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Simulation of Lignin Degradation During Chlorine Dioxide Delignification Stage

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The chlorine dioxide reaction with residual lignin of chemical pulp during delignification stage was simulated using phenolic and non-phenolic lignin model compounds applying various amounts of chlorine dioxide. Based on the reaction of model compounds and measurement of inorganic chlorinated species, three reaction phases were established for degradation of lignin model compounds. It was found that after the degradation of free phenolic units, the reaction of primary oxidized products by ClO₂ competed with the oxidation of non-phenolic aromatic structure. The results obtained by lignin model compounds were compared with the pulp delignification results. This comparison indicated two special phases for the reduction of the kappa number. The initial phase corresponded to the oxidation of phenolic units without secondary reactions. The second phase corresponded to the oxidation of the non-phenolic units in competing with secondary reactions. The results of this confirmed the over consumption of chlorine dioxide by primary oxidized lignin in the secondary reactions.

Keywords: Lignin, bleaching, efficiency, muconic acid derivatives, secondary reactions.

1 Introduction

Lignin, the second most abundant biomacromolecule is a complex aromatic polymer acting as a cementing material for lignocellulosic fibers. To obtain high-quality paper pulps, firstly, 92% to 95% of lignin is depolymerized and removed from lignocellulosic materials during chemical pulping processes. Then, the production of fully bleached pulps involves the removal of residual lignin from unbleached chemical pulp and the destruction of chromophores by bleaching processes, using a series of oxidizing chemical products, e.g., chlorine dioxide, oxygen, ozone, and hydrogen peroxide. During the past twenty years, chlorine dioxide has been the major reagent used to bleach chemical wood pulps. In a classical D₀ED₁ED₂ bleaching sequence, chlorine dioxide is applied in D₀ stage as a delignification agent and in D₁ and D₂ stages as a bleaching agent. During the delignification stage (D₀), chlorine dioxide oxidizes the aromatic units of lignin, e.g., phenolics and non-phenolics, to muconic acid derivatives as the primary oxidized products

(1–3). This is enough for the degradation and elimination of lignin during the subsequent alkali extraction (E) stage. However, it has been shown that the derivatives of muconic acid are also subject to subsequent reaction with ClO₂ in the non-desired secondary reactions (1, 4). This means that in most bleaching mills, chlorine dioxide is over-consumed and at least 40% or more, is not used to open the aromatic rings of lignin but wasted in the secondary reactions (3–5). It is well known that the reaction of the phenolic units of lignin with ClO₂ is much faster than the reaction of the non-phenolic ones (1, 2). Moreover, the oxidation of the free phenolic units of lignin occurs prior to the non-desired secondary reactions (4).

Since there are few studies available in the literature concerning the importance of the secondary reactions and their effects on the consumption of ClO₂ during the delignification stage, a better understanding of the chlorine dioxide delignification stage and a proper estimation of the starting point and the extent of secondary reactions may lead to a more efficient use of ClO₂ in bleaching chemical pulps. In this study, to determine the contribution of each species (phenolic, non-phenolic and primary oxidized products) to the consumption of chlorine dioxide in D₀ stage, the reaction of a mixture containing phenolic and non-phenolic lignin model compounds, as function of chlorine dioxide charge, was investigated under different pH values. As a

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result, the relative amounts of chlorine dioxide consumed by the primary oxidized products in the inutile secondary reactions will be clarified and discussed.

2 Experimental

All chemicals and model compounds used in this study were analytical grade, commercially available, and used without further purification. Pure aqueous ClO_2 solution was prepared by acidification of saturated aqueous NaClO_2 with 2M sulfuric acid and ClO_2 gas absorption in pure cold water.

In this study, vanillyl alcohol (3-methoxy, 4-hydroxy benzyl alcohol) and veratryl alcohol (3, 4-dimethoxy benzyl alcohol) were respectively selected as the phenolic and non-phenolic (phenol-ether) units of lignin. These models have been used in several studies as the residual phenolic and non-phenolic lignin structures in unbleached pulps (2, 4, 6). A mixture of model compounds containing 50% phenolic model compound and 50% non-phenolic one was reacted with various amounts of ClO_2 . It was chosen to approach the aromatic structure of the residual lignin of unbleached kraft pulp, typically containing 35–60% free phenolic rings after pulping (6).

The treatment of lignin model compounds was carried out in 50 mL glass flasks, capped with Teflon, and placed in a thermostatic bath. At the initial time, a known amount of ClO_2 was added to the mixture under magnetic stirring, and the reaction was done at a constant temperature (60°C) for 60 min. This time is sufficient for full consumption of applied chlorine dioxide (2). At the end of the reaction, a sample of 20 ml was taken for the titration of inorganic chlorine species (ClO_2 , ClO_2^- , HClO , and ClO_3^-). The titration was made by iodometry with dilute sodium thiosulfate (0.05 M, daily prepared) and thiodene as the indicator, employing a modified three-step titration method (7). The amounts of organic compounds were quantified before and after reaction by HPLC (P1500 pump, AS 300 Injector, UV 2000 detector from Spectra-Physics (Thermoelectron Co.) and ERC-7500 refractometer). All model compounds (phenolic and non-phenolic) were analyzed using an Alltima C18 column ($150 \times 4.6 \text{ mm} - 5 \mu\text{m}$ - Alltech Co.). The mobile phase was acetonitrile-water (10:90 v/v) and 0.1% acetic acid with flow rate 0.3 mL min^{-1} ; temperature 50°C , and UV detection at 280 nm.

To compare the obtained results from the model compounds study with the response of chlorine dioxide on pulp, an unbleached softwood kraft pulp (kappa no. 25) was treated with ClO_2 in the conventional D_0 stage conditions followed by a conventional extraction stage. D_0 stage was performed with various amounts of ClO_2 at 60°C for 60 min (10% consistency). The alkali extraction stage was done with 1.2% NaOH based on the dry weight of the pulp, 10% consistency, 70°C for 60 min.

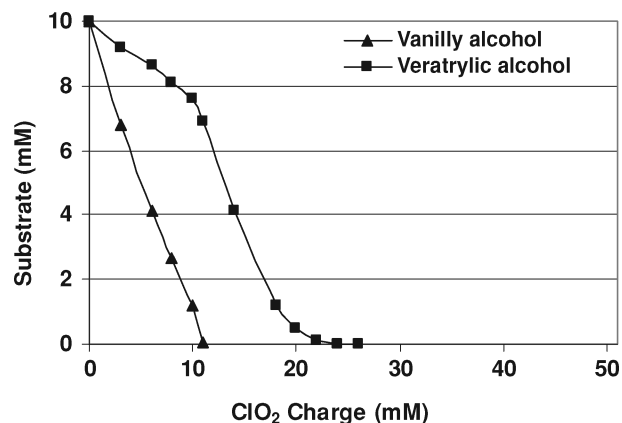


Fig. 1. Reaction of phenolic and non-phenolic model compounds of lignin by various amounts of chlorine dioxide (no pH control, 60 min, 60°C).

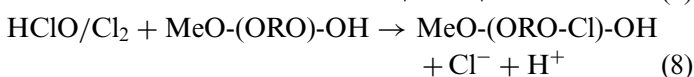
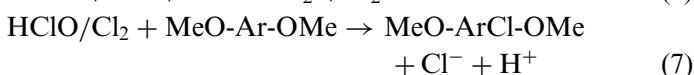
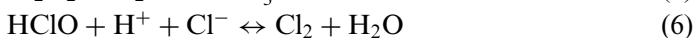
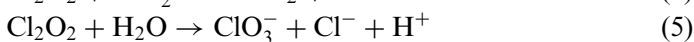
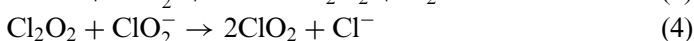
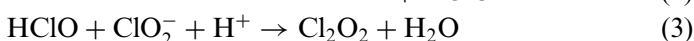
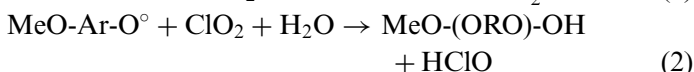
3 Results and Discussion

3.1 ClO_2 Reaction with a Mixture of Phenolic and Non-Phenolic Model Compounds at Uncontrolled pH

The concentration of model compounds and the ratio of ClO_2 /model compound were chosen to simulate the delignification stage of an unbleached pulp of kappa number 25. As seen in Figure 1, increasing amounts of chlorine dioxide were added to the mixture containing 10 mM/l of each type of the model compounds.

During the initial reaction phase, 1 mol of the phenolic compound fully degraded by approximately 1.2 mol of chlorine dioxide, whereas just 0.25 mol of the non-phenolic one reacted. After the complete degradation of the phenolic model, the ratio of residual non-phenolic model degradation versus chlorine dioxide charge was similar to the phenolic model ones. At the end, the curve flattened, and reaching the total degradation of the lignin model compounds required some excess charge of ClO_2 (Fig. 2).

According to the literature (7–10), a complete reaction scheme of ClO_2 with free phenolic compounds of lignin at acidic pH can be given as follows:



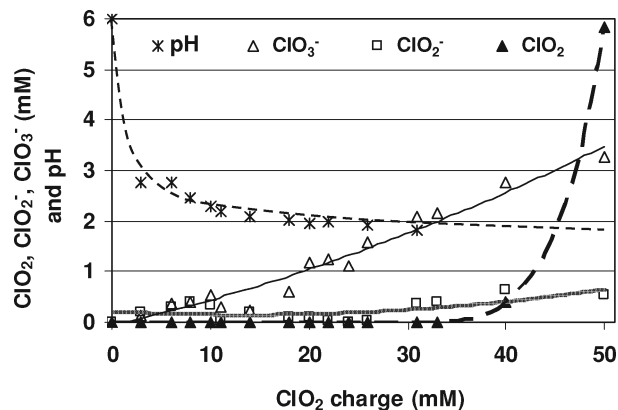


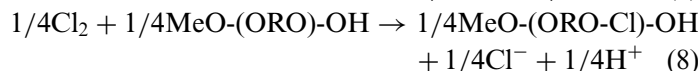
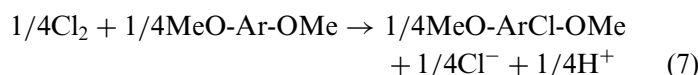
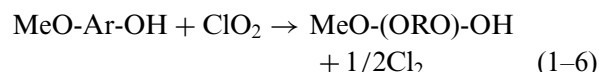
Fig. 2. Evolution of pH and inorganic chlorine species during the reaction of the equimolar mixture of phenolic and non-phenolic model compounds of lignin with various amounts of chlorine dioxide (no pH control, 60 min, 60°C).

(MeO-Ar-OH: guaiacyl phenolic moiety; MeO-(ORO)-OH: muconic acid methyl ester moiety; MeO-Ar-O[•]: phenoxy radical).

The formation of chlorinated inorganic species generally fit the above mechanism (Fig. 2). PH noticeably decreased with the increase of ClO₂ amount. Chlorite residuals were always low even at high chlorine dioxide ratios (about 2% of the applied ClO₂). The mechanism of ClO₂ regeneration caused by reactions [3–4] was fairly active in acidic medium, while reaction generating chlorate [reaction 5] was rather inactive (only 7% ClO₂ converted to chlorate at the highest charge of ClO₂). One interesting feature was that, after the disappearing of aromatic compounds, chlorine dioxide still reacted, and an excess amount of ClO₂ appeared just after 34 mmol/L of ClO₂ was applied.

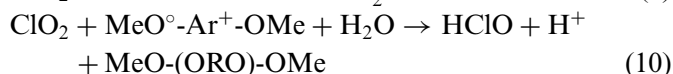
Due to the very high reactivity of ClO₂ with phenols and phenoxy radicals, it is likely that the applied ClO₂ initially reacts with these species and doesn't with non-phenolic compounds, producing 10 mM/1 muconic acid methyl ester moiety. Despite the fact that hypochlorous acid contributes to ClO₂ regeneration [3–4], the non-phenolic molecules may react with the hypochlorous acid continuously produced and remaining in excess. Hypochlorous acid is in equilibrium with molecular chlorine and globally 1/2 mol of HClO/Cl₂ per mol of ClO₂ is available for other reactions. Svenson *et al.* (8, 9) in a study on the treatment of non-phenolic compounds with ClO₂ indicated that the generated chlorine mainly reacted for the chlorination of non-phenolic substrates. The results of Seger (11) also confirmed the production of considerable amounts of chlorinated aromatic rings during the treatment of non-phenolic compounds with ClO₂. Regarding the Cl₂ generation and the presence of identical amounts of muconic acid methyl ester moiety and non-phenolic compounds in the reaction medium, the following stoichiometry can therefore be established for the reaction of phenolic and non-phenolic

units of lignin during the initial reaction phase:



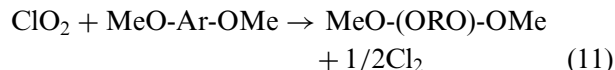
As illustrated above, one can conclude that during the initial reaction phase, the entire phenolic compound was destroyed in the oxidation reactions, while 25% of the non-phenolic one participated only in chlorination reactions.

As displayed in Figure 1, after the phenolic model was completely degraded, the reaction was followed through the reaction of non-phenolic compound in the second phase of reaction. This involves an attack of ClO₂ on one ether linkage and leads to a di-ester compound [12]:

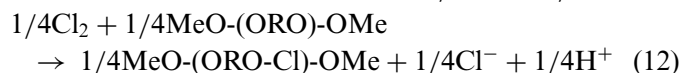
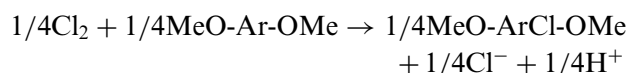


(MeO-Ar-OMe: guaiacyl non-phenolic moiety; MeO-(ORO)-OMe: muconic acid dimethyl ester structure).

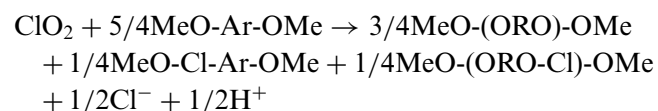
Allowing for further reactions of HClO (ClO₂ regeneration reactions [3–4] and reaction [6]):



Finally, if chlorination reactions follow:



The global stoichiometry is obtained:

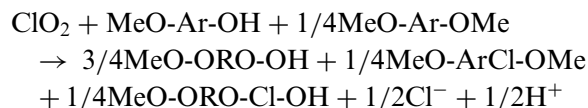


As a result, during the second phase, the consumption ratio of model compound/ClO₂ should be 1.25 which was comparable to the ratio slightly higher than 1.2 obtained in Figure 1. Thus, during the two steps approximately 50% of the starting non-phenolic compound (presented in Fig. 1) was degraded due to chlorination and the remaining 50% due to oxidation.

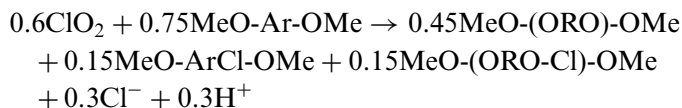
Figure 2 also illustrates that chlorine dioxide could react (3rd reaction phase) even after the two models disappeared. The substrates were then the primary model oxidation products and the chlorinated non-phenolic compounds. An excess of ClO₂ appeared only after consumption of approximately 34 mmol/L of ClO₂. Since no remaining active chlorine except a trace amount of unreacted chlorite was

titrated in the medium and accounting the small chlorate formation (2 mM), the delignification stoichiometry could be summarized according to the following equations:

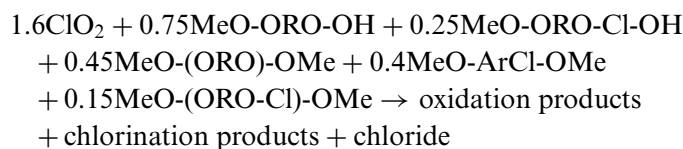
1st phase, oxidation of the phenolic units and chlorination a part of the non-phenolic units:



2nd phase, reaction of the remaining non-phenolic (MeO-Ar-OMe) units:



3rd phase, reaction of the chlorinated non phenolic, muconic acid, and muconic acid methyl ester units:



In the above stoichiometric scheme, the reaction of muconic acid type moieties attributes to the general reaction scheme presented by Brage *et al.* (13) which involves the successive attacks of two molecules of ClO_2 on the $\text{C}=\text{C}$ double bonds followed by the release of HClO and HClO_2 in various proportions, depending on the decomposition path of the chlorite ester intermediate.

From this scheme, a total number of 32 mM of ClO_2 would be consumed for 20 mM of aromatic units. This indicated the transfer of 8 electrons per aromatic unit as the active oxidizing power, and a waste of 0.6 electron as chlorate. Therefore, the total oxidizing power consumption reached more than twice the number theoretically required for the full reaction of aromatic units. This result was in general agreement with the values reported in literature for delignification stage, typically 8–10 eq/mol of aromatic units (calculations are given in appendix 1).

3.2 ClO_2 Reaction with a Mixture of Phenolic and Non-Phenolic Model Compounds at pH 4.2

One important point in the delignification stoichiometry appeared to be the important role of HClO/Cl_2 as the intermediates. Based on the above mechanism, at a pH above 4 and in the presence of small amounts of chloride (which may not reflect the real case of mill liquors generally enriched in chloride due to recirculation loops), equilibrium reaction [6] should be displaced towards the left, and small amounts of molecular chlorine should be present in the medium. According to Svenson *et al.* (8, 9) and Gunnarson *et al.* (14), the reaction of HClO/Cl_2 with organic substrates depends on pH values. At lower pH values, high amounts of chlorinated products were obtained via Cl_2 reaction in the

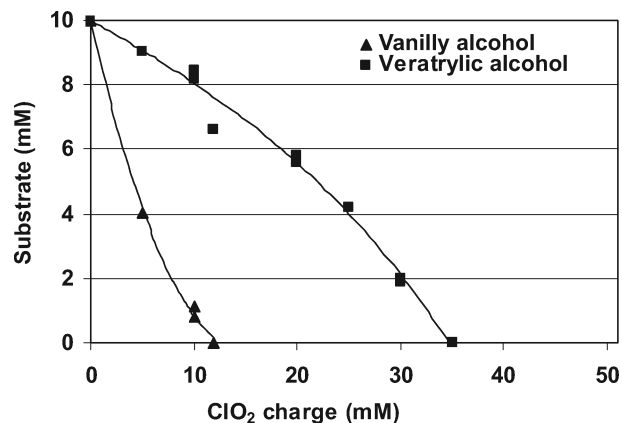


Fig. 3. . Reaction of phenolic and non-phenolic model compounds by various amounts of chlorine dioxide (buffered milieu at pH 4.2- acetate buffer, 60 min, 60°C).

treatment of non-phenolic compounds with ClO_2 (8, 9, 14). However, higher end pH resulted in a greater amounts of oxidized products via HClO reaction, because hypochlorous acid has the highest oxidation potential among inorganic chlorine agents, i.e., $E_0 = 1.49$ volts vs 1.36 volts for Cl_2 . Thus, higher pH limits chlorination reactions, and the degradation of non-phenolic compounds could be attributed mainly to oxidation reactions.

In Figures 3–4, the evolutions of organic and inorganic compounds at a buffered pH of 4.2 (acetate buffer) can be compared to the plots of Figures 1–2 at uncontrolled, more acidic pH.

The reaction of the phenolic compound was not affected by pH change, and the same amount of ClO_2 consumed for total reaction. Conversely, the reaction of the non-phenolic compound significantly decreased. Total degradation of the both compounds required approximately 36 mmol of ClO_2 . A modified value of 33 mmol of ClO_2 was found after the correction of the remaining chlorine dioxide, chlorite, and chlorate at the end of the reaction (Fig. 4). It is interesting

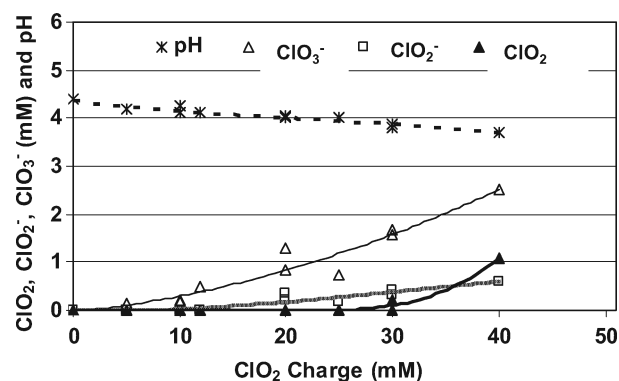


Fig. 4. Evolution of pH and inorganic chlorine species during the reaction of phenolic and non-phenolic compounds (buffered milieu at pH 4.2-acetate buffer, 60 min, 60°C).

to notice that this value was close but slightly higher than the value of 32 mmol obtained at uncontrolled pH.

Since the full degradation of non-phenolic compound has combined with the ClO_2 appearing, it could be concluded that the primary reaction products, namely the muconic acid type structures, were degraded together with the non aromatic unit oxidation. This appeared as an important result, suggesting that the oxidation rate of non-phenolic rings was similar to the reaction rate of muconic acid type structures.

It is also interesting to note that the evolution of the inorganic compounds only slightly changed with pH change from 2 to 4.2. The only significant difference was a slightly higher amount of chlorite, with no significant difference of chlorate formation, therefore indicating that the regeneration mechanism of ClO_2 through reactions [3–4] still occurred well at this pH.

3.3 Effect of pH on the Reaction of Pure Veratryl Alcohol with ClO_2

The effect of pH and the role of HClO as oxidant or Cl_2 as the chlorination agent of non-phenolic groups were tested by studying the reaction of pure veratryl alcohol with ClO_2 . The results (Fig. 5) showed that the effect of pH was significant. At buffered pH 4.2, the rate of veratryl alcohol degradation was approximately 2:1 mol ClO_2 /mol substrate. Since the ClO_2 regeneration mechanism was active (no chlorite at the end, full consumption of ClO_2 and little chlorate), the consumption of 2 mol of ClO_2 for the reaction of 1 mol of veratryl alcohol confirmed that the reaction rate of ClO_2 with the primary reaction products of veratryl alcohol was more or less similar to the oxidation rate of veratryl alcohol by chlorine dioxide.

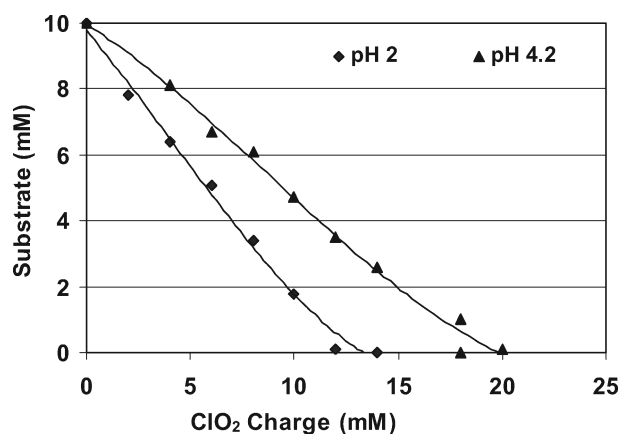


Fig. 5. Reaction of veratryl alcohol with various amounts of ClO_2 at different pH values (60 min, 60°C).

3.4 Comparison of the Stoichiometry Observed in the Model Compounds with ClO_2 Delignification of Kraft Pulp

In order to compare the obtained results based on model compounds with chlorine dioxide response on pulp, a 25 kappa number unbleached softwood kraft pulp was treated by ClO_2 in the conventional D_0 stage conditions followed by a conventional extraction stage in pure water. This pulp contained 52% of free phenolic units, a value measured on extracted lignin (acidolysis) by ^{13}C NMR spectroscopic analysis (5, 6, 15).

In Figure 6, the stoichiometric response can be compared by plotting the variation of the aromatic unit of lignin in the pulp against the molar charge of ClO_2 . The calculation was based on the molar mass of aromatic unit of lignin as 200 g/mol. It can be observed that the behavior of delignification followed two different phases. A linear kappa number reduction was observed until reaching a ClO_2/C_9 ratio of about 0.5. This corresponded to about 50% elimination of aromatic units, i.e., all phenolic groups were oxidized to muconic acid type compounds which were fully extracted from the fiber matrix in the alkaline extraction medium. After this phase, the secondary reduction of kappa number corresponded with the reduction of the non-phenolic compounds due to oxidation. In this phase, ClO_2/C_9 ratio increased and extended oxidation by higher charge of chlorine dioxide seemed necessary to reach a desired kappa number after the alkaline extraction stage.

The comparison of the reaction of model compounds and pulp with chlorine dioxide showed that the free phenolic groups would be degraded in the initial and very efficient phase of pulp delignification. The released chlorine would participate mainly in the chlorination of non-phenolic aromatic units.

In the second phase of pulp delignification, the competitive reactions of ClO_2 with the non-phenolic groups and primary reaction products of phenolic oxidation decreased

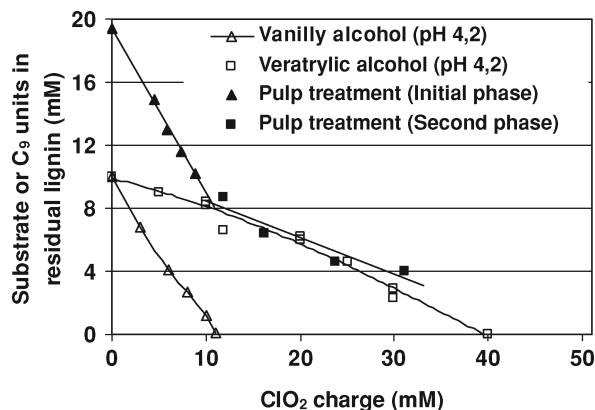


Fig. 6. Comparison of the degradation of lignin model compounds and residual lignin of kraft pulp (D_2 stage in pure water, pulp consistency 10%, 60 min, 60°C).

the ClO_2 efficiency, and a desired kappa number after alkaline extraction could be obtained only after the complete oxidation of all aromatic units. This suggests that the alternative low-charges of ClO_2 and E treatments of the type dEdE... (d = D at low charge), would results in a significant decrease in chlorine dioxide consumption and could be considerably more advantageous compared to a single D_0E treatment.

4 Conclusions

This study showed that the stoichiometric behavior of ClO_2 delignification during D_0 stage can be simulated by the behavior of mixtures of phenolic and non-phenolic lignin model compounds. The effect of pH was important since it determined the probable route of the chlorination and oxidation of non-phenolic units. The results indicated that the reaction of muconic acid type structures with ClO_2 competed with the oxidation of non-phenolic aromatic structures after the degradation of free phenolic units. The stoichiometry observed on pulp was close to that of model compounds. A desired kappa number level can be observed after the complete oxidation of all aromatic units.

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Appendix 1.

Assuming,

- I. That a chlorine multiple of 0.20 applied in D_0 on a kappa no. 25 softwood unbleached pulp typically produces a reduction of 20 kappa number units,
- II. That a lignin content/kappa number ratio of 0.155 is a good estimate for softwood unbleached kraft pulp,
- III. That the average molecular weight of an aromatic C_9 unit is within the range [185–200] g/mol,

One finds that, in 100 g of pulp, containing 3.1 g of lignin, i.e., [15.5–16.7] mmol of lignin are oxidized; the applied ClO_2 as active chlorine on pulp is 5%, i.e., 141 meq; thus the oxidation ratio is within the range [8.4–9.1] eq/mol of aromatic unit (corresponds to 1.7–1.8 mol ClO_2 /mol aromatic unit). This is exactly the same range as with the mixture of model compounds that simulates lignin oxidation.