

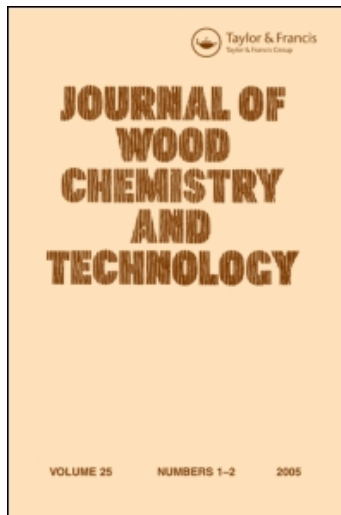
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Comparative Studies of Chlorine Dioxide Reactions with Muconic Acid Derivatives and Lignin Model Compounds

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Abstract: The reaction of chlorine dioxide with different types of lignin model compounds was investigated in order to compare the kinetics and to evaluate the amount of oxidant consumed by the different substrates. Complete reaction of lignin model compounds was observed at ClO₂-to-substrate molar ratios of 0.9–1.2, which corresponds to an electron transfer varying between 5–6 equivalents per mole of substrate. Muconic acid derivatives also fully reacted, at a ClO₂-to-substrate molar ratio of 1.2, with the oxidant consumption being about 4 equivalents per mole of substrate. The reaction of mixtures of phenolic, non-phenolic, and muconic acid type substrates showed that the reaction rates of non-phenolic and muconic acid type substrates were rather similar. This study suggests that further reaction between ClO₂ and the primary lignin oxidation products, such as muconic acid type structures could be the cause of overconsumption of oxidant in a D stage.

Keywords: Chlorine dioxide, delignification, efficiency, muconic acid derivatives, lignin model compounds

INTRODUCTION

Numerous studies have been devoted to understanding the chlorine dioxide bleaching mechanism. This has been generally done by treating lignin

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model compounds under bleaching conditions. It was established that the major oxidation pathways were the conversion of lignin aromatic rings to o-quinone or muconic acid type structures, involving the exchange of two or four electrons respectively.^[1-4] In this process, chlorous and hypochlorous acids are released and the subsequent oxidation of chlorous acid by hypochlorous acid regenerates chlorine dioxide, which reacts further with the lignin. The amount of ClO_2 needed for aromatic rings opening and the formation of muconic acid type structures, which involves the exchange of four electrons per aromatic unit, should theoretically be sufficient for lignin solubilization. However, it is frequently observed that the amount of ClO_2 applied for lignin extraction reaches more than twice the calculated theoretical amount.^[5-7] The reasons why ClO_2 is overconsumed and why its oxidation efficiency on the organic matter decreases beyond a certain charge are not fully understood. It is well established that ClO_2 reacts rapidly with free phenolic units in lignin and their reaction products accumulate in the reaction medium. In an unbleached kraft pulp, the latter represent 40 to 50% of the total aromatic units of residual lignin. Thereafter, in the absence of free phenolic units, delignification should proceed through reactions of non-phenolic units. It is suggested that reactions of non-phenolic units compete with reactions of the primary products (secondary reaction) of the reactions of the free phenolic units.

Recently, some hypotheses for ClO_2 overconsumption by organic compounds in pulps have been discussed.^[5] It was shown that during a D_0 stage, secondary reactions could be partly avoided by splitting the ClO_2 charge to several successive (DE) (DE) (DE) stages. This reduced the total consumption of ClO_2 by at least 20%.

The reactions of ClO_2 with the primary products formed during delignification have not been extensively investigated. Barton^[8] attributed the presence of oxalic and fumaric acids in the effluents of a chlorite delignification stage to the oxidation of muconic acid resulting from the oxidation of lignin by ClO_2 generated from chlorite decomposition. Studying the reactions of lignin model dimers (5-5', 5- CH_2 -5', and β -O-4 structures), McKague et al.^[9,10] attributed the formation of maleic acid derivatives to oxidative cleavage of muconic acid by ClO_2 . Another study^[11] on the reaction of ClO_2 with a hardwood lignin model compound (4-methylsyringol) showed that one mole of this compound reacted with two moles of ClO_2 , which led to the formation of 2,3-dihydroxy-5-methyl-1,4 benzoquinone, whereas three moles of ClO_2 led to a ketoacid ester and maleic acid, which implied that primary products were being further degraded. According to Masschelein,^[12] when the molar ratio of chlorine dioxide to phenolic compounds is greater than 5, the main reaction products are oxalic, maleic, and fumaric acids. The reaction of chlorine dioxide with muconic acid structures is analogous to the reaction of ClO_2 with the hexenuronic acids present in some kraft pulps.^[13,14] Muconic and hexenuronic acids have structural similarities with double bonds conjugated to carboxylic groups. All these

studies have shown that part of the oxidizing power of ClO₂ could be consumed in useless reactions because conversion of the phenolic structures into muconic acid structures should be sufficient for lignin solubilization.

In this study, the number of oxidant equivalents necessary to fully oxidize lignin model compounds of phenolic or non-phenolic types was determined. Then, the reaction of muconic acid derivatives with chlorine dioxide was investigated. Finally the competition between reactions of different model compounds was studied.

RESULTS AND DISCUSSION

Reaction of Lignin Models Compounds with ClO₂

First, the amount of chlorine dioxide required for complete reaction of the lignin model compounds was studied. In separate experiments, vanillin, vanillyl alcohol and veratryl alcohol were treated using ClO₂-to-substrate molar ratios of 0.2 to 1.5. The remaining substrate was quantified by HPLC and the loss of oxidizing power due to the formation of chlorate and chlorite was determined. The ClO₂ applied was fully consumed. At low ClO₂ charges, quantities of chlorate and chlorite were negligible, whereas at higher charges, about 7% of the initial ClO₂ was transformed into chlorite and chlorate. Figure 1 shows the quantity of chlorine dioxide required for complete consumption of the lignin model compounds. The substrates were completely consumed when a molar ratio of 0.9 to 1.2 was applied.

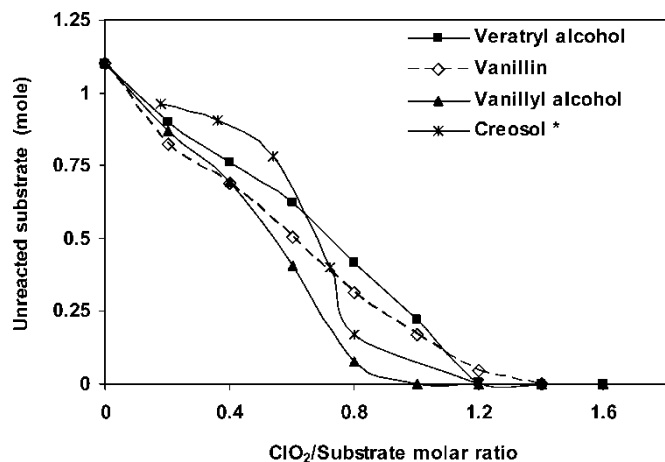


Figure 1. Reaction of lignin model compounds at various chlorine dioxide charges (initial concentration of substrate 10 mmol/L, temperature 70°C, reaction time 30 min). *Data for creosol from Nonni and Dence.^[15]

The low molar ratio (0.9) obtained for vanillyl alcohol could be due to the fact that ClO_2 reacts with it much faster than with its reaction products, thus consuming less ClO_2 . The higher ClO_2 consumption by veratryl alcohol and vanillin indicated that secondary reactions must be involved more extensively. In previous studies, Svenson et al.^[16] and Gunnarsson et al.^[17] also found that veratryl alcohol was totally consumed at a (ClO_2 :substrate) molar ratio of 1.25. The time required for complete reaction of the substrate was 30 min. The higher ClO_2 consumption by veratryl alcohol can be explained by the much lower reactivity of the non-phenolic unit, increasing the competition with the oxidation of the primary reaction products. This is supported by the results obtained by Seger et al.^[18] who identified extensively oxidized products when 3,4-dimethoxybenzoic acid was reacted with ClO_2 at 70°C. In the case of vanillin, oxidation of the aldehyde group may have competed with ring opening reactions.^[3,12]

Oxidant consumption by the substrates after correction for chlorate and chlorite formation is reported in Table 1. The oxidant required for the complete degradation of veratryl alcohol, vanillin, and vanillyl alcohol was about 5.9, 6.1, and 4.9 equivalents, respectively. A higher ClO_2 charge led to further oxidation of the primary products, which increased the oxidant consumption to values as high as 11.3 equivalents at a ClO_2 molar ratio of 2.4 in the case of vanillin. The fact that some chlorination of organic material occurred during ClO_2 delignification, due to the action of hypochlorous acid intermediate, could explain that the oxidant consumed by vanillyl alcohol was 4.9 instead of the theoretical 4 value. The rate of ClO_2 reaction with nonphenolic units is very low and takes place at the side chain when the pH is higher than 5.^[16] This could explain the 3.4 equivalents consumed at the 0.2 ClO_2 /substrate ratio. At higher charges (lower pH) aromatic ring oxidation, involving four-electron transfer, would be more dominant.

Table 1. Oxidant consumption by substrates at different charges of ClO_2 (eq/mole)

ClO_2 /substrate molar ratio	Veratryl alcohol	Vanillin	Vanillyl alcohol
0.2	3.4	6.1	5.0
0.4	5.6	6.3	5.0
0.6	5.8	6.0	4.9
0.8	5.7	6.1	4.2
1	5.9	6.1	4.9
1.2	6.2	6.1	5.9
1.4	6.8	6.9	6.7
1.6	7.8	7.9	7.7
2.4	—	11.3	—

Nonni and Dence^[15] reported that creosol was completely degraded to non-aromatic products (Figure 1) at a ClO₂ molar ratio of 1.2. This result showed that the full conversion of creosol involved around 6 equivalents of oxidant.

Reaction of Maleic and Muconic Acids with ClO₂

Additional evidences of chlorine dioxide consumption by primary oxidation products can be provided by studying the reaction of maleic and muconic acid type model compounds with ClO₂ in aqueous medium. It was found that maleic acid treated with an excess of ClO₂ was stable during several hours even at high temperature. Under the same condition, methyl maleic acid reacted slowly with chlorine dioxide. These results are consistent with studies of the reactions of lignin model compounds with an excess of ClO₂ where maleic acid was found as a final product.^[9,10,12]

Results for muconic acid treatments with ClO₂ are presented in Figure 2. The ClO₂ reacted with muconic acid at a rate that depended strongly on temperature and substrate concentration. At the highest muconic acid concentration (19 mmol/L) and at the highest temperature (80°C), muconic acid was almost totally consumed after 5 h.

Kinetic experiments with muconic acid were also performed in the presence of dimethylsulfoxide (DMSO) as a trapping agent for intermediate

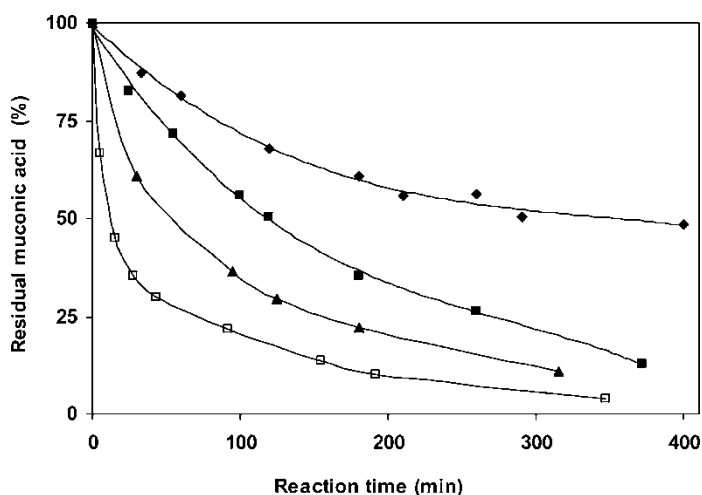


Figure 2. Reaction of ClO₂ with muconic acid in aqueous medium; molar ratio ClO₂ to substrate = 7; initial muconic acid concentration of 4 mmol/L and temperatures of 50°C (◆), 70°C (■) and 80°C (▲); initial muconic acid concentration of 19 mmol/L and temperature 70°C (□).

Cl_2 and HClO possibly generated during the reaction with ClO_2 .^[19] Results in Figure 3 show that the reaction rate was only slightly affected by the presence of DMSO, which is consistent with the main degradation pathway being the reaction between muconic acid and chlorine dioxide itself. Similar results have recently been reported by Torngren et al.^[13] who studied the reaction between hexenuronic acid and chlorine dioxide. They also found that it was not significantly hindered by the presence of sulfamic acid, a masking agent of hypochlorous acid. Lindgren and Svahn^[20,21] showed that the reaction of cyclohexene and methyl oleate with chlorine dioxide led to cleavage of the double bond as a result of direct attack of chlorine dioxide itself.

The concentrations of inorganic species such as chlorine dioxide, chlorite, and chlorate during the reaction were also analyzed (Figure 4). The rate of ClO_2 consumption followed that of muconic acid degradation. Chlorite was detected and its concentration increased slowly with reaction time until a maximum of 0.3 mmol/L. Interestingly, it was found that about 30% of the ClO_2 was converted into chlorate. The chlorate may be formed by reaction of chlorine dioxide with free radicals such as ClO^\bullet or other organic radicals.^[16,17,22,23]

Reaction of Dimethyl Muconic Acid with ClO_2

Results in the previous section have shown that ClO_2 reacted with muconic acid at lower rates than with aromatic model compounds. In

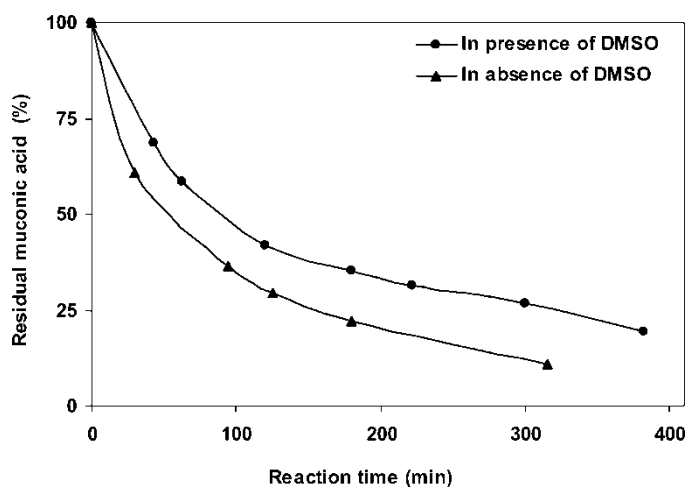


Figure 3. Effect of HClO trapping by dimethylsulfoxide (DMSO) on the reaction rate of ClO_2 with muconic acid at 80°C with initial concentrations of muconic acid and ClO_2 of 4 mmol/L and 28 mmol/L, respectively.

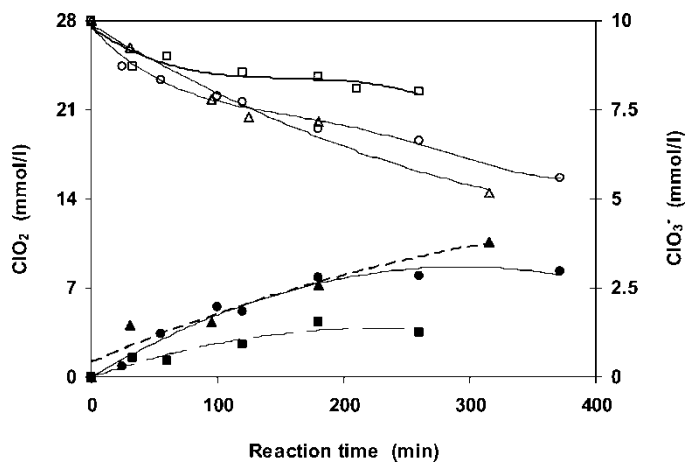


Figure 4. Inorganic species generated during the reaction of muconic acid (4 mmol/L) with ClO₂ (28 mmol/L): ClO₂ concentration at 50°C (□), 70°C (◇), and 80°C (▲); chlorate concentration at 50°C (■), 70°C (◆), and 80°C (▲).

fact, the structure of unsubstituted muconic acid is too simple and may not be representative of substituted structures likely to be found in primary lignin oxidation products. Because the initial attack of chlorine dioxide is electrophilic in nature, the reactivity of ClO₂ on the carbon-carbon double bond in organic compounds should depend on the electron-donating character of substituents at positions adjacent to the double bond.

For this reason the reactivity of ClO₂ with dimethyl muconic acid (DMMUA) was investigated to see the effect of an electron-donating group (-CH₃) α to the double bond. DMMUA reacted much faster than unsubstituted muconic acid. The reaction occurred even at room temperature and with small amounts of chlorine dioxide. The amount of residual DMMUA reacted versus ClO₂ charge is shown in Figure 5.

DMMUA was completely degraded when a ClO₂-to-substrate molar ratio of 1.4 to 1.6 was applied. The equivalents of oxidant consumed by DMMUA, after correction for chlorate and chlorite formation, showed that at low ClO₂ charges (<equimolar amount of ClO₂), the reaction of DMMUA resulted in a two-electron transfer process. At higher charges, oxidation was more extensive and approximately 4 oxidant equivalents per mole of DMMUA were consumed. It may be concluded that, in general, the reaction of the DMMUA with ClO₂ followed pathways analogous to those described for olefinic structures.^[24,25] For example, at the lower amounts of chlorine dioxide, only one of the double bonds was transformed by a 2 electron exchange leading to products with a diol structure. At higher charges the other double bond would react in the same way.

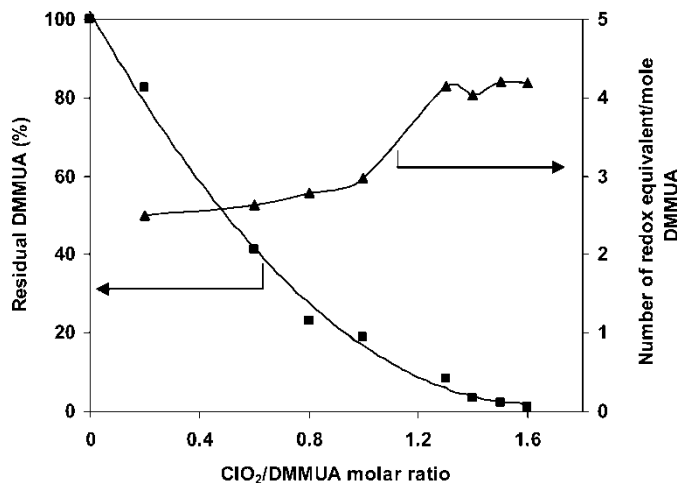


Figure 5. Reaction of chlorine dioxide with dimethyl muconic acid (DMMUA) at various ClO₂ charges (initial concentration of DMMUA 19 mmol/L, temperature 70°C, reaction time 10 min).

Competing Reactions of ClO₂ with Dimethyl Muconic Acid and Veratryl Alcohol

These experiments were carried out to see how the reaction of ClO₂ with DMMUA could affect the efficiency of ClO₂ reaction on lignin model compounds. A mixture containing equimolar amounts of veratryl alcohol and DMMUA were oxidized with various amounts of chlorine dioxide. The unreacted compounds were quantified by HPLC (Figure 6). As can be seen by comparing Figures 1 and 6, the presence of DMMUA hindered the oxidation of veratryl alcohol. To degrade veratryl alcohol alone, 1.2 moles ClO₂ was required whereas in the presence of DMMUA about 2 moles of ClO₂ had to be applied. On complete degradation of the veratryl alcohol about 50% of DMMUA was also consumed. This indicates that DMMUA and veratryl alcohol do compete for the ClO₂.

Competing Reactions of ClO₂ with Dimethyl Muconic Acid, Veratryl Alcohol, and Vanillin

Vanillin was added to the previous mixture of veratryl alcohol and DMMUA. The results of the oxidation of an equimolar mixture of the model compounds are shown in Figure 7. The ClO₂ necessary to fully degrade vanillin was increased compared to the case of pure vanillin. The ClO₂-to-substrate molar ratio was increased from 1.2 (Figure 1) to 1.8 (Figure 7).

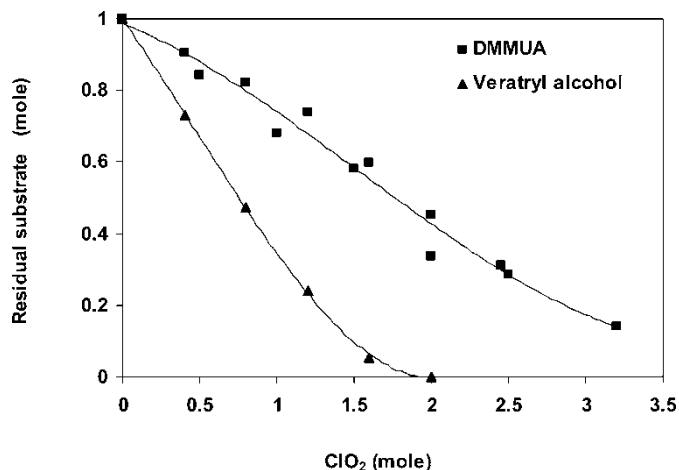


Figure 6. Competing reactions of ClO₂ with an equimolar mixture of veratryl alcohol and DMMUA at various ClO₂ charges (initial concentration of model compounds was 19 mmol/L, temperature 70°C, and reaction time 60 min).

When DMMUA was present, a charge of 2.7 mole of ClO₂ was necessary to fully degrade both vanillin and veratryl alcohol. According to Figure 1 a total of 2.4 moles of ClO₂ should have been enough to degrade these 2 compounds by themselves. This indicates that DMMUA competed for the ClO₂ with the two other compounds.

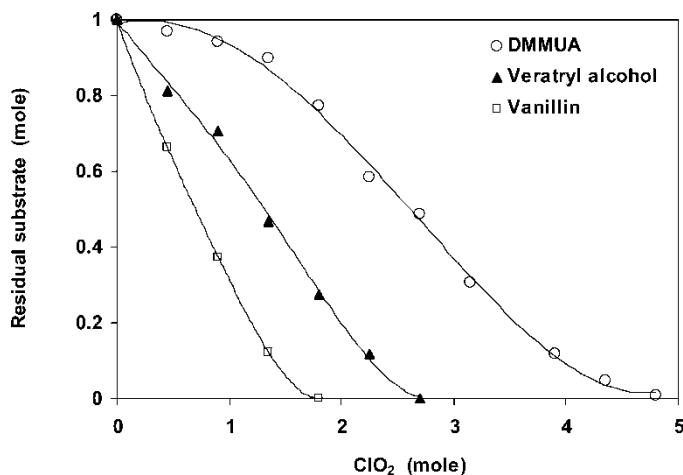


Figure 7. Competing reactions of ClO₂ with an equimolar mixture of vanillin, veratryl alcohol, and DMMUA at various ClO₂ charges (initial concentration of model compounds was 10 mmol/L, temperature 70°C, and reaction time 60 min).

Comparison of the curves shows that under the conditions of the present study, the reaction rate of the non-phenolic compound (veratryl alcohol) was still higher than the rate for the muconic acid derivative (DMMUA). However, during kraft pulp delignification by ClO_2 , other kinds of structures can be involved and some muconic acid structures might react as rapidly as non-phenolic rings. This point of view was supported by the study of McKague et al.^[9] where the muconic acid structure formed by the opening of free phenolic rings in a β -O-4 dimer underwent stepwise oxidative degradation yielding maleic acid derivatives, whereas the second aromatic ring (nonphenolic) remained essentially stable. This higher reactivity of the muconic acid structure may be attributed to the electron-donating effect of the aromatic ring related to the double bond which enhances the reactivity. Moreover, the reactivity of muconic acid structures and non-phenolic ring are also affected by pH variations. As the pH is increased, the reaction rate of non-phenolic structures decreases^[16,17] whereas the reactivity of muconic acid structures is not affected.^[22] Therefore, a higher pH would enhance secondary reactions during ClO_2 delignification.

EXPERIMENTAL

All chemicals and model compounds used in this study were commercially available. The pure ClO_2 solution was prepared by acidification of a saturated NaClO_2 solution with 2M sulfuric acid. The treatments of model compounds with pure chlorine dioxide were performed in a 50 mL glass flask placed in a thermostated water bath. A calculated amount of ClO_2 was added to an aqueous solution of model compound under magnetic stirring and the reaction was allowed to proceed at constant temperature. At the end of the reaction period, a 10 mL sample was taken for inorganic analysis (ClO_2 , ClO_2^- and ClO_3^-) using modified iodometry.^[23,26]

Amounts of organic compounds were quantified before and after reaction by HPLC (P1500 Pump, AS 300 Injector, and UV 2000 detector from Spectra-Physics, ERC-7500 refractometer). Lignin model compounds (phenolic or non-phenolic) were analyzed on an Alltima C18 column (150 mm \times 4.6 mm – 5 μm – Alltech), using a mobile phase composed of acetonitrile-water (10 : 90) (vol) and 0.1% acetic acid, a flow rate of 0.3 mL/min, a temperature of 50°C, and UV detection at 280 nm. Muconic acid derivatives were analysed using a RT 300-6.5 Polyspher OAHY column (Merck) and the eluting solvent was 0.01 N H_2SO_4 at 0.3 mL/min, a temperature of 50°C, and refractometry detection. In the case of model compound mixtures (studies of competing reactions), the organic compounds were analyzed using the same conditions as for phenolic compounds.

CONCLUSIONS

During ClO₂ delignification the reactions of primary lignin oxidation products such as muconic acid derivatives can be significant and compete with reactions of nonphenolic structures. As a consequence more oxidant must be applied for delignification than that necessary for just opening of aromatic rings. This study also suggests that any excess of ClO₂ should be avoided, which explains the benefit of sequential addition of small charges of chlorine dioxide separated by alkaline extraction.

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