

# Fenton's Reagent–Mediated Degradation of Residual Kraft Black Liquor

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## Abstract

In this work, the effect of Fenton's reagent on the degradation of residual Kraft black liquor was investigated. The effect of Fenton's reagent on the black liquor degradation was dependent on the concentration of H<sub>2</sub>O<sub>2</sub>. At low concentrations (5 and 15 mM) of H<sub>2</sub>O<sub>2</sub>, Fenton's reagent caused the degradation of phenolic groups (6.8 and 44.8%, respectively), the reduction of reaction medium pH (18.2%), and the polymerization of black liquor lignin. At a high concentration (60 mM) of H<sub>2</sub>O<sub>2</sub>, Fenton's reagent induced an extensive degradation of lignin (95–100%) and discoloration of the black liquor. In the presence of traces of iron, the addition of H<sub>2</sub>O<sub>2</sub> alone induced mainly lignin fragmentation. In conclusion, Fenton's reagent and H<sub>2</sub>O<sub>2</sub> alone can degrade residual Kraft black liquor under acidic conditions at room temperature.

Index Entries: Fenton's reagent; free radicals; hydrogen peroxide; hydroxyl radical; Kraft black liquor; lignin degradation; pulp mill effluent treatment.

## Introduction

Black liquor, an intermediate product of the Kraft process for production of pulp, is one of the most important industrial fuels (1). It is burned in recovery boilers with the objective of simultaneous recovery of heat and chemicals (sodium and sulfur) (1). However, in most developing countries.

Kraft plants are not always fully equipped with recovery units. Therefore, the pulp industry in these countries produces high amounts of residual Kraft black liquor, which are rather difficult to dispose of and represent an environmental problem. On the other hand, Kraft black liquor has valuable chemical compounds that could be utilized such as lignin and some metals (2).

Fenton's reagent has been widely used to treat a variety of industrial wastes containing a range of toxic organic compounds such as phenols, formaldehydes, pesticides, and wood preservatives (3–10). This reagent has been applied to induce organic pollutant destruction, reduction of toxicity, improvement in biodegradability, removal of biologic oxygen demand/chemical oxygen demand, and removal of odor and color. Fenton's reagent (11), a

40 combination of hydrogen peroxide and a ferrous salt, is a potent oxidizing agent of organic  
41 compounds in acidic aqueous solution (12–15). Fenton's reagent generates a highly reactive  
42 free radical, hydroxyl radical (16,17), which reacts with various wood compounds, including  
43 lignin (18–21). However, to date there is little knowledge about the effects of the Fenton's  
44 reaction on the industrial black liquors. Thus, the general aim of the present investigation  
45 was to study Kraft black liquor degradation by Fenton's reagent. The objective was to  
46 examine the effect of H<sub>2</sub>O<sub>2</sub> concentration on the performance of Fenton's reagent under  
47 acidic pH in order to establish its optimum conditions for the degradation of Kraft black  
48 liquor.

## 49 **Materials and Methods**

### 50 **Materials**

51 All reagents were of the highest quality available. Hydrogen peroxide (30% [w/w] H<sub>2</sub>O<sub>2</sub> in  
52 water) solution and mannitol were purchased from Sigma (St. Louis, MO), and FeCl<sub>2</sub>·4H<sub>2</sub>O  
53 (99%) was obtained from Fluka.

54 All solutions were prepared with Millipore-quality water (Milli-Q plus, Ultrapure water  
55 system, 18 M $\Omega$ ·cm).

### 56 **Residual Kraft Black Liquor**

57 Residual Kraft black liquor was kindly provided by Smurfit-Mocarpel pulp mill (Venezuela).  
58 This black liquor is derived from the digestion of Caribbean pine (*Pinus caribaea*) and was  
59 taken from the recovery plant at the process line, where the total solid content was 32.7%,  
60 density was 1.2 g/mL, and pH was 12.5. The Kraft lignin content was determined to be 17.8%  
61 according to Kim's method (22).

### 62 **Degradation of Kraft Black Liquor by Fenton's Reagent**

63 Hydroxyl radical was generated by the Fenton's reagent ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ )

64 (16). Fifteen microliters of black liquor were added to 5 mL of an aqueous solution of FeCl<sub>2</sub>  
65 (1 mM). With the solution stirring at room temperature, 570  $\mu\text{L}$  of H<sub>2</sub>O<sub>2</sub> (for final  
66 concentrations of 5, 15, 30, and 60 mM) were added over 1 min. The vessels were capped,  
67 and the reaction mixture was under continuous agitation for 20 min.

### 68 **UV/VIS Spectrophotometer Analysis**

69 For UV/VIS spectrophotometric analysis, a Lambda 3B spectrophotometer was used.  
70 Samples were prepared as follows: to 200  $\mu\text{L}$  of black liquor sample was added 1.8 mL of  
71 0.1 N NaOH. Samples were scanned over the wavelength range from 200 to 400 nm using  
72 the PECSS program (Perkin-Elmer<sup>®</sup> Computerized Spectroscopy Software, version 3.2). In  
73 some experiments, the absorbance maximum of Kraft lignin was measured at 280 nm (23).

### 74 **Size-Exclusion Chromatography**

75 Size-exclusion chromatography (SEC) was employed to obtain information on the  
76 molecular weight distribution of residual black liquor samples. The high-performance SEC  
77 of black liquor was performed on a high-performance liquid chromatograph with a size-  
78 exclusion column (310  $\times$  10 mm id, Superose<sup>®</sup> 12HR 10/30; Pharmacia Biotech), a binary  
79 pump (LC Pump 250; Perkin-Elmer) with a manual injector (Rheodyne), and a UV detector  
80 (UV/VIS Detector LC 295; Perkin-Elmer) at 280 nm connected to a PC (PE NELSON, model

81 1022; Perkin-Elmer). The optimum conditions for black liquor analysis were as follows: the  
82 mobile phase was 0.1 N NaOH, flow was 0.4 mL/min, injection volume was 20  $\mu$ L, and black  
83 liquor dilution was 200  $\mu$ L of sample and 200  $\mu$ L of 0.1 N NaOH (24). Prior to SEC, all samples  
84 were filtered through 0.45-  $\mu$ L Millipore membranes. A calibration curve was done to obtain  
85 the molecular weight distribution of black liquor samples using sodium polystyrene  
86 sulfonate standards (Poly- sciences) (24–27).

### 87 **Determination of Phenolic Groups**

88 Phenolic groups were measured using the procedure of Markwell et al.(28) with a solution  
89 of known concentration of precipitated Kraft black liquor as standard.

### 90 **Determination of Iron Ions**

91 The determination of iron in the black liquor was performed by atomic absorption  
92 spectroscopy with an absorption/emission spectrophotometer 200-A (Buck Scientific).

### 93 **Sample Color**

94 Photographs of all preparations were taken to keep a record of the sample color. A  
95 commercial camera with Gold Kodak<sup>®</sup> film was employed.

### 96 **Statistical Analyses**

97 Results were expressed as the mean  $\pm$  SE of three different preparations. Data was analyzed  
98 by student's t-test (GraphPad, Prism<sup>®</sup>, Version 2.01). The level of significance was accepted  
99 as  $p < 0.05$ .

## 100 **Results and Discussion**

### 101 **Effect of Time and H<sub>2</sub>O<sub>2</sub> Concentration on pH of Incubation Medium**

102 Since the optimum pH for the completion of Fenton's reaction is found over the range of  
103 acidic pH (12,16,29–34), the incubation medium's pH was adjusted to approx 5.5 with 250  
104 mM H<sub>2</sub>SO<sub>4</sub>. Then, ferrous iron as FeCl<sub>2</sub> (final concentration: 1 mM) was added to the  
105 incubation medium. This addition caused a low reduction in medium pH, which could be  
106 owing to traces of

107 H<sub>2</sub>SO<sub>4</sub>, contained in FeCl<sub>2</sub> (16,30). When the H<sub>2</sub>O<sub>2</sub> was added to the incubation medium,  
108 a further reduction in pH occurred. This change in pH happened within 2 min after adding  
109 the H<sub>2</sub>O<sub>2</sub>. This decrease in pH has been attributed to the fragmentation of organic material  
110 into organic acids (12,16,30). After the incubation for 20 min, the pH value was unchanged  
111 (Fig. 1). Samples without FeCl<sub>2</sub> did not show any significant change in pH. The same pattern  
112 of pH changes was observed for all concentrations of H<sub>2</sub>O<sub>2</sub> (Fig. 1).

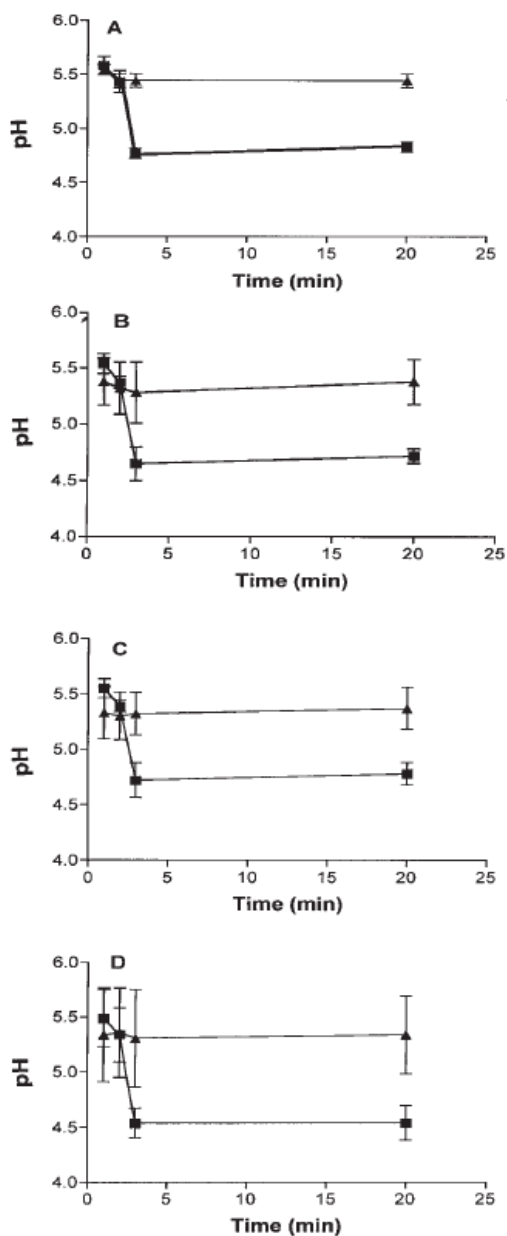
### 113 **Effect of H<sub>2</sub>O<sub>2</sub> Concentration on pH**

114 Fenton's reagent caused a change in pH, which was negative; for example, the final pH was  
115 lower than the initial one. As discussed, this change was explained by the fact that during  
116 the Fenton's reaction acidic compounds (organic acids) formed, as has been proposed by  
117 other investigators (12,16,30). The highest concentration of H<sub>2</sub>O<sub>2</sub> (60 mM) produced the  
118 largest change in pH (Fig. 2). The samples of black liquor that were treated with increased  
119 concentrations of H<sub>2</sub>O<sub>2</sub> alone did not show any change in pH (Fig. 2).

### 120 **Effect of H<sub>2</sub>O<sub>2</sub> Concentration on Phenolic Groups of Kraft Black Liquor**

121 Lignin is considered the main organic compound in the black liquor (2,25), and it is well  
122 known that lignin has phenolic hydroxyl groups in its structure (35). Therefore, it was  
123 decided to investigate the effect of Fenton's reagent on phenolic hydroxyl groups of black  
124 liquor lignin. Increased concentrations of H<sub>2</sub>O<sub>2</sub> in the Fenton's reagent induced the  
125 degradation of black liquor phenolic groups (Fig. 3). From a chemical point of view, this is  
126 not surprising because these functional groups have a very high affinity for reactive oxygen  
127 species (ROS) (18). This degradation reached its maximum at a concentration of 60 mM  
128 H<sub>2</sub>O<sub>2</sub> (Fig. 3). On the other hand, H<sub>2</sub>O<sub>2</sub> alone caused only a partial degradation of black  
129 liquor phenolic groups (Fig. 3).

130



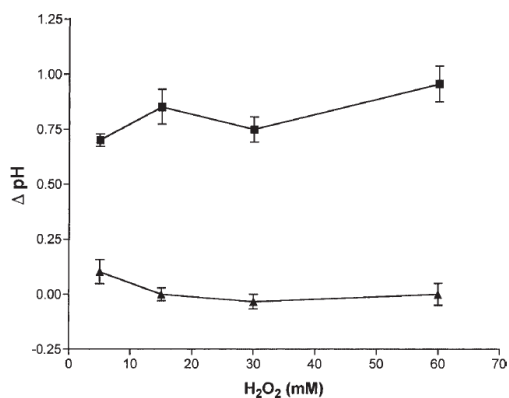
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133 Fig. 1. Effect of time on pH of incubation medium. (■) Black liquor samples were treated  
134 with Fenton's reagent containing different concentrations of H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20

135 min at room temperature; (-) black liquor samples were treated with different  
136 concentrations of H<sub>2</sub>O<sub>2</sub> alone for 20 min at room temperature. (A) 5 mM H<sub>2</sub>O<sub>2</sub>; (B) 15 mM  
137 H<sub>2</sub>O<sub>2</sub>; (C) 30 mM H<sub>2</sub>O<sub>2</sub>; (D) 60 mM H<sub>2</sub>O<sub>2</sub>.

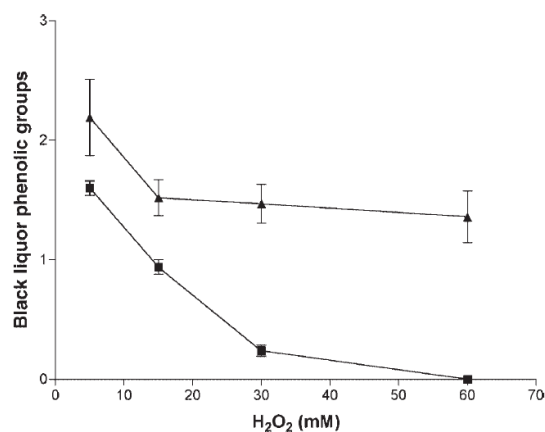
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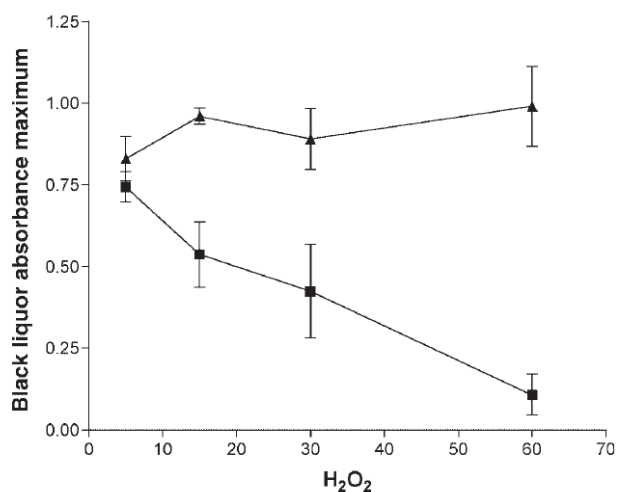
141 Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> concentration on pH. (■) Black liquor samples were treated with  
142 Fenton's reagent containing different concentrations (5, 15, 30, 60 mM) of H<sub>2</sub>O<sub>2</sub> and 1 mM  
143 FeCl<sub>2</sub> for 20 min at room temperature; (-) black liquor samples were treated with different  
144 concentrations of H<sub>2</sub>O<sub>2</sub> alone for 20 min at room temperature.



145

146

147 Fig. 3. Effect of H<sub>2</sub>O<sub>2</sub> concentration on black liquor phenolic groups (g/L). (■) Black liquor  
148 samples were treated with Fenton's reagent containing different concentrations (5, 15, 30,  
149 60 mM) of H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20 min at room temperature; (-) black liquor samples  
150 were treated with different concentrations of H<sub>2</sub>O<sub>2</sub> alone for 20 min at room temperature.



151

152 Fig. 4. Effect of H<sub>2</sub>O<sub>2</sub> concentration (in mM) on black liquor absorbance maximum (280  
 153 nm). (■) Black liquor samples were treated with Fenton's reagent containing different  
 154 concentrations (5, 15, 30, 60 mM) of H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20 min at room temperature;  
 155 (-) black liquor samples were treated with different concentrations of H<sub>2</sub>O<sub>2</sub> alone for 20  
 156 min at room temperature.

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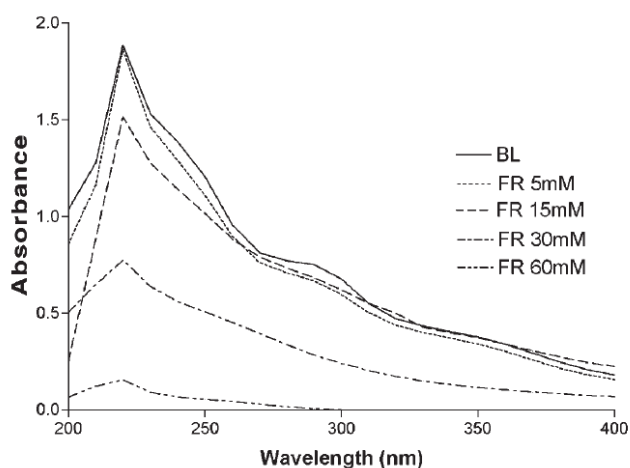
#### 158 **Effect of H<sub>2</sub>O<sub>2</sub> Concentration on UV Absorbance of Kraft Black Liquor Lignin**

159 The molecule of Kraft lignin absorbs over the UV range and has an absorbance maximum at  
 160 280 nm (23). When the pH of the incubation medium was adjusted to approx 5.5, the  
 161 increase in H<sub>2</sub>O<sub>2</sub> concentration caused a decrease in the maximum of lignin absorbance  
 162 of black liquor samples treated with Fenton's reagent (Fig. 4). This indicated that the  
 163 hydroxyl radical generated by Fenton's reagent was very effective in degrading the black  
 164 liquor lignin. It has been demonstrated by other investigators that ROS, particularly hydroxyl  
 165 radical and singlet oxygen, are able to react with lignin, causing its chemical degradation  
 166 (18,36–41). On the other hand, absorbance did not change when samples were treated with  
 167 H<sub>2</sub>O<sub>2</sub> alone (Fig. 4). It is noteworthy to underline that those changes observed in samples  
 168 treated with Fenton's reagent were not owing to a shift in lignin spectra as shown in Fig. 5.

#### 169 **Effect of H<sub>2</sub>O<sub>2</sub> Concentration on Molecular Weight Distribution of Black Liquor Lignin**

170 The increase in H<sub>2</sub>O<sub>2</sub> concentration induced a reduction in both average molecular weight  
 171 (M<sub>w</sub>) and number average molecular weight (M<sub>n</sub>) of black liquor samples treated with  
 172 Fenton's reagent (Table 1). Interestingly, at low concentrations of H<sub>2</sub>O<sub>2</sub>, the values of M<sub>w</sub>  
 173 and M<sub>n</sub> of samples

174



175

176

177 Fig. 5. Effect of H<sub>2</sub>O<sub>2</sub> concentration on UV spectrum of black liquor. BL, black liquor alone;  
 178 FR, black liquor samples treated with Fenton's reagent containing different concentrations  
 179 (5, 15, 30, 60 mM) of H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20 min at room temperature.

180

181 Table 1

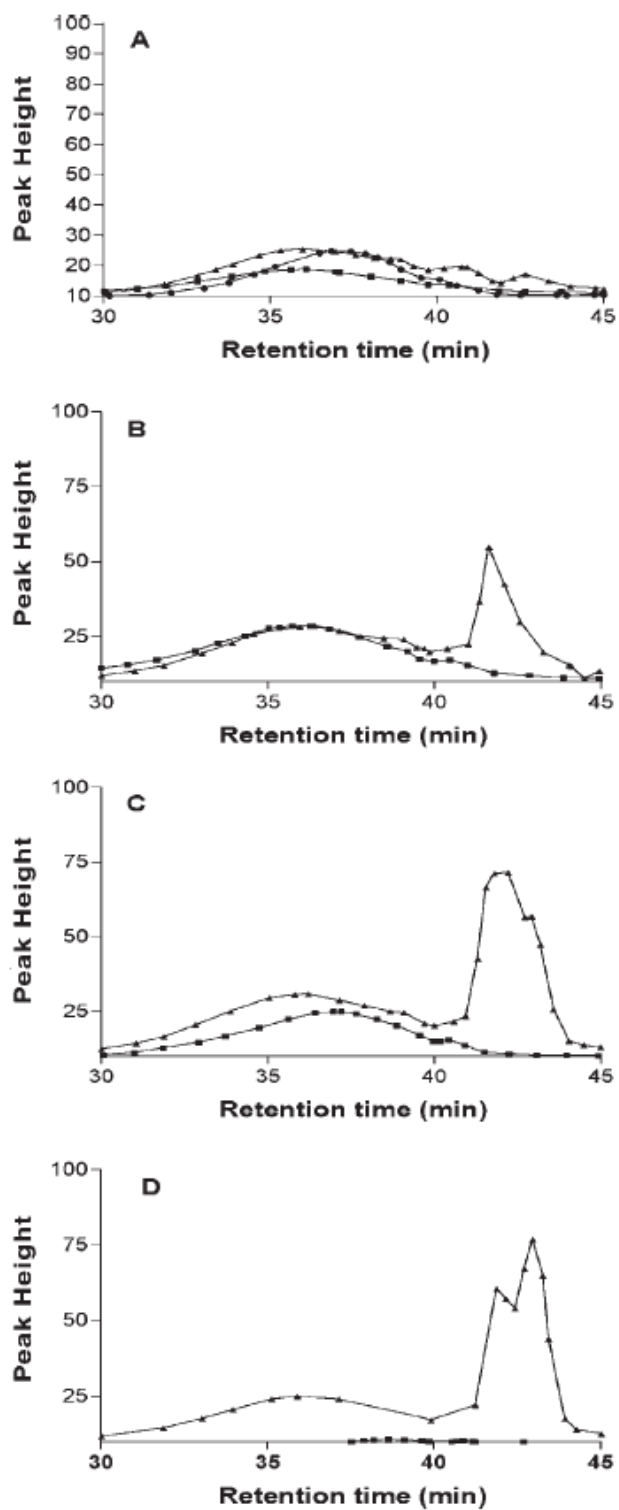
182 Effect of H<sub>2</sub>O<sub>2</sub> Concentration on Weight Average Molecular Weight (*M<sub>w</sub>*), Number Average  
 183 Molecular Weight (*M<sub>n</sub>*), and Dispersity (*D*) of Black Liquor

Treatment [H <sub>2</sub> O <sub>2</sub> ] <sup>a</sup>	<i>M<sub>w</sub></i>	<i>M<sub>n</sub></i>	<i>D</i> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> )
Black liquor alone	1561.1 ± 62.3	720.0 ± 5.8	2.2 ± 0.1
5 mM FR	2961.2 ± 321.0	1200.0 ± 57.8	2.5 ± 0.4
15 mM FR	2408.7 ± 76.6	1133.3 ± 33.4	2.1 ± 0.03
30 mM FR	1906.1 ± 9.7	1233.3 ± 33.4	1.6 ± 0.03
60 mM FR	867.6 ± 45.6	820.0 ± 61.2	1.1 ± 0.03
5 mM H <sub>2</sub> O <sub>2</sub>	1847.9 ± 33.4	793.3 ± 12.0	2.4 ± 0.03
15 mM H <sub>2</sub> O <sub>2</sub>	1628.5 ± 140.3	643.3 ± 78.9	2.6 ± 0.1
30 mM H <sub>2</sub> O <sub>2</sub>	1309.7 ± 89.0	503.3 ± 23.4	2.6 ± 0.03
60 mM H <sub>2</sub> O <sub>2</sub>	1152.6 ± 73.1	456.7 ± 16.7	2.5 ± 0.03

<sup>a</sup>FR, samples treated with Fenton's reagent; H<sub>2</sub>O<sub>2</sub>, samples treated with H<sub>2</sub>O<sub>2</sub> alone.

184

185 This result could indicate that the molecule of lignin was fragmented by the Fenton's  
 186 reagent and then these fragments copolymerized, creating compounds with higher  
 187 molecular weight, as shown by SEC (Fig. 6). It has been proposed that unlike other natural  
 188 polymers, lignin cannot be degraded to give structurally intact precursors. This is owing to  
 189 the presence of many reactive sites in the molecule; therefore, hydrolysis reactions are  
 190 often coupled to condensation reactions (42).



191

192

193 Fig. 6. Effect of H<sub>2</sub>O<sub>2</sub> concentration on molecular weight distribution of black liquor. (■)  
 194 Black liquor samples were treated with Fenton's reagent containing different  
 195 concentrations of H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20 min at room temperature; (-.) black liquor  
 196 samples were treated with different concentrations of H<sub>2</sub>O<sub>2</sub> alone for 20 min at room  
 197 temperature; (●) black liquor alone incubated for 20 min at room temperature. (A) 5 mM  
 198 H<sub>2</sub>O<sub>2</sub>; (B) 15 mM H<sub>2</sub>O<sub>2</sub>; (C) 30 mM H<sub>2</sub>O<sub>2</sub>; (D) 60 mM H<sub>2</sub>O<sub>2</sub>.

199

200 In the samples treated with H<sub>2</sub>O<sub>2</sub> alone, although there was a small reduction in Mw and  
201 Mn values, SEC clearly showed that there was a frag- mentation of black liquor lignin  
202 molecules, and the appearance of a peak over the range of lower molecular weights (Table  
203 1 and Fig. 6). It seems that H<sub>2</sub>O<sub>2</sub> alone only caused the fragmentation of lignin molecules,  
204 whereas the

205 Fenton's reagent induced an initial fragmentation, which was rapidly folded by the  
206 polymerization of lignin fragments at low concentrations of H<sub>2</sub>O<sub>2</sub>. At the highest  
207 concentration of H<sub>2</sub>O<sub>2</sub>, Fenton's reagent could readily degrade lignin molecules (Fig. 6) and  
208 the decrease in Mw and Mn was approx. 50% (Table 1).

209 Since black liquor sample treated with H<sub>2</sub>O<sub>2</sub> alone showed a fragmentation of lignin  
210 molecules (Fig. 6), it was decided to measure iron ions in the black liquor stock solution by  
211 atomic absorption spectrometry. The concentration of iron ions was 0.842 ppm in the black  
212 liquor stock solution. It is possible that these traces of iron were sufficient to reduce H<sub>2</sub>O<sub>2</sub>  
213 and produced hydroxyl radical, which then reacted with lignin and caused it fragmentation  
214 into molecules with lower molecular weight. An alternative explanation for the  
215 fragmentation of lignin is the action of cationic species. Cationic species are formed by the  
216 protonation of H<sub>2</sub>O<sub>2</sub> under acidic conditions, and they can react with the  $\pi$  electrons of the  
217 benzene ring, resulting in ring cleavage reactions of lignin molecules (43,44).

218 As shown in Table 1, Fenton's reagent also produced a reduction in  
219 dispersity (D) of approx. 50%, whereas H<sub>2</sub>O<sub>2</sub> alone did not modify this parameter. The value  
220 of D of black liquor lignin was similar to those values reported by other investigators (25)  
221 and was close to what would be expected from a polymer degraded through a random  
222 process.

223

#### 224 **Effect of H<sub>2</sub>O<sub>2</sub> Concentration on Black Liquor Color**

225 Black liquor solution darkened on the addition of H<sub>2</sub>O<sub>2</sub> and cleared up as the Fenton's  
226 reaction reached completion. Samples with H<sub>2</sub>O<sub>2</sub> alone also darkened on the addition of  
227 H<sub>2</sub>O<sub>2</sub>, but their clearance was not completed (results not shown). It has been reported that  
228 in certain conditions H<sub>2</sub>O<sub>2</sub> induces the formation of chromophoric species such as  
229 quinones, cinnamaldehyde, and ring-conjugated ketones (44,45).

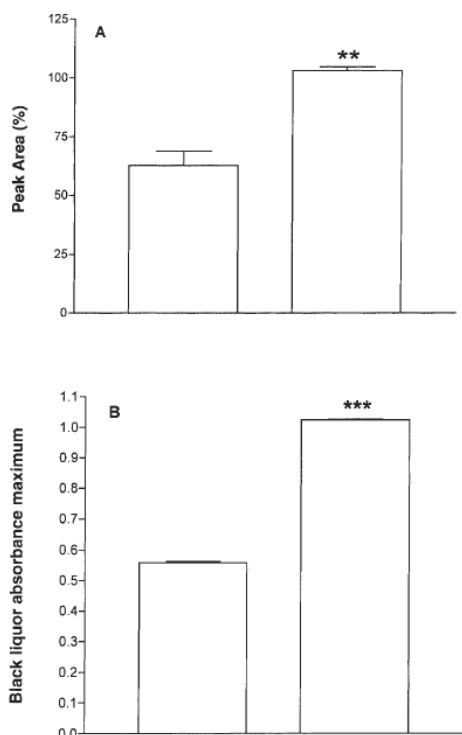
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#### 231 **Effect of Mannitol (100 mM) on Degradation of Kraft Black Liquor**

232 Mannitol is widely used as a hydroxyl radical scavenger to demonstrate the formation of this  
233 radical under certain experimental conditions (36,46). Therefore, to ensure that hydroxyl  
234 radical was formed in our conditions, the effect of mannitol on Fenton's reagent-mediated  
235 black liquor degradation was studied. Mannitol was able to prevent the degradation of black  
236 liquor by Fenton's reagent (about 30–45% of protection) as shown by the inhibition of  
237 reduction in area under the curve and absorbance maxi- mum loss (Fig. 7). This result  
238 confirmed that hydroxyl radical was formed during Fenton's reaction under the conditions  
239 of this investigation. However, the partial protection brought about by mannitol might  
240 indicate that the formation of hydroxyl radical occurred very close to the lignin molecule

241 and mannitol was unable to interact with this radical. Another explanation was that other  
242 ROS were involved in black liquor degradation; however, they were not quenched by  
243 mannitol.

244



245

246

247 Fig. 7. Effect of mannitol (100 mM) on black liquor degradation. Samples were treated with  
248 Fenton's reagent containing 30 mM H<sub>2</sub>O<sub>2</sub> and 1 mM FeCl<sub>2</sub> for 20 min at room temperature.  
249 (A) Area under the curve from sample size-exclusion chromato- grams (\*\*p < 0.001, in  
250 relation to samples without mannitol); (B) absorbance maximum of samples (\*\*p < 0.0001,  
251 in relation to samples without mannitol).

252

253 Conclusion

254 The degradation of residual Kraft black liquor by Fenton's reagent was investigated at room  
255 temperature under acidic conditions and was found to be easily degraded. In the presence  
256 of Fenton's reagent and at a low concentration of H<sub>2</sub>O<sub>2</sub>, the main degradation products  
257 seemed to polymerize and form molecules with higher molecular weight, whereas at a high  
258 concentration of H<sub>2</sub>O<sub>2</sub>, black liquor lignin appeared to be converted into compounds with  
259 lower molecular weight. By contrast, the use of less reactive reagent (H<sub>2</sub>O<sub>2</sub> and traces of  
260 iron) could fragment lignin molecules and produce intermediate products of lower  
261 molecular weight.

262 The problem of environmental pollution has led to a growing interest in the potential use of  
263 different treatments for the degradation of lignin containing industrial waste. This  
264 investigation showed that Fenton's reagent could be an efficient treatment for the  
265 degradation of industrial black liquors.

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