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Bangladesh J. Sci. Ind. Res. **52(4)**, 247-252, 2017

BCSIR

BANGLADESH JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

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Modification of chlorine dioxide bleaching of *Gmelina arborea* (gamar) pulp

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Abstract

Elemental Chlorine Free (ECF) pulp bleaching is now the dominant pulp bleaching process in globally. In most bleachery, chlorine dioxide is over-consumed. About two thirds of the chlorine dioxide is wasted in useless side reactions. In the study, kraft pulp from *Gmelina arborea* (gamar wood) was bleached by ECF bleaching in modified sequences. Oxygen prebleaching was carried out to decrease ClO_2 requirement, which reduced kappa number of kraft pulp by 47.6% and increased pulp brightness by 21.7 percent points. Several sequences were tested based on the application of limited charges of ClO_2 during successive ClO_2 and extraction stage. Application of this concept allowed a 33% reduction of ClO_2 to reach target brightness. The kraft pulp could not reach target brightness of 80% in DED sequences using even 30 kg ClO_2 /ton of pulp, while splitting of same amount of ClO_2 charge into DEDED sequences reached the pulp brightness to 81.1%. But oxygen delignified kaft pulp reached 79.6% brightness using 25 kg ClO_2/ton of pulp in DED sequences. In the splitting of ClO_2 charge into DEDED sequences, Oxygen pulp reached to 85% brightness by using only 20 kg ClO_2/ton pulp.

Keywords: Pulp bleaching; *Gmelina arborea* (gamar); Chlorine dioxide; Chlorine dioxide Splitting and Brightness

Introduction

Gmelina arborea (gamar) as the main wood source for pulping in Karnaphuli Paper Mills (KPM), the only pulp mill in Bangladesh, cooked by kraft process. Unfortunately, the brightness of the produced pulp can't meet the consumer demand. Pulping conditions can affect residual lignin nature, which may play a key role in pulp brightness development (Jahan *et al*., 2007). The bleachability of bamboo pulp was improved when pulping was done with a higher active alkali charge and sulphidity (Jahan *et al.,* 2007).

Chlorine dioxide (ClO_2) is the dominant chemical pulping process golbally. Oxidation of lignin with ClO_2 is the main reaction to reach delignification and brightness target levels. Despite the occurrence of several side reactions it seems that the main mechanism is the ring opening of the free phenolics (Lachenal and Chirat, 1999). In most bleaching mills, chlorine dioxide is over-consumed and the oxidant charge generally applied for delignification is more than twice the theoretical oxidizing power necessary to convert free phenolic groups to soluble oxidized units bearing carboxylic functions (Chirat and Lachenal, 1999; Lachenal and Chirat, 2000). Good results are observed at low ClO_2 charge in order to make reactions on free phenolic groups selective and avoid secondary reactions. To avoid secondary reactions, splitting the full chlorine dioxide charge into subdivided stages at low charge is a good option in ECF bleaching (Hamzeh *et al*., 2007). So, in this study ClO_2 charge was splitted into subdivided stages.

To reduce effluent load in Elemental Chlorine Free (ECF), prebleaching have been studied extensively (Ikeda *et al*., 1999; Jahan *et al*., 2006, 2013). Oxygen delignification is the most common and environmental friendly process employed prior to ECF and TCF bleaching sequences for continuance of delignification to reduce lignin in pulp by 35-55% prior to bleaching (Samuelson, 1994). The oxygen delignification modifies residual lignin through increase of carboxyl groups and a decrease in free phenolic groups (Gellerstedt *et al*., 1986).

In this study, gamar wood chips was cooked by kraft process in mill conditions and the produced pulp was oxygen delignified prior to ECF bleaching. Kraft and oxygen delignified pulps were ClO_2 bleached by splitting total ClO_2 charge.

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The delignification and brightness after D_0E in varying ClO_2 charge were determined. The final brightness and effluent load after splitted ClO_2 charge were also studied.

Materials and methods

Raw materials

Gamar wood chips were collected from Karnaphuli Paper Mills (KPM) and cooked by kraft process. The cooking was carried out in thermostatically control digester, rotating at 1 rpm. The cooking conditions were 170 °C for 120 min, liquor to material ratio 4, active alkali charge 18% (as Na_2O) on oven dried (o.d.) wood basis.

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.

Oxygen delignification

Oxygen delignification (OD) was carried out in thermostatically control digester, rotating at 1 rpm. OD conditions were 110 °C, retention time 60 min, pulp consistency 10 %, NaOH 2 %, $MgSO_4$ 0.3 % and O_2-pressure 3.5 kg cm^{-2}. The kappa number, viscosity and brightness of the resulting pulp was determined in accordance with Tappi Test Methods (T 236 om-99), (T 230 om-99) and (T 452 om-92), respectively.

Bleaching

Kraft and oxygen delignified pulps were bleached by $D_0E_pD_1$ and $D_0E_pD_1ED_2$ bleaching sequence. The ClO_2 charge was varied from 0.5% to 2.5% and temperature was fixed at 70 °C for 45 min in the D_0 stage. The pH was adjusted to get end pH 2.5 by adding dilute H_2SO_4. In alkaline extraction stage, temperature was 70 °C for 120 min and NaOH and H_2O_2 charges were 2% and 0.5%, respectively. Using same the ClO_2 charge, DED sequences were splitted into DEDED sequences. In the final D_1 and D_2 stage, the pH was adjusted to get end pH 4.5 and 6.5, respectively, by adding dilute NaOH and temperature was 70°C for 120 min. 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.

Results and discussion

Oxygen delignification

The yield of kraft pulp from gamar wood with 18% active alkali was 48.2% The kappa number of the pulp was 18.3 and viscosity 16.2 mPa.s. Oxygen delignification of the produced pulp was carried out in order to reduce kappa number. The kappa number was reduced by 47.6%, while the overall pulp yield was reduced by 2 percent unit. The degree of oxygen delignification is dependent on initial kappa number (Vu *et al*., 2004). Vu and co-workers showed that pulps with an initial kappa number of 11–22, the degree of delignification was between 44 and 48%. These results indicated that kraft pulps with a low kappa number could also be readily delignified by oxygen delignification. It is established that the effectiveness of an oxygen delignification stage is limited to 50% delignification. Beyond this level, severe cellulose degradation takes place, resulting in the deterioration of pulp viscosity and strength characteristics (McDonough, 1996; Masura, 1993). Oxygen delignification of soda-AQ bagasse pulp reduced kappa number by almost 50% with marginal yield loss (Mohta *et al.,* 1998). Oxygen delignification significantly increased unbleached pulp brightness from 18.3% to 40.0% (Table I).

Delignification of DE in varying ClO_2 charges

Several D_0E stages at varying ClO_2/pulp charges (0.5 to 2.5% on o.d. pulp) were carried out on the unbleached and oxygen delignified pulp and shown in Table II and Fig. 1. It shows that the kappa number decreased rapidly and linearly up to 1% ClO_2 charge followed by a slower and flattened decreased (Fig. 1). McDonough *et al.* (2000) also showed that 95% delignification after D_0E could be reached in only one minute. This was due to the oxidizing efficiency of ClO_2 severely decreases at a higher charge (Hamza *et al*., 2007). Hamza and co-workers showed the minimum of about 5 eq/mol of C_9 at the lowest ClO_2 charge. Above 0.6% ClO_2 charge, the oxidizing power increased and reached 10 eq/C_9 at high ClO_2 charge. The theoretical value for the formation of muconic acid moieties is 4 eq/C_9, which was lower than the 5 eq/C_9. This indicates that increasing quantity of ClO_2 was consumed by non-useful reactions. It is suggested that ClO_2 reacts with already oxidizable lignin mucomic acid structure (Ni and Heiningen, 1992). It is believed that when the ClO_2 consumption in D_0 reaches a certain level, it is beneficial to remove the oxidizable lignin which accumulates and reactive with ClO_2. Extraction stage can do it. Therefore, D and E stages were splitted to several stages, which are discussed in later section.

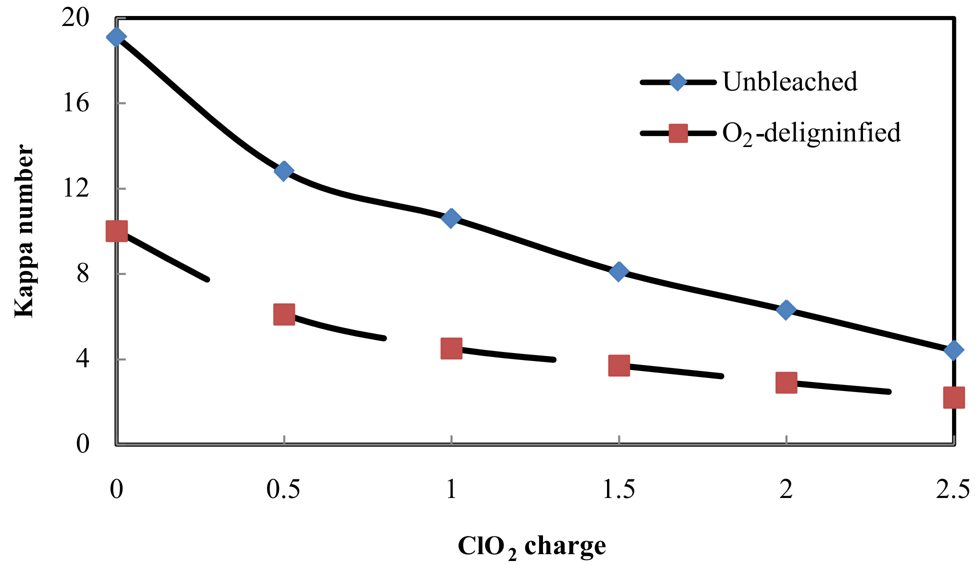

Fig. 1. Effect of chlorine dioxide charge on the D_0E stage kappa number

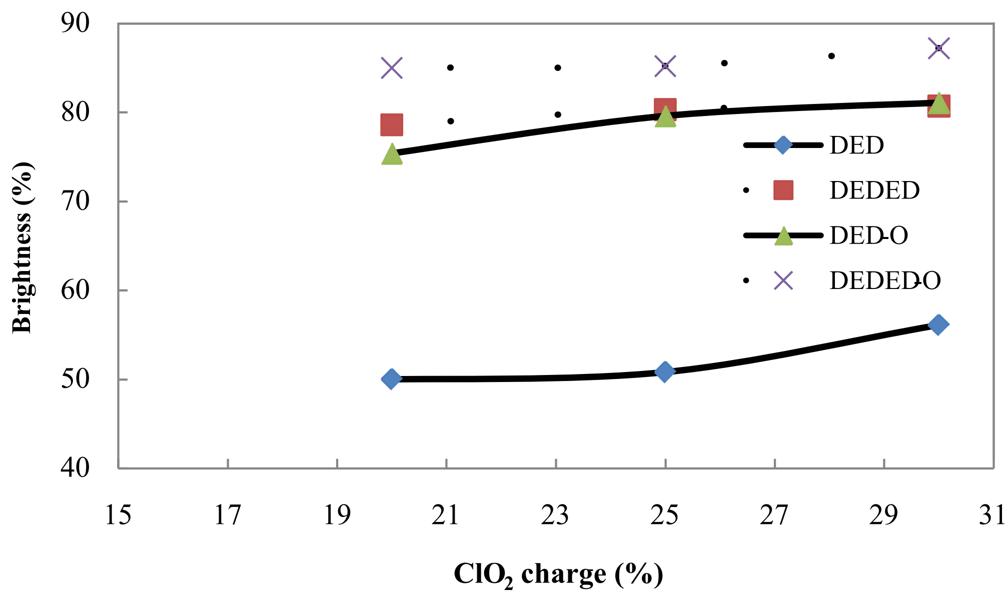

Fig. 2. Final brightness after DED and DEDED sequences of kraft and oxygen delignified pulps

As shown in Table 2, yield after D_0 stage was not dependent by ClO_2 charge. Both unbleached and oxygen delignified pulp showed around 94% yield. The pulp viscosity after D_0 stage decreased by 12.3% for unbleached and 35.8% for oxygen delignified pulp at 0.5% ClO_2 charge. But the viscosity did not decrease with increasing further ClO_2 charge. The pulp brightness increased from 21.1% to 37.3% for unbleached and 49.5% to 73.7% for oxygen delignified pulp with increasing ClO_2 charge from 0.5% to 2.5%.

Splitting of ClO_2 charge

Table III shows the advantages obtained by splitting a DED stages into DEDED stages in which one third of the chlorine dioxide was applied three times with intermediate extraction and washing. At the same ClO_2 consumption, the splitting process showed higher brightness and similar viscosity. Kraft pulp could not reach the target brightness of 80% in applied total ClO_2 charges in DED bleached sequences. Splitting of

Table I. Pulping and oxygen delignification of Gamari wood

	Pulp yield (%)	Kappa number	Brightness (%)	Viscosity (mPa.s)
Kraft	48.2	19.1	18.3	16.2
O_2- delignification	95.5 (46.0)	10.0	40.0	12.3

Table II. Effect of ClO_2 charge on the pulp properties after D_0E stage

	ClO_2 charge (%)	Yield (%)	Kappa number	Viscosity (mPa.s)	Brightness (%)
Unbleached	0.5	94.4	12.8	14.2	21.2
	1.0	94.6	10.6	15.4	22.9
	1.5	94.7	8.1	15.1	25.6
	2.0	94.1	6.3	15.6	29.4
	2.5	94.0	4.4	15.8	37.3
Oxygen delignified	0.5	94.2	6.1	7.9	49.5
	1.0	94.1	4.5	8.0	62.1
	1.5	94.8	3.7	7.8	69.5
	2.0	94.4	2.9	7.4	71.4
	2.5	94.5	2.2	7.4	73.7

Table III. Splitting of DED bleaching stages into DEDED

	Splitting	Total ClO_2 charge (kg/MT pulp)	Viscosity (mPa.s)	Brightness (%)
Unbleached	DED	30	10.1	56.1
		25	10.7	50.8
		20	10.8	50.0
	DEDED	30	9.9	80.7
		25	10.5	80.3
		20	10.5	78.6
Oxygen delignified	DED	30	4.6	81.1
		25	5.1	79.6
		20	5.4	75.4
	DEDED	30	5.4	87.2
		25	5.5	85.2
		20	5.5	85.0

DED stages into DEDED stages increased pulp brightness from 51% to 80% using 25 kg ClO_2/ton of pulp. Oxygen delignified pulp was easier to brighten as shown in Fig. 2. In the DED bleaching sequences, final pulp brightness reached to 75.4% using total ClO_2 of 20 kg/ton of pulp; further increase of ClO_2 to 30 kg/ton of pulp increased pulp brightness to 80.7%. But splitting of ClO_2 charges, pulp brightness reached to 85% by using only 20 kg /ton of pulp. The better delignification and higher brightness were likely the result of removing solubilized lignin by-products, which otherwise would have consumed some ClO_2. Similar results were observed elsewhere (Chirat *et al*., 2000; Jahan *et al*., 2006). Intermediate alkaline stages should not only extract the ClO_2 reaction products but also reactivate the pulp residual lignin by regenerating free phenolic groups (Berry, 1996; McKague *et al.,* 1995).

Conclusions

Kraft pulp from *Gmelina arborea* was bleached by ECF bleaching in modified sequences. Oxygen delignification reduced kappa number by 47.6%. D_0E kappa number decreased rapidly at low ClO_2 charge followed by slower decrease, which indicated over consumption of ClO_2 by non-useful reactions. Splitting of DED stages into DEDED stages increased pulp brightness from 51% to 80% using 25 kg ClO_2/ton of pulp for kraft pulp. Splitting of ClO_2 charges, pulp brightness reached to 85% by using only 20 kg /ton of pulp only for oxygen delignified pulp. Splitting of ClO_2 charge, reduced over consumption of ClO_2 through removing solubilized lignin by-products (like mucomic acid) resulted better delignification and higher brightness of the bleached pulp.

Acknowledgement

The authors wish to thank BCSIR Laboratories, Dhaka, for providing the necessary funds to carry out this research.

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Received: 23 April 2017; Revised: 02 May 2017;
Accepted: 29 May 2017.