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Elemental Chlorine Free Delignification of Chemical Pulp in Flow Through Reactor

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Abstract: Based on the known mechanisms of lignin degradation by ClO_2 , it has been shown that in conventional ECF delignification stage a significant part of applied chlorine dioxide is consumed in secondary reactions without significant effect on bleaching. This problem contributed to the principle of a typical batch reactor used for pulp bleaching in which primary reaction products can easily react with ClO_2 . In this study the strategy of pulp delignification in flow through reactor used to limit secondary reactions. The main feature of this reactor is its capability to remove the primary reaction products from the reaction zone by displacement flow. The obtained results showed that the global ClO_2 efficiency in flow through reactor depended on the temperature and chlorine dioxide concentration used for delignification. Compared to conventional batch reactor, flow through reactor enhanced significantly the effective ClO_2 efficiency toward non oxidized lignin. However, the loss of oxidizing power was considerable due to chlorate formation that restricted improvement of the global efficiency of chlorine dioxide.

Key words: Bleaching, ECF process, effective efficiency, secondary reactions, chlorate, oxidant losses, batch reactor, flow through reactor

INTRODUCTION

Several studies on the chemistry of chlorine dioxide delignification have indicated that during chlorine dioxide delignification stage, oxidation of aromatic moieties to muconic acid derivatives with only four electron transformations per aromatic ring is the main oxidation mechanism of lignin (Dence and Reeve, 1996). Theoretically, this reaction is enough for lignin extraction during following alkali stage. On the other hand, in most bleaching mills, ClO_2 is over-consumed and generally ClO_2 applied for delignification is more than twice the necessary requirement to convert aromatic groups to soluble oxidized units (Lachenal and Chirat, 2000).

During chlorine dioxide bleaching one part of chlorine dioxide loss is attributed to chlorate which is the inactive species under bleaching conditions. In the typical multi-stages $\text{D}_0\text{ED}_1\text{ED}_2$ pulp bleaching sequences, chlorate formation is occurred principally during the bleaching stages (D_1 and D_2 stages) and small amount of chlorate is formed during delignification (D_0) stage (Svenson *et al.*, 2005).

The over consumption of ClO_2 during delignification stage has been contributed to ineffective secondary

reactions in which ClO_2 reacts with initial reaction products (Lachenal and Chirat, 2000, 1999). Our previous study confirmed the reaction of ClO_2 with muconic acid derivatives as the main primary oxidation products of lignin. It was showed that muconic acid type compounds compete with non phenolic rings of lignin for chlorine dioxide consumption (Hamzeh *et al.*, 2006).

It is assumed that over consumption of ClO_2 associate to the typical pulp delignification in batch towers. Generally, conventional bleaching process is preceded by continuous mixing of ClO_2 with pulp and then fed into a batch reactor to complete the reaction time. In such conditions, the secondary reactions take place through simultaneous reactions of unconsumed ClO_2 by non oxidized non-phenolic rings and primary reaction products.

To limit the ClO_2 over consumption, it is necessary to separate primary reaction products from ClO_2 . The sequential additions of optimized small charges of ClO_2 separated by intermediate alkali extraction stages reduced significantly the consumption of ClO_2 (Hamzeh *et al.*, 2007; Lachenal *et al.*, 2007).

The secondary reactions can be limited through delignification of pulp in the flow through reactor in

which the primary reaction products can be successfully eliminated from reaction zone before over-oxidation. The potential of flow through reactor to limit secondary reactions was investigated in this study at different conditions of ClO₂ charges and temperatures. The results of delignification performance were compared with conventional DE and modified (dE)(dE)(dE) batch sequences.

MATERIALS AND METHODS

In this study, several experiments were done on a 25 kappa number mill unbleached softwood kraft pulp. The equipment used for pulp delignification consists of a water-jacked glass cylinder reactor. The interior diameter of the reactor is 6 cm and its height is 20 cm. The reaction chamber is closed at the bottom by a fixed fritted glass dick with porosity No. 2 and at the top by a removable fritted glass disk with the same porosity. The homogeneous fixed beds of pulp were formed as follows. Initially, the pulp was disintegrated in distillate water in a stainless steel blender and then diluted to 0.03% consistency. Fixed beds of pulp were formed by simultaneous draining the diluted pulp suspension and compression of formed bed to the desired consistency. This operation was repeated to obtaining a bed height of 20 cm. At the 10% consistency, the reactor holds about 56 g of the dry pulp.

The preparation of pure aqueous ClO₂ solutions proceeded by acidification of saturated aqueous NaClO₂ with 4N sulphuric acid and ClO₂ gas absorption in pure refreshed water. The prepared chlorine dioxide solution does not contain any dissolved elementary chlorine. The desired temperature (45, 55 and 70°C) of fibre bed was achieved via thermostatic bath water circulation. Delignification experiments were carried out by pumping 1200 mL chlorine dioxide solution into the reactor at a constant flow rate. The flow rate was set to provide a plug flow in the reactor (Re<0.1) (Mortha and Hamzeh, 2003). After adding chlorine dioxide solution, 600 mL of distillate water was pumped into the reactor to provide complete passage of applied chlorine dioxide through the reactor.

For each experiment, 20 mL samples were taken from each 100 mL effluent left from the reactor for pH measurement and inorganic chlorine compounds (ClO₂, ClO₂⁻, HClO and ClO₃⁻) analysis. The titration of inorganic chlorine compounds were made with dilute sodium thiosulfate (0.01 M, daily prepared) and thiodene as indicator by a modified three-step titration method according to Wartiovaara (Wartiovaara, 1982; Mortha *et al.*, 1990).

After the D stage, pulp was discharged from the reactor and washed with distillate water. Then alkali

extraction stage was carried out using 1.2% NaOH (based on dry pulp), at 10% consistency, 60°C for 60 min. The conventional bleaching stage and alkali extraction stage were performed at 10% consistency in polyethylene bags in a temperature controlled water bath. After washing and drying the pulp in ambient conditions, the kappa number of delignified pulp was determined according to T 236 om-99 Tappi Test Method.

RESULTS

Pulp delignification in batch reactor: Figure 1 shows the kappa number drop against the ClO₂ consumed in conventional batch reactor. As delignification proceeded, the delignification efficiency of chlorine dioxide decreased as a result of chlorine dioxide participation in the secondary reactions.

The linear part of the curve corresponds to the free phenolic rings oxidation with high efficiency of ClO₂. The free phenolic rings of lignin oxidized very rapidly with ClO₂ and their reaction products accumulate in the reaction medium. After oxidation of free phenolic groups, delignification proceeds through the reaction of non-phenolic units at a limited rate. The former reactions compete with the primary products oxidation produced from free phenolic rings for ClO₂ consumption (Hamzeh *et al.*, 2007).

Pulp delignification in flow through reactor: The results obtained from pulp delignification in the flow through reactor were summarized in Table 1. The results showed that the global efficiency of ClO₂ in flow through reactor depended on the temperature and chlorine dioxide concentration used for delignification. Under low charge and moderate temperature conditions, flow through reactor improved the efficiency of ClO₂. Moreover, under elevated ClO₂ charges and temperature conditions, flow through reactor contributed an extra delignification of pulp and significant improvement in ClO₂ efficiency observed. However, when high temperature and small charges of ClO₂ was applied, higher DE kappa numbers

Table 1: Comparison of DE kappa number after delignification of softwood kraft pulp in conventional batch and flow through reactor

ClO ₂ Charge (%)	Batch reactor	Flow through reactor		
		45	55	70
		----- (°C) -----		
0.0	25.0	25.0	25.0	25.0
0.5	16.7	16.0	16.3	17.4
1.0	11.3	10.3	11.6	12.2
1.5	7.8	7.1	7.6	8.0
2.0	5.3	5.0	5.4	6.0
2.5	4.8	-	3.7	3.4
3.0	4.3	-	2.7	2.3

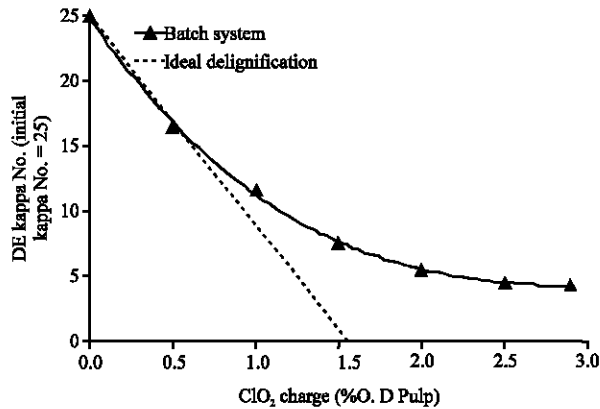


Fig. 1: Kappa number drop after DE as a function of the ClO_2 charge, D stage 70°C , 10% consistency for 1 h, E stage: 1.2%NaOH same conditions as D

DE kappa number were obtained in flow through reactor compared to batch. These results indicated that temperature played an important role in delignification performance in flow through reactor.

Inorganic chlorine compounds evolution in flow through reactor: Under acidic bleaching condition, principal reactions of chlorine dioxide with lignin can be summarized as follows (Yoon *et al.*, 2004; Svenson *et al.*, 2002, 2006).

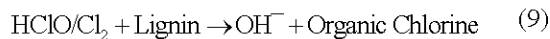
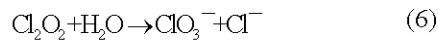
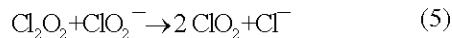
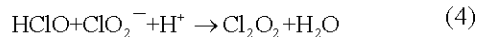
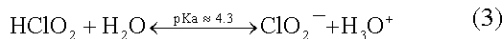
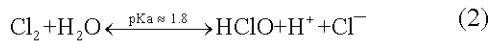
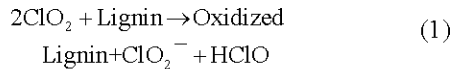


Figure 2 shows a typical example of inorganic chlorine species formed during delignification of pulp in flow

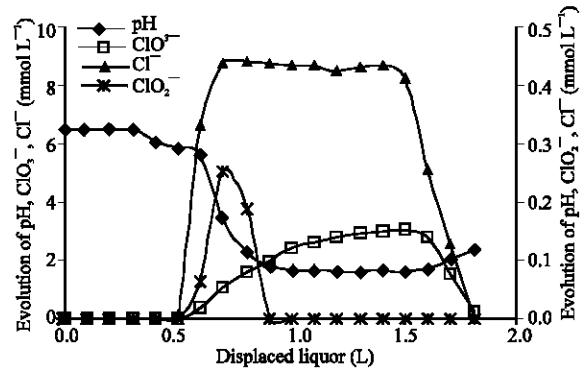


Fig. 2: Inorganic chlorinated species present after chlorine dioxide delignification of 25 kappa No. softwood kraft pulp in fixed bed (pulp consistency; 10%, ClO_2 charge; 2%, 55°C , 1200 mL ClO_2 solution + 600 mL distilled water, flow rate 25 mL min^{-1})

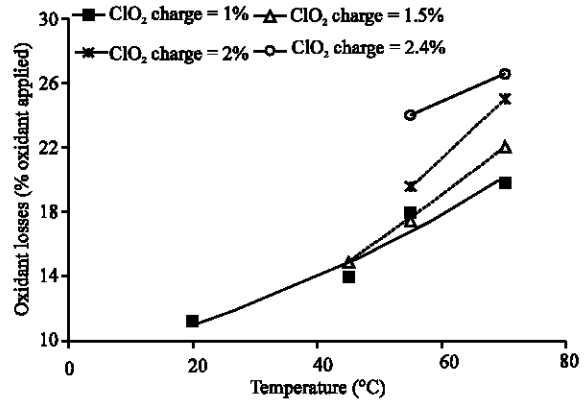


Fig. 3: Active chemical losses due to chlorate formation in function of chlorine dioxide charge and temperature, expressed as % initial chlorine dioxide oxidizing power

through reactor. These results were determined by titration of the samples taken from the reactor effluent.

Initially, the reaction front moved up and effluent came out from the top of reactor after displacement of 600 mL filtrate through the reactor. As pH dropped, the chlorite formed during the initial reaction (reaction 1) participated in several reactions resulting in ClO_2 regeneration (reactions 4-5) and chlorate formation (reaction 6, 8). During delignification the chloride ion is produced from several intermediate reactions (reactions 2, 5, 6). As shown in Fig. 3, the Cl^- concentration increased rapidly. Based on this behavior, it is concluded that the displacement of reaction front through the bed is sharp and channeling in the fiber bed and mixing in the reaction

front are small. Similar results was obtained in bleaching of mechanical pulps using the displacement system (Li *et al.*, 1996) This result confirmed our previous study on the hydrodynamic behavior of fibrous fixed bed in which small axial dispersion was seen (Mortha and Hamzeh, 2003).

As delignification preceded the chlorate formation increased progressively, then it decreased slowly during washing with distillate water. There are several inorganic reactions that attribute to ClO₃ formation (reactions 6, 7 and 8). In acidic conditions, the reactions of hypochlorous acid with ClO₂ (reaction 7) and ClO₂⁻ (reactions 4 followed by reaction 6) have been identified as the major sources of chlorate formation (Ni *et al.*, 1993). However, these reactions compete with HClO reactions with organic compounds (reaction 9).

Increasing chlorate formation with delignification in progress was attributed to the flow through reactor structure and the relative reaction rate of hypochlorous acid with organic and inorganic compounds. When delignification progresses, the ClO₂ solution has to travel a longer distance to the reaction zone thus prolonging the exposure of ClO₂ to high temperature. Moreover the small amount of non oxidized lignin remaining in the delignified zone contains essentially low reactive non phenolic rings. These conditions provide convenient conditions for ClO₂ and ClO₂⁻ oxidation with hypochlorous acid to produce chlorate.

Figure 3 shows the loss of ClO₂ oxidizing power due to chlorate formation in flow through reactor. The chlorate formation increased significantly when temperature and chlorine dioxide concentration increased. From the Figure 3, 13 to 27% of ClO₂ oxidizing power was transformed to chlorate. Contrary, in batch conditions small amounts of chlorate was formed during delignification stage. At the highest charge of ClO₂, only 7% of ClO₂ oxidizing power converted to chlorate and generally the chlorate formation was lower than 5% (Svenson *et al.*, 2005; Lindgren and Nilsson, 1975).

The higher loss of ClO₂ oxidizing power explains the results presented in the Table 1. Considering this, the comparison of batch and flow through reactor based on global efficiency of ClO₂ do not exactly indicate the flow through reactor capability to limit secondary reactions. To further analyze, comparison of the two reactors was done based on the effective oxidizing power consumed for organic materials oxidation.

Comparison of two reactors based on effective oxidation charge: The effective oxidation power is equal to applied oxidizing power as chlorine dioxide minus ClO₂ oxidizing power loss as chlorate, chlorite and residual chlorine dioxide. This can be calculated based on the number of

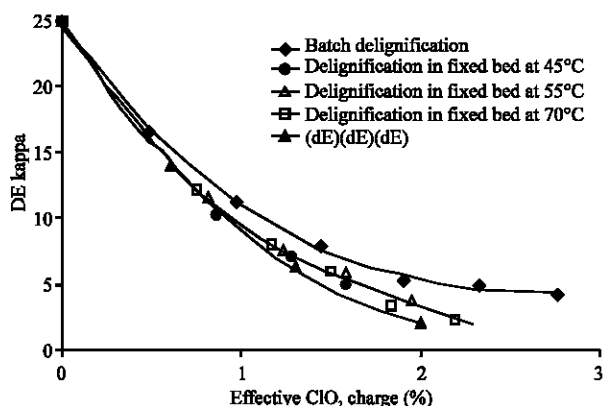


Fig. 4: Comparison of delignification efficiency based on the effective ClO₂ charge in conventional batch, subdivided D stage in batch and flow through reactor

electrons (Ne) consumed by organic materials according to equation 1 and expression the results as effective chlorine dioxide charge (Where N expresses the number of mol and 5 is the equivalent oxidation capacity of ClO₂).

$$Ne = \frac{5N_{ClO_2} - 6N_{ClO_3} - 4N_{ClO_2} - 2N_{HClO} - 2N_{Cl_2}}{5} \quad (1)$$

Figure 4 shows the comparison of batch, modified batch sequences and flow through reactor delignification based on the effective ClO₂ charge. These results differ significantly from those of earlier shown in Table 1.

Figure 4 shows that the effective efficiency of the flow through reactor is independent of reaction temperature. In equal effective ClO₂ charges, the capability of flow through reactor to eliminate primary reaction products led to lower DE kappa number. This confirmed that flow through delignification improves significantly the reaction selectivity toward non oxidized lignin compared to the conventional batch process. The modified sequences (dE)(dE)(dE) sequences improved the selectivity of ClO₂ more than that for a flow through reactor. This can be attributed to improved separation of primary reaction products in intermediate alkali extraction stages compared to acidic conditions applied in flow through reactor.

DISCUSSION

In this study flow through reactor delignification applied to limit inefficient secondary reactions during ClO₂ delignification stage. In spite of elimination the primary reaction products form reaction zone, obtained results

indicated that this technique did not improve the global efficiency of chlorine dioxide. Inorganic chlorine compounds investigation showed however, the loss of oxidizing power was considerable due to high amount of chlorate formation. This restricted the global efficiency of chlorine dioxide in flow through reactor.

CONCLUSION

This study confirmed the ineffective oxidizing power of consuming secondary reactions that occurred during pulp delignification of pulp in batch conditions. The delignification of pulp in flow through reactor increases chlorine dioxide selectivity toward non oxidized lignin and improves the effective oxidation of chlorine dioxide. Since this system involved higher undesirable chlorate formation compared to conventionally batch reactor, this technique could not be improved the global efficiency significantly.

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