_2SO_4 catalyst

The breaking length, burst index and tear index increased with increasing formic acid concentration up to 90 % (Table I). The properties were decreased at 100 % formic acid concentration. These results are in agreement with rice straw cooking in acetic acid.[10] There was no significant change in double fold number with the change of formic acid concentration. Highest properties were obtained at 90 % formic acid. At 90 % concentration breaking length, burst index and tear index were 4.7 Km, 3.2 $kPa.m^2/g$ and 7.8 $mN.m^2/g$, respectively.

Table II shows the effect of cooking time on strength properties of bagasse pulp from formic acid process. The strength properties increased with increasing cooking time up to 90 min, with further increase of cooking time the properties decreased. The breaking length was increased from 4.3 to 4.8 Km, burst index from 2.2 to 3.2 $kPa.m^2/g$ and tear index from 5.6 to 7.8 $mN.m^2/g$ with the increase of cooking time from 30 to 90 min. An addition of H_2SO_4 decreased all strength properties (Table II).

Pulp obtained using 90 % formic acid in 90 min of cooking was further treated with peroxyformic acid at 80^{O} C. The peroxyformic acid was prepared by adding 4 % H_2O_2 to 90 % formic acid. Such a mixture of formic acid, H_2O_2 and peroxyacid proved to be efficient in delignification of unbleached pulp through the combined action of the peroxyacids as oxidizing agent and formic acid as solvent for the lignin.[14] The test results of begasse pulp obtained in formic acid cooking showed that this oxidizing medium decreased residual lignin significantly. Peroxyformic acid treatment reduced the kappa number to 14.5 from 26.1 in the unbleached state and brightness improved to 52.4 % from 24.8 % (data not shown). The bleaching of peroxyformic acid treated pulp was done by an alkaline peroxide treatment. The final brightness reached to 83 %. The bleaching improved strength properties of formic acid pulp (Table III). The reason may be the damage of the fibers caused by acidic pulping. The hydroxyl group of cellulose was formylated, which inhibits fiber bonding. During bleaching, formyl group was hydrolysed to hydroxyl group, thus increased fiber bonding.[15] This may be another reason of better strength after bleaching of organic acid pulp. Recently SAS-AQ process shows better performance over soda process for bagasse pulping.[16] So in Table III, formic acid bleached pulp is compared with SAS-AQ bleached bagasse pulp. Formic acid pulp was quite comparable with SAS-AQ pulp.

Appendix 1. Schematic flow diagram of formic acid pulping of bagasse

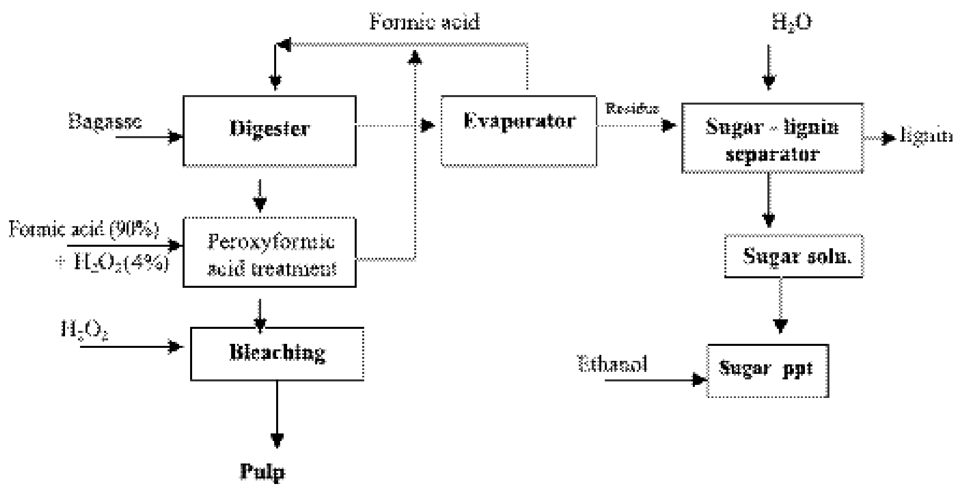

Table III. Strength properties of bleached formic acid and SAS-AQ pulp

	Formic acid pulp	SAS-AQ[16]
Breaking length, Km	5.1	5.4
Burst index, kPa.m^2/g	4.1	2.8
Tear index, mN.m^2/g	7.3	4.0
Double fold number	57	-
Brightness, %	83.1	83.1

Appendix 1 : Appendix 1 shows the flow diagram of formic acid pulping. In this process, pulp obtains from the bottom of digester and formic acid can be regenerated from the spent liquor by evaporation. The dissolved lignin and hemicelluloses in the formic acid are collected as concentrated slurry from the evaporator. The concentrated slurry is mixed with water, lignin is separated as precipitate and the hemicelluloses remain in water solution. The hemicelluloses are precipitated in ethanol. Therefore, we can utilize all fraction of biomass in the formic acid pulping.

Conclusions

- The pulp yield and kappa number decreased with increasing formic acid concentration or cooking time.
- The best strength properties were obtained at 90 % formic acid in 90 min of cooking.
- Addition of H_2SO_4 catalyst decreased pulp yield, kappa number and strength properties rapidly.

- Formic acid pulp responded very well on total chlorine free bleaching. The final brightness was reached to 83 %.

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