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Effect of acid leaching of bamboo and hardwood chips on kraft pulping and pulp bleaching

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Abstract

Acid leaching of chips prior to pulping is a proven method to reduce non-process elements in kraft pulping process. In this paper, acid leaching of bamboo and hardwood chips was carried out at pH 2 for 1h at 80 °C prior to kraft pulping. Calcium removal in acid leaching from wood chips was 52.6% while for bamboo was only 17.4%. Acid leaching also reduced potassium (K) from 1258 mg/kg to 495.7 mg/kg for bamboo and 928 mg/kg to 562.5 mg/kg for wood chips. The effects of acid leaching on pulping, pulp bleaching, and papermaking characteristics were also determined. Acid leaching of both kinds of chips prior to kraft cooking resulted in a significant increase in the rate of delignification. Acid leached chips showed higher screen pulp yield and lower rejects at any kappa number. There was no significant difference of papermaking properties between pulps obtained from acid leached and non-leached chips. Using same ClO₂ charge, acid leaching improved pulp brightness by 1% and 1.1% for hardwood and bamboo, respectively. Acid leaching improved pulp viscosity from 10.1 mP.s to 12.1 mP.s for hardwood.

Keywords: Bamboo and hardwood chips; Acid leaching; Pulp yield; Pulp bleaching

Introduction

Most of the non-process elements (NPEs) usually come to the process through wood chips, make-up chemicals, make-up lime (Rocha *et al.*, 1998; Taylor and McGuffie, 2006; Ulmgren, 1987) process water, bleaching chemicals, and with recycled effluent streams and biosludge (Tran and Vakkilainen, 2007). However, close system tends to limit some NPEs. Accumulation of NPEs in the pulping process may cause deposits/corrosion in the liquor recovery cycle and in various parts of the bleach plant, such as washer screens, filtrate tanks, nozzles, repulpers, pumps, piping and instrumentation and can affect bleaching chemical consumption, especially when hydrogen peroxide is used.

Transition metals participate in a large number of chemical oxidations capable of pulp color formation (Colodette *et al.*, 1989a; Colodette *et al.*, 1989b). Transition metals-catalyzed decomposition of hydrogen peroxide results in reagent loss and formation of free radicals that degrade cellulose. Since peroxide is also generated during bleaching with oxygen, the presence of transition metals, especially iron, manganese and copper is undesirable during this stage.

It is found that acid leaching of wood chips is a promising technology for reducing NPEs in kraft pulping, consequently increasing the rate of delignification, unbleached pulp brightness and improve pulp bleachability (DelAntonio *et al.*, 2011; Lundqvist *et al.*, 2006). Recently Santose *et al.* (2015) also showed that acid leaching of eucalyptus wood chips considerably reduced NPEs. Humar *et al.* (2004) leached chromate-copper-borate treated wood sample using five different agents, namely, water, an aqueous solution of oxalic or acetic acid, and an aqueous solution of oxalic or acetic acid with ammonia. The highest chromium leaching was achieved with the aqueous solution of oxalic acid.

Kharnaphuli Paper Mills (KPM)- only pulp mill in Bangladesh has recently installed oxygen delignification plant. Bamboo and mixed hardwoods are used in this mill. No study has been made on the NPEs of these raw materials. Therefore, in this study acid leaching of industrial chips of bamboo and mixed hardwoods was carried out with acidic water. The main objectives were to determine the impact of acid leaching on the kraft pulping and bleaching.

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Materials and methods

Raw materials

Bamboo and mixed hardwood chips were collected from the KPM for acid leaching and subsequent pulping experiment.

Acid leaching

The acid leaching experiment of bamboo and mixed hardwood chips was carried out separately by acidic water in polyethylene bag. The chips (250g od basis) were treated with sulfuric acid-water under the following conditions: 1:10 material to liquor ratio, 80 °C, 60 min and pH 2.0. After acid leaching, the liquor was collected for NPEs determination and chips were washed with distilled water.

Pulping

Acid leached and non-leached bamboo and mixed hardwood chips were used for subsequent pulping experiment. Pulping was carried out by kraft process in a thermostatically controlled electrically heated digester with capacity of 5 litres. Pulping conditions were as follows:

- Active alkali was 16, 18 and 20 % on oven-dry (o.d) raw material as Na₂O
- Cooking time was fixed for 2 h at maximum temperature (170 °C), with 90 min to raise maximum temperature (170 °C) from room temperature.
- Liquor to material ratio was 4.
- Sulphidity 25 % for kraft process.

After digestion, pulp was washed until free from residual chemicals, and screened in a flat vibratory screener (Yasuda, Japan). The screened pulp yield, total pulp yield and screened reject were determined gravimetrically as percentage of o.d. raw material. The kappa number (T 236 om-99) of the resulting pulp was determined in accordance with Tappi Test Methods. Three replicates of all experiments were done and average reading was taken.

Evaluation of pulps

Pulps were beaten in a PFI mill to get drainage resistance (°SR) 25 and hand sheets of about 60 g/m² were made in a Rapid Kothen sheet making machine. The sheets were tested for tensile (T 494 om-96), burst (T 403 om-97) and tear

strength (T 414 om-98) according to TAPPI Standard Test Methods.

DEpD bleaching

The acid leached and non-leached bamboo and mixed hardwood pulps were bleached by D₀EpD₁ bleaching sequences (where D represents chlorine dioxide and Ep represents peroxide reinforced alkaline extraction). The ClO₂ charge was 2% and temperature was 70°C for 45 min in the D₀ stage. The pH was adjusted to 2.5 by adding dilute H₂SO₄. Alkaline extraction was carried out with 2% NaOH and 0.5% H₂O₂ charge, temperature was 70°C for 120 min. In the D₁ stage, ClO₂ charge were 0.5, pH was adjusted to 4.5 by adding dilute alkali. The pulp consistency was 10% in all the stages. The brightness (T 452 om-92) and viscosity (T 230 om-99) of the bleached pulp were determined in accordance with Tappi Test Methods.

NPEs determination

NPEs were determined by atomic adsorption spectrophotometer at the soil science laboratory of BCSIR Laboratories, Dhaka.

Results and discussion

Acid leaching

Acid leaching may cause acid hydrolysis of carbohydrate consequently decrease pulp yield and strength properties in subsequent pulping. Axegard (2003) showed that acid hydrolysis of carbohydrate leaching was minimum at temperature lower than 100 °C and no negative effect of strength properties of pulp. It was also observed that considerable amount of NPEs were removed from wood chips by leaching at pH 2-3. Therefore, in this study, acid leaching was carried out at 80 °C with pH 2.

Acid leaching of bamboo and hardwood chips resulted in weight loss of 2.1 and 2.0%, respectively. The composition of the organic material lost was not determined. Acid leaching results are shown in Table I. As shown in Table I, acid leaching efficiently removed metals from the bamboo and hardwood chips and contributed to improving chips characteristics prior to pulping. Leaching resulted in reduction potassium (K) from 1258 mg/kg to 495.7 mg/kg for bamboo

Table I. Effect of acid leaching on the non process elements of bamboo and wood

NPEs	Bamboo			Wood		
	Without Leaching(mg/kg)	On Leaching(mg/kg)	% removal	Without Leaching (mg/kg)	On Leaching (mg/kg)	% removal
Ca	223	185	17.4	721	342.1	52.6
Mg	325	253	22.2	443	304.9	31.1
Fe	48.3	14.7	69.6	48.8	6.3	87.1
Mn	60.2	29.3	51.3	16.84	4.7	72.1
K	1258	495.7	60.6	928	562.5	39.4

and 928 mg/kg to 562.5 mg/kg for wood chips, which accounted 60.6% and 39.4%, respectively. K impacts negatively on thermal properties of recovery boiler deposits and even in small quantities can accelerate obstruction of flue gas passages by reducing deposit melting point (Ulmgren, 1997).

Calcium removal in acid leaching from wood chips was 52.6%, while for bamboo was only 17.4%. Presence of calcium favors formation of calcium oxalate, one of the hardest and most difficult deposits to remove (Silva *et al.*, 2002). Furthermore, calcium carbonate (CaCO₃) found in industrial white liquor can increase deposit formation problems in the digester. Even at low concentrations, CaCO₃ readily precipitates in white liquor storage tanks, forming deposits that can be carried over to the cook. Additionally, reduction in black liquor soluble calcium will avoid super concentration of sodium salts in the first effects of the evaporation plant. This in turn will impede massive precipitation of salts such as sodium bicarbonate that can cause deposits, reduce heat exchange coefficients and compromise plant operations (Verrill and Frederick, 2005). It has also been suggested that calcium may have a negative effect on wood delignification (Lundqvist *et al.*, 2005). Thus, acid leaching is advantageous for subsequent pulping.

Acid leaching removed manganese from 60.2 mg/kg to 29.3 mg/kg for bamboo and from 16.8 mg/kg to 4.7 mg/kg for wood chips. Manganese has deleterious effects on elemental chlorine free (ECF) and total chlorine free (TCF) bleaching since they catalyze decomposition of oxygen based bleaching reagents.

Manganese also catalyzes cellulose depolymerization reactions during oxygen delignification and alkaline peroxide bleaching stages, and degrades hydrogen peroxide solutions (Ulmgren, 1997).

Acid leaching also removed part of magnesium was from bamboo (22.2%) and wood chips (31.1%). Magnesium protects carbohydrate degradation during oxygen delignification and peroxide bleaching (Kolar, 1997).

Pulping

Acid leached wood and bamboo chips were cooked by kraft process with varying alkali charge. The results are compared with the non-acid leached wood and bamboo chips data (Table II). Acid leached chips showed higher screen pulp yield and lower rejects than the non-leached counterpart. At the 18% active alkali charge, screened pulp yield was 33.9%

Table II. Effect of acid leaching on the pulping of hardwood and bamboo

	Alkali charge (%)	Without leaching			Kappa number	On leaching			Kappa number
		Yield (%)				Yield (%)			
		Screened	Reject	Total		Screened	Reject	Total	
Wood	16	34.8	3.1	37.9	16.1	35.2	2.7	37.9	15.1
	18	33.9	2.2	36.7	15.4	34.7	0.7	35.4	14.0
	20	33.0	1.5	34.5	12.3	33.9	0	33.9	12.0
bamboo	16	39.8	0	39.8	12.5	39.9	0	39.9	11.9
	18	35.3	0	37.4	10.2	37.3	0	37.4	9.6
	20	34.6	0	34.6	9.3	34.2	0	34.2	9.4

and 35.3% for acid leached hardwood and bamboo, respectively. The pulp yields were lower than expected, which due to inferior quality of chips. The screened yields were 0.4% and 2.1% higher than non-leached chips. Acid leached hardwood had lower reject than non-leached hardwood. Acid leaching reduced kappa number (Table II). Similar results were obtained for birch wood chips (Lundqvist *et al.*, 2006). Moreira *et al.* (2008) also showed that acid treatment improved delignification rate. Acidic leaching of both the chips prior to cooking resulted in a significant increase in the rate of delignification at a lower alkali charge. But it had no effect as it approaches the residual delignification phase (Fig. 1). The screened yield gain and improved delignification can be explained by the fact that acid leaching removed material, which would otherwise be removed during cooking.

Papermaking properties of unbleached pulp

The pulp obtained from acid leached and non-leached bamboo and hardwood chips were beaten to drainage resistance ($^{\circ}$ SR) 25 and papermaking properties were determined. The results are given in Table III. There was no significant difference observed between pulps obtained from acid leached and non-leached chips. At 18% active alkali charge, acid leaching increased tensile index by 3.3% for hardwood while decreased tear index by 12.7%. On the other hand, no difference in tensile index was found for bamboo pulp.

Bleaching

As shown in Table IV, acid leaching of both wood and bamboo chips had positive effects on bleaching, especially with

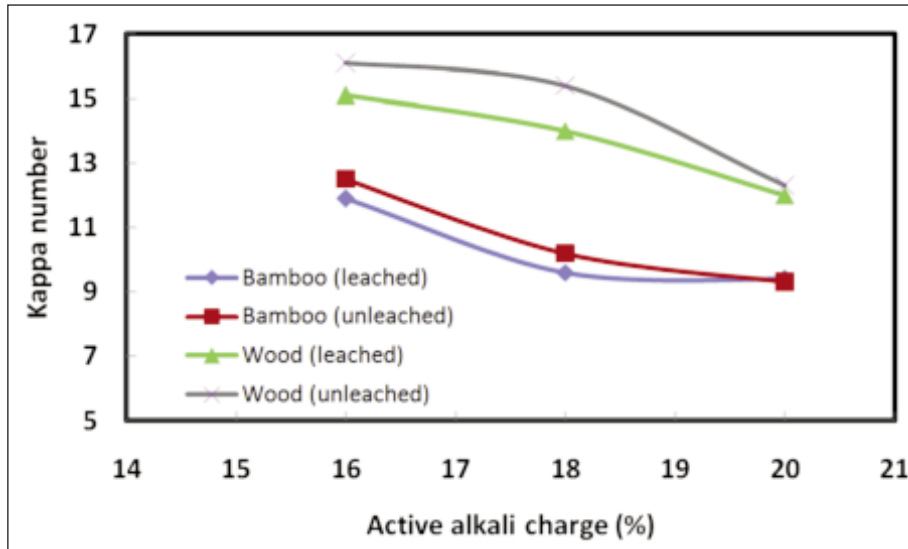


Fig. 1. Effect of acid leaching on the delignification of bamboo and hardwood chips by kraft process

Table III. Effect of acid leaching on the papermaking properties of unbleached pulp

	Alkali charge (%)	Without leaching			On leaching		
		Tensile index (N.m/g)	Burst index (kPa.m ² /g)	Tear index (mN.m ² /g)	Tensile index (N.m/g)	Burst index (kPa.m ² /g)	Tear index (mN.m ² /g)
Wood	16	33.3	2.5	9.8	34.5	2.5	9.7
	18	33.1	2.4	10.2	34.2	2.4	8.9
	20	33.0	2.6	9.7	34.0	2.3	8.5
bamboo	16	24.4	2.3	17.4	24.3	2.1	17.2
	18	24.8	2.1	17.8	24.9	2.2	16.8
	20	24.4	2.2	17.5	24.6	2.2	16.4

Table IV. Effect of acid leaching on the bleaching of bamboo and wood pulp

	Without leaching			On leaching		
	Brightness (%)		Viscosity mPa.s	Brightness (%)		Viscosity mPa.s
	Unbleached	Bleached		Unbleached	Bleached	
Wood	16.4	75.5	10.1	16.2	76.2	12.1
Bamboo	23.2	85.4	12.1	23.3	86.5	12.3

regard to brightness and final pulp viscosity. Unbleached pulp brightness was not improved on acid leaching. But acid leaching improved pulp brightness by 1% and 1.1% for hardwood and bamboo, respectively, using same ClO_2 charge. DelAntonio *et al.* (2011) also observed positive effects of acid leaching on pulp brightness of two eucalyptus species. Moreira *et al.* (2008) also showed that the pulp from acid leached chips showed improved performance during bleaching over the reference pulp. Acid leaching improved pulp viscosity from 10.1 to 12.1 mPa.s for hardwood and from 12.1 to 12.3 mPa.s from bamboo. Lundquist *et al.* (2006) showed that acid leaching increased pulp viscosity for birch wood while the viscosity of eucalyptus pulp did not increase.

Conclusions

Acid leaching of calcium is more difficult with bamboo chips compared to hardwood chips. Potassium, magnesium and manganese are leached similarly for both the chips. Acid leaching significantly improved delignification in subsequent kraft pulping. Acid leaching also reduced screening reject and slightly improved pulp yield. Improved pulp brightness and viscosity were observed on acid leached hardwood and bamboo chips. From the above results, it can be concluded that acid leaching of bamboo and hardwood chips prior to pulping is advantageous kraft pulping.

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