

## The Synergistic Effect in Oxidative Lignin Degradation by the Biomimetic Gif System

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A degradação oxidativa de ligninas [obtidas de *E. grandis* (processo acetosolv) e de *P. sylvestris* (processo organocell)] pelo sistema Gif foi testada usando peróxido de hidrogênio com cloreto férrico, cloreto cúprico ou a mistura cloreto férrico-cloreto cúprico, todos em piridina/ácido acético. Os melhores resultados foram obtidos empregando 80 mmol de peróxido de hidrogênio sob atmosfera inerte por 6 h. Para a lignina organocell, foi obtido um aumento dos produtos fenólicos (acima de 500 mg) juntamente com mais de 200 mg de bipyridilas, para a razão Fe/Cu de 1:1. Para a lignina acetosolv, 90 mg de produtos fenólicos e 40 mg de piridínicos foram observados nas mesmas condições. As quantidades de produtos obtidos com cloretos férrico ou cúprico sozinhos foram significativamente menores.

The oxidative degradation of lignins [obtained from *E. grandis* (acetosolv process) and *P. sylvestris* (organocell process)] by the Gif system was tested using hydrogen peroxide with ferric chloride, cupric chloride or a mixture of ferric and cupric chloride, using a pyridine/acetic acid solvent. The best results were obtained using 80 mmol of hydrogen peroxide in an inert atmosphere for 6 h. For organocell lignin an increase of the phenolic products (up to 500 mg) was obtained together with up to 200 mg of bipyridyls when a Fe/Cu ratio of 1:1 was used. For acetosolv lignin, 90 mg of phenolic and 40 mg of pyridine products were observed under the same conditions. The quantities of products obtained with either ferric or cupric chloride alone were much lower.

**Keywords:** synergistic effect, oxidative degradation, lignin, Gif system

### Introduction

Lignin, cellulose and polyoses are the main polymers of wood<sup>1</sup>. Since cellulose is the raw material for the paper industry, there is a growing interest in using clean industrial processes for wood delignification. In the Kraft process, used for the manufacture of high quality paper, most of the lignin is removed by reaction with alkaline sulfide<sup>2</sup>. At the elevated temperatures used in pulping, chemical reactions of lignin give rise to highly colored conjugated aromatic structures which remain in the wood cell (fiber) walls. The purpose of bleaching is to degrade or remove these chromophores along with the remaining lignin<sup>3</sup>.

A present pulps are bleached with elemental chlorine and chlorine dioxide<sup>4</sup>. Reactions of elemental chlorine with the chromophores and residual lignin generate chlorinated aromatics and dioxins<sup>5</sup>. The oxidative chlorine degradation of

lignin in white paper manufacturing produces 4-5 kg of chlorinated phenolic residues per metric ton of treated pulp<sup>6</sup>. The obvious alternatives (bleaching with dioxygen, peroxides or enzymatic systems) are difficult to control under the extreme conditions required to achieve high brightness. A solution for this problem may be the use of water-soluble catalysts to enhance the selectivity and effectiveness of the reaction of dioxygen or peroxides with lignin.

We have studied the possibility of using a methane monooxygenase model system [Gif system, using iron(III) chloride (GoAgg) or copper(II) chloride (GoChAgg) in pyridine / acetic acid with hydrogen peroxide] for the oxidative degradation of lignins obtained by both the organocell (from *P. sylvestris*) and acetosolv (from *E. grandis*) processes. Reactions with tryptophan dioxygenase suggest that species containing both iron and copper are catalytically more active<sup>7</sup>. We used iron and copper chlorides in different ratios in order to evaluate the existence of a synergistic effect.

## Experimental

The lignins studied were obtained from *Pinus sylvestris*, by the organocell process (methanol, NaOH)<sup>8</sup> and from *Eucalyptus grandis*, by the acetosolv process (93% acetic acid, HCl)<sup>9</sup>. One g of each lignin was refluxed for 2 h in 33 mL of pyridine/acetic acid (4:1, mol:mol). The refluxed solution was cooled to room temperature and filtered in a Büchner funnel. The filtered solution was transferred to an Erlenmeyer containing iron and/or copper chloride in various ratios (Table 1).

The reactions were initiated at room temperature and with magnetic stirring under an inert atmosphere by the addition of 2 mL (20 mmol) of hydrogen peroxide. The reaction time was 6 h. An additional 20 mmol of hydrogen peroxide was added every 90 min. The reaction mixture was then filtered in a Büchner funnel and the solvent was removed in a rotary evaporator under reduced pressure. The oils obtained were distilled at 0.1 mmHg in a short pathway apparatus by slowly increasing the bath temperature (2 °C min<sup>-1</sup>) to 190 °C. The volatiles were collected in a Schlenk immersed in a liquid nitrogen bath. They were then analyzed using an HP5890 gas chromatograph fitted with a 25 m x 0.2 mm HP-1 column and coupled to an HP5970A mass detector operating at 70 eV. The products were semi-quantified by integration of the chromatograms.

## Results

In preliminary experiments using 1 mmol of iron chloride alone, the addition of four consecutive portions of 2 mL of hydrogen peroxide gave rise to a ten fold increase in phenolic products over those from a single addition of 2 mL of hydrogen peroxide. The quantity of pyridinic products increased even more, thus reducing the selectivity of the reaction (defined as the ratio of phenolic to pyridinic products) from 0.6 to 0.2 for the organocell lignin<sup>10</sup>. Using an inert atmosphere the quantity of pyridinic products was

Table 1. Quantities and molar ratio of iron and copper chloride used.

FeCl <sub>3</sub> .6H <sub>2</sub> O (mg)	CuCl <sub>2</sub> .H <sub>2</sub> O (mg)	Fe:Cu (mol:mol)
0.00	170.40	0.00:1.00
54.06	136.32	0.20:0.80
90.10	113.60	0.33:0.66
108.12	102.24	0.40:0.60
121.63	93.72	0.45:0.55
135.15	85.20	0.50:0.50
148.66	76.68	0.55:0.45
162.18	68.16	0.60:0.40
180.20	56.80	0.66:0.33
216.24	34.08	0.80:0.20
270.30	0.00	1.00:0.00

considerably reduced, giving a much better selectivity of 1.3<sup>10</sup>. With 1 mmol of cupric chloride, in place of the ferric chloride, the quantity of phenolic products and the selectivity were lower, but the results were similar<sup>10</sup>. Therefore, in the experiments described here we always used the consecutive addition of four portions of hydrogen peroxide under an inert atmosphere.

For molar ratios of Fe/Cu between 40 and 60% a considerable increase in the yield of phenolic products and in the selectivity was observed (Fig. 1). The best result was obtained for 50% iron in the catalyst. This produced 500 mg of phenolic and 208 mg of pyridinic products (selectivity of 2.4). For acetosolv lignin the quantity of phenolic products was lower, as the acidic pulping process used caused cross-linking of the lignin, thus reducing its reactivity. Fe/Cu mixtures also significantly improved the results. With 60% iron (Fe/Cu ratio 3:2), 96 mg of phenolic products were produced, with a selectivity of 2.4 (Fig. 2).

A typical chromatogram of the products is shown in Fig. 3. Phenol and guaiacol, partly substituted in the 4-position, are the principal phenolic products, while bipyridyls, obtained by oxidative coupling, are the principal pyridinic products. As the pyridine also coupled oxidatively to the residual lignin, the distillate residues (1-3 g) were typically higher than the quantity of lignin used (1 g).

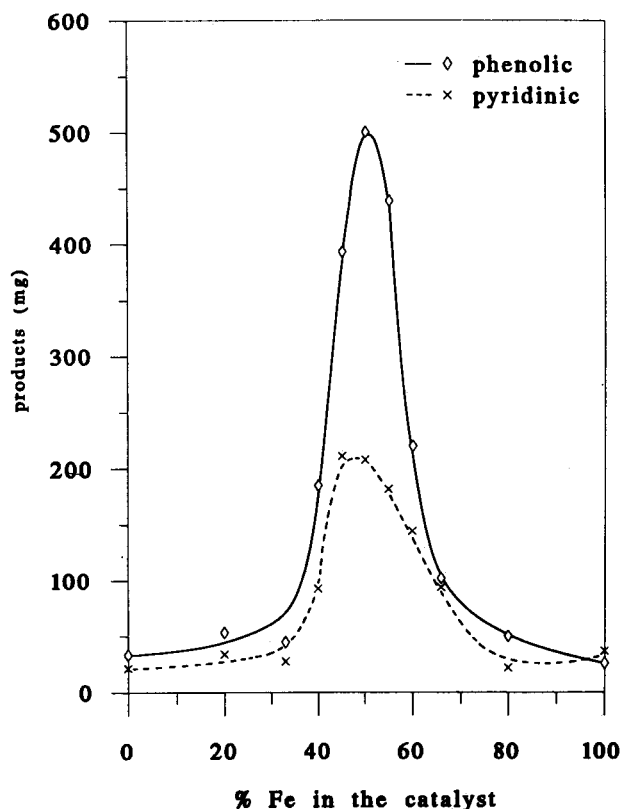


Figure 1. Products obtained from organocell lignin as a function of the percentage of iron in the catalyst.

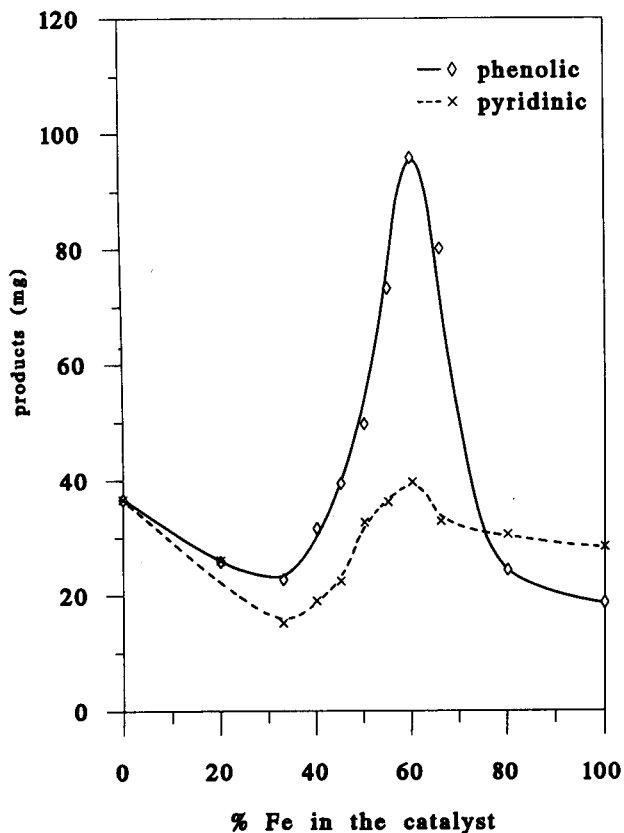


Figure 2. Products obtained from acetosolv lignin as a function of the percentage of iron in the catalyst.

## Discussion

Alkane oxidations by the GoAgg and the GoChAgg systems are non-radical processes which do not form pyridinic coupling products<sup>11</sup>. This is certainly not true for the oxidation of lignins. Hydrogen peroxide, together with the metal salts, form radicals which result in pyridine incorporation in the distillate residues and the formation of bipyridyls. The use of an inert atmosphere minimizes this process, but cannot prevent it. Furthermore, the quantity of hydrogen peroxide used in the lignin oxidation is very high, thus favoring radical reactions. Although it is not possible to calculate the oxidation efficiencies of these reactions, they are certainly lower than 10%, compared to 91% obtained in the oxidation of cyclohexane by the GoAgg system<sup>12</sup>. These low efficiencies and the formation of coupling products of pyridine make the Gif system inappropriate for pulp bleaching.

On the other hand, the combination of iron and copper chloride as the catalyst not only increases the quantity of phenolic products (and thus the oxidation efficiency), but also the selectivity of the process, thus showing that the predominantly radical reaction, observed for iron or copper alone, has become more specific, as is expected for enzymes. For both lignins the best results occurred with Fe/Cu ratios close to 1:1, which suggests that the catalytically active species for the non-radical process is a  $\mu$ -peroxy iron-copper complex, which decomposes forming singlet

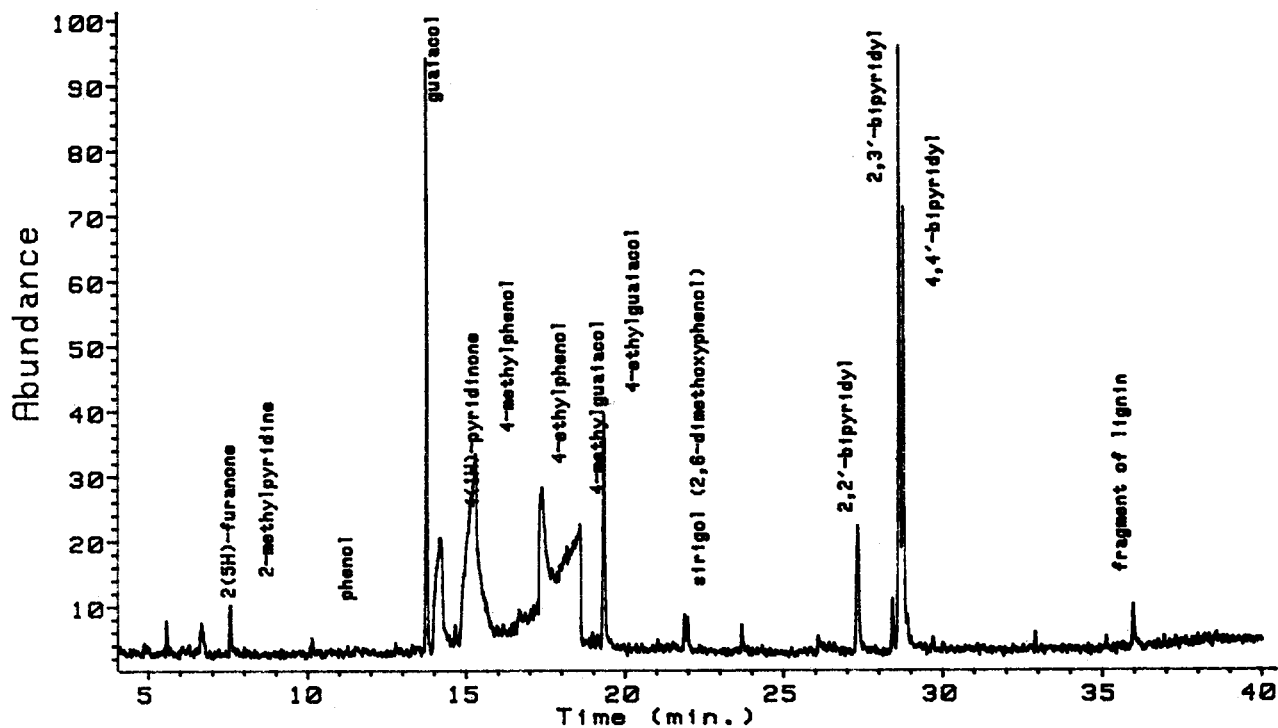
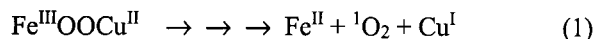


Figure 3. Chromatogram obtained from the volatile products of the oxidation of organocell lignin using 60% iron in the catalyst.

oxygen<sup>7</sup> (Eq. 1), which is much more effective and selective in the degradation of lignins.



To the best of our knowledge, this is the first time that a synergistic effect of iron and copper has been observed in an enzyme model system. Although this result may not be very interesting for lignin degradation, it opens a new possibility for the selective oxidation of hydrocarbons. Preliminary results show that this effect is also observed in the oxidation of cyclohexane by molecular oxygen/metallic zinc using a catalyst obtained by the co-impregnation of iron and copper chloride on silica<sup>13</sup>.

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