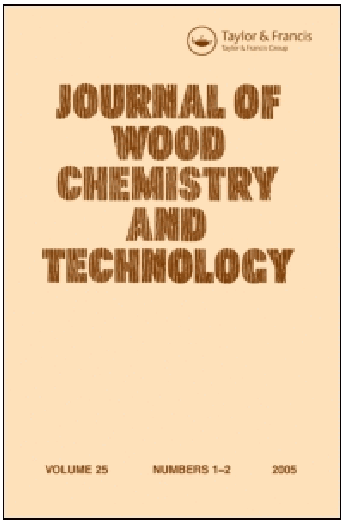

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OXIDATION OF HARDWOOD KRAFT-LIGNIN TO PHENOLIC DERIVATIVES.NITROBENZENE AND COPPER OXIDE AS OXIDANTS

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ABSTRACT

A hardwood kraft lignin (obtained by precipitating an industrial black liquor with a solution of calcium salt in alcohol) was oxidized in alkaline medium to obtain phenolic compounds (syringaldehyde, vanillin, syringic acid and vanillic acid). Nitrobenzene and copper (II) oxide were the oxidants employed. Influence of temperature, reaction time and oxidant concentration on yield and product distribution were studied. The results show that nitrobenzene is a more effective oxidant (15-18 % of aldehydes on kraft lignin) than copper (II) oxide (7-8 %). Product distribution showed the highest aldehyde selectivity for nitrobenzene, due to the presence of two additional oxidation products in the copper oxide oxidations. In the oxidation to aldehydes, the alcohol-calcium precipitated kraft lignin is a better raw material than other precipitated kraft lignin.

INTRODUCTION

Lignin is the main component in the black liquors from the production of chemical pulps. In kraft pulp mills, concentrated black liquors are burned in the recovery furnace to recover chemicals and produce energy. However, the recovery furnace limits the solid charge in black liquors and therefore, the increase of production, or some modifications involving intensive delignification are not always possible.

Lignin derivatives (kraft lignin and mainly lignosulfonates) have industrial interest as surface active agents and as raw material in the production of chemicals. Utilization of lignin as a raw material in the chemical industry is reduced to the production of vanillin (from lignosulfonates) and dimethyl sulfide (from kraft lignin)[1,2]. Other possibilities as hydrogenation, oxidation or pyrolysis have been also considered.

Lignosulfonates have more applications than other lignin derivatives. The main differences to alkali-lignins are a higher molecular weight, better solubility in water and a lighter color. However, as a consequence of the large production of kraft pulps, alkali-lignins are the more available derivatives. In this work the utilization of alkali-lignin as a source of chemicals is considered. Lignin oxidation to phenolic compounds is one of the possibilities to make lignin valuable. Products such as vanillin (V) and vanillic acid (VA) could be obtained in the oxidation of softwood lignin. In addition to these products, syringic aldehyde (S) and syringic acid (SA) are obtained when a hardwood lignin is employed.

The market of vanillin is in the foodstuff and pharmaceutical industry, where it is employed as an intermediate in the synthesis of a diversity of products for the treatment of infections of the respiratory system, hypertension and Parkinson disease. Other uses are for herbicides, vulcanization inhibitors, antifoaming and in the preparation of tanning creams. Vanillic acid and its esters also have preservative and disinfectant properties and can be used as ingredients in pharmaceutical products and sun creams. Syringaldehyde has a similar chemical structure as vanillin and similar properties and because of this has similar application. Pharmaceutical uses have been recently proposed, in which syringaldehyde is employed to synthesize drugs for cancer treatment[3,4].

Lignin Recovery from Kraft Black Liquors

The recovery of kraft lignin has been carried out by acid precipitation or by ultrafiltration. Acid precipitation with carbon dioxide or sulfuric acid removes most of lignin from black liquors. Complete precipitation of lignin is only achieved when pH is in the range of 2-3. At low pH, the precipitate becames difficult to filter and it is necessary to operate at temperatures near 80°C[5,6]. To improve the filterability Whalen[7] has proposed to add to the acid suspension of lignin a non soluble organic solvent. The effect observed by Whalen was the acceleration of the filtration and the reduction of the liquid retained by the precipitate. However, the method employs a great volume of solvent to obtain the desired effect.

Ultrafiltration removes the fraction of high molecular weight lignin, being more useful for lignin breaking-up than for removing lignin. In ultrafiltration there is no consumption of chemicals but it is a more expensive technique. Membranes must be alkali resistant and the ultrafiltrate flow could decrease if pore and molecules have similar size. In this situation, molecules are retained in pores hindering the flow.

In a previous paper[8], a procedure to precipitate solids from black liquors was presented. The procedure consists of the addition, to the black liquor, of a calcium salt dissolved in a water soluble alcohol. Under these conditions, most of the solids are recovered in a precipitate that contains about 90 % of the original kraft lignin. The calcium salt added controls the amount of precipitated solids and can be adjusted to obtain the maximum precipitation of lignin. Filterability of the precipitate depends on the alcohol-black liquor ratio, which permits improving the velocity of filtration by increasing the volume of alcohol. This effect is explained by modifications in the Z-potential caused by the alcohol addition, improving particle agglomeration and precipitation.

In this work, the kraft lignin obtained by this method has been tested as raw material for oxidation to phenolic compounds (aldehydes and acids). It could be expected that the alcohol-calcium precipitated lignin shows a higher yield in these derivatives than acid precipitated lignin (whose structure is modified during the isolation procedure) and could be used as raw material in the production of chemicals.

Oxidation

Different oxidants have been employed in lignin oxidation, yielding a large diversity of products. Lignin oxidants could be classified by the reaction produced from lignins, strong oxidants (permanganate, chlorine, chlorine dioxide, or hypochlorite) destroy the aromatic ring and low molecular weight acids are obtained. Milder oxidants do not break the aromatic ring and oxidation occurs at the side chain. Simultaneously, depolymerization of lignin macromolecule is favored by the oxidation, which breaks the ether bonds between two phenyl-propane units.

Nitrobenzene, some metal oxides and oxygen, all of them in alkaline medium, are mild oxidants. In the oxidation of softwood lignin, they produce vanillin and vanillic acid as the main products, utilization of hardwood lignin yields syringaldehyde and syringic acid in addition to the former products. The relative amount of aldehydes and acids depends on the oxidant. In the nitrobenzene oxidation aldehydes are the main products, while oxidation with mercury oxide or silver oxide give acids in higher yield[9]. Copper(II) oxide and oxygen show intermediate product distribution[10].

Many papers have been published about lignin oxidation, using different lignocellulosic materials. Table 1 shows those works carried out employing nitrobenzene as oxidant, most of them taken from Brauns and Brauns[11]. The most significative result is the large range of aldehyde yield obtained, that varies from 1.5 to 50%(weight on lignin). However, comparisons have been made between different lignin samples, with different reactivity towards nitrobenzene oxidation. Samples of similar origin showed less difference in aldehyde yield, 18-28% for

TABLE 1
Lignin Oxidation with Nitrobenzene-Alkali

Ref.	Raw Material	Type of Lignin	Oxidation Conditions[a]	Yield[b]
16	Eucalyptus	Methanol lignin		27% ph. ald.
17	Eucalyptus	Protolignina		11-44% S; 6-9% V
18	Red pine	Alkali lignin	180°C; 2h.	11% V
	Red pine	Thiolignin		6.6% V
19	*Picea abies L.*		180°C; 2h.;3.3 NB/LIG;2N NaOH	28% V; 4.8% AV
20	SW	Protolignin		26-27% ph. ald.
	HW	Protolignin		40-47% ph. ald.
21	SW	Black liquor thiolignin		1.8% VA; 0.3% V
22	Spruce	Protolignin		22% V
	Spruce	Cuoxam lignin		17% V
	Spruce	Alkali lignin		14% V
	Spruce	Klason lignin		1.5% V
23	*Cryptomeria japonica*	Protolignin	0.43 Na MNB/LIG 2.5% NaOH; 140°C; 5h.	10% V
24	Aspen	Protolignin	170-180°C; 2.5 h.	15% V; 36% S
	Aspen	Alkali lignin		10% V; 25% S
25	Spruce	Native lignin		25% V
	Spruce	Alkali lignin		14% V
26	Spruce	Dioxan lignin		23% ph. ald.
	Oak	Dioxan lignin		45% ph. ald.
27	SW	Thiolignin	160-170°C	5-6% V
	SW	Protolignin	180°C; 2h.; 2.4 NB/LIG	19% V
	SW	Cuoxam lignin	2N NaOH	19% V
28	Bamboo	Protolignin	160°C; 3h.; 2N NaOH	13% S; 8.5% V
29	Larix	Protolignin	160°C; 4h.; 6.5 NB/LIG	4% V
	Larix	Alkali lignin		3% V
30	HW	Kraft lignin	180°C; 2h.; 2N NaOH	2% V, 4.4% S
31	HW	Protolignin	180°C; 2h.; 2.6 NB/LIG 2N NaOH	8% V, 13% S

[a] NB/LIG ratio expressed in mL/g. [b] expressed as percentage on lignin

softwood lignin and 27-50% for hardwood lignin in protolignin and dioxan lignin oxidations (two lignin forms without chemical modifications). Other lignin preparations also showed similarities in yield: cuoxam lignin 17-19%, alkali-lignin 11-14% (for softwoods) and thiolignin 2-6%. According to these results, the aldehyde yield decreases when the lignin sample is modified, and therefore the lignin preparation method seems to be a critical factor in the nitrobenzene oxidation.

In nitrobenzene reduction, nitrosobenzene, phenylhydroxylamine and aniline are the consecutive reduction products, condensation between them can occur[10], what complicates the reaction scheme and recovery of the oxidant. As the result of these reactions, lignin is oxidized to give aromatic aldehydes as principal products, in addition, the corresponding carboxylic acids are also obtained in lower yields.

Cu(II), Ag(I) and Hg(II) oxides have also been employed to oxidize lignin to phenolic compounds: among these oxides, copper(II) produces the highest aldehyde yield. Pearl et al.[9,12,13] employed silver oxide in lignosulfonate oxidation, at 105 °C the main oxidation product is vanillic acid (or syringic acid from hardwood lignosulfonates). Mercury(II) oxide gives aldehydes and acids in similar proportions, the total yield was about 30 % on lignin[14,15]. Other oxides such as vanadium, chromium or nickel oxides, have been also applied as lignin oxidants[10], however, the results are not promising.

Table 2 shows a summary of some experiences on lignin oxidation with CuO, as in nitrobenzene oxidation, protolignin is again the most useful material for oxidation but the yield is now reduced with respect to nitrobenzene.

In alkaline CuO oxidation, copper(II) sulfate is normally used as the chemical. When the suspension of copper(II) sulfate is heated, the color turns from blue to black, due to the conversion of copper(II) sulfate into copper(II) oxide. Oxidation with copper has the advantage over nitrobenzene of not producing harmful byproducts and being easy to recover[17-19].

TABLE 2
Lignin Oxidation with Copper Oxide-Alkali

Ref.	Raw Material	Type of Lignin	Reaction Conditions[a]	Yield[b]
35	Spruce	Protolignin		7.3% V
36	*Abies sachalinensis*	Protolignin	160°C; 1-3h; 2.4N NaOH; 4 Cu/LIG	20% ph. ald.
37		Protolignin		7.8% V; 0.5% VA
		Klason lignin		10% V; 0.5% VA
		Alcohol lignin		7.4% V; 0.7% VA
38	*Criptomeria japonica*	Native lignin	160°C; 4h; 2.5N NaOH; 4 Cu/LIG	17% V; 1.5% VA
		Klason lignin		11% V; 1.4% VA
		Periodate lignin		18% V; 1.4% VA
		Phenol lignin		8.6% V; 1.0% VA
33		Sulfate black liquor	3 Cu/LIG	13% V
34	Spruce, Pine	Protolignin	160-180°C; 2-2.5h 2-2.5N NaOH	14-20% V
		Hydrolysis lignin		2-3% V
9	Aspen	Spent sulfite liquor	170°C; 2h.; 2N NaOH 3 CuO/solids	3.2% V; 4.1% S on solids
13	Aspen	Spent sulfite liquor	170°C; 2h.; 2N NaOH 2.7 CuO/solids	9-14% V; 10-17% S on ether sol. comp.
39	Spruce	Protolignin	180°C; 2h.; 2N NaOH 5.6 Cu/LIG	15% V
	Spruce	Dioxan lignin		9% V
40		Soda liquor		5% V
30	HW	Kraft lignin	180°; 2h.; 2N NaOH 0.7 Cu/LIG	1% V; 3% S
41	Beech		170°C; 3h.; 2N NaOH	30% ph. comp.
	Pinus sylvestris			15% ph. comp.

[a] Cu/LIG ratio expressed in mol/mol, CuO/solids in g/g.

[b] expressed as percentage on lignin

In this work, nitrobenzene and copper(II) oxide are used to oxidize an industrial eucalyptus kraft lignin to obtain phenolic compounds (aldehydes and acids). For each oxidant, oxidation variables have been modified to study the response to these changes. Yield, selectivity (for each product) and lignin conversion were the responses studied. The lignin, precipitated from the black liquor with a solution of calcium chloride in alcohol, is expected to yield a higher amount of phenolic aldehydes than acid precipitated lignins.

EXPERIMENTAL

A solution of calcium chloride in methanol (47.7 g/L; 17.2 g Ca/L) was employed to precipitate lignin from an industrial eucalyptus black liquor (Total Solids: 199 g/L; Lignin: 50 g/L) as it was described in a previous paper[8]. The alcoholic solution removes most of the black liquor lignin (75-95%), which precipitates as calcium salt. The precipitate was filtered and solids were air-dried for two weeks. The dry solids (Lignin: 42%; Ca: 9%) were then redissolved in about 600 mL 2N NaOH solution, a vigorous stirring was maintained for 60 minutes to promote complete lignin redissolution. The insoluble material was filtered and washed with two 2N NaOH portions (25 mL each one) that were added to the lignin solution. Lignin solution is then oxidized in a Burton-Coblin autoclave. The installation (see Figure 1) permits heating the vessel up to the oxidation temperature and then addition of the oxidant to begin the reaction at constant temperature, pressurizing with nitrogen. Samples were taken at different time intervals (from 0 to 150 minutes) and phenolic compounds analyzed by HPLC. Sample preparation and HPLC conditions are shown in Table 3.

According to the literature, those variables affecting the aldehyde yield have been identified. For the nitrobenzene oxidation they are: temperature, reaction time, nitrobenzene concentration and NaOH concentration[24,29,42]. Oxidation with copper(II) oxide showed similar behavior, and temperature, time, NaOH concentration, and CuO/lignin ratio are the more important variables[39,43].

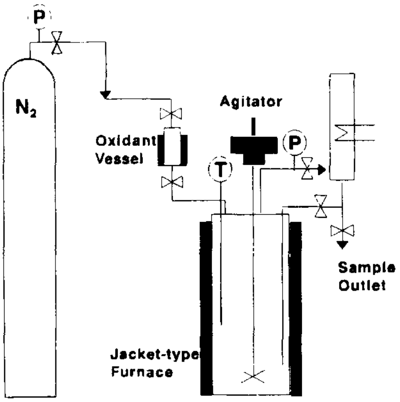


FIGURE 1. Experimental set-up employed for lignin oxidation.

TABLE 3
Oxidation Products Analysis

Sample preparation	HPLC Analysis
Put 1 mL of lignin solution into a vial	Eluent: 75% CH_3OH
Add concentrated H_2SO_4 (up to pH 3)	25% PO_4H_3 solution (pH 2.7)
Add chloroform (5 mL)	flow: 1mL/min.
Add $(NH_4)_2SO_4$ (0.3 g)	
	Column Reverse Phase C_{18}
Shake the mixture for 4 hours	Column Temperature: 45 °C
Take 50 μL of the chloroform phase	
Dilute with 1 ml of benzene	Detector UV 288 nm
Analyzed by HPLC	Elution Order: VA, SA, V, S

Temperatures in the range 160 to 190 °C have been normally employed with both oxidants. In nitrobenzene oxidation, some authors[24,42] agree that 180 °C is the optimum to obtain a high yield. Low temperature (160 °C) requires larger reaction times[29], while a very high temperature can degrade the reaction products more. Oxidation with copper(II) oxide runs at the same temperatures than nitrobenzene[39,43], so both oxidants were tested at the same temperatures: 170, 180 and 190 °C.

Reaction is carried out for 120 to 240 minutes, although larger times are employed when reaction temperature is 160 °C[29]. For the optimum temperature range, reaction is usually maintained for 120 to 150 minutes, so for both oxidants the oxidized samples have been collected at intervals between 10 and 120 minutes from the oxidant income.

Nitrobenzene/lignin ratios in the range 1.5 to 5 mL/g LIG were found in the literature, the highest values were employed in the oxidation of a kraft lignin, which obtained a low aldehyde yield. So the nitrobenzene/lignin ratios used in this work (that also employs a kraft lignin as substrate) are always higher than 5 mL/g LIG, 6.3, 9.4 and 12.6 were the values employed.

For the CuO oxidation, there is little information about the most suitable CuO/lignin ratio and very large[43] (14 mol CuO/mol LIG) or moderate values[36] (4 mol CuO/mol LIG) have been reported. By supposing 195 g/mol as the average molecular weight for the lignin monomer, the CuO/lignin ratio has been fixed at 1.33, 2.66 and 3.99 mol CuO/mol LIG, which favours the total income of oxidant into the reactor.

In nitrobenzene and CuO oxidation, NaOH concentration and solution volume were 2N and 65-70 mL/g LIG respectively. These variables do not seem to be as critical as the previous ones and their effect has not been considered. Authors agree to employ 2N as the most effective NaOH concentration to get an optimum aldehyde yield.

Oxidation products were analyzed by HPLC, a previous extraction step was neccesary to isolate the products from the rest of solids. Extraction procedure is reproduced in Table 3, the method was tested in a set of trials that employed oxidation product samples in a 2N NaOH solution, product recovery was always

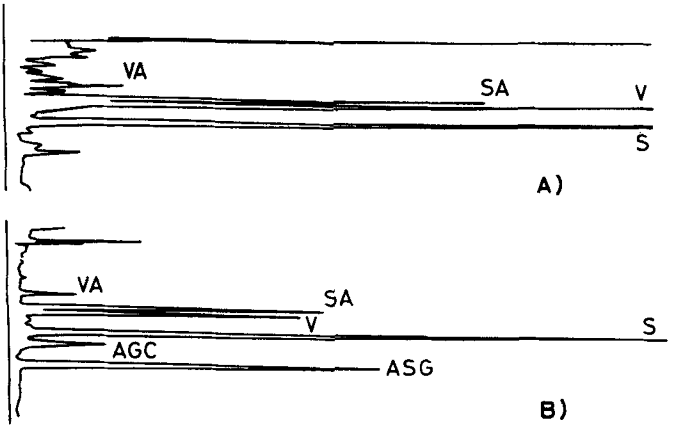


FIGURE 2. Chromatograms of HPLC obtained in the analysis of nitrobenzene oxidation (A) and copper oxidation (B).

higher than 92%. HPLC conditions are also shown in Table 3. Figure 2 shows the chromatograms from nitrobenzene and copper(II) oxide oxidation respectively. Two additional products acetoguaiacone (AGC) and acetosyringone (ASG) are obtained when copper oxide is employed instead nitrobenzene.

RESULTS AND DISCUSSION

To compare the action of the two oxidants, lignin conversion, yield and selectivity were calculated from the product concentration data. Lignin conversion gives information about the reaction extension, that is, how much has the reaction proceeded, yield and selectivity measure the absolute and relative abundance for a product.

Lignin conversion calculation needs to measure the lignin concentration at different reaction times. The lignin analysis is difficult to perform because of the heterogeneous structure. Chemical or spectrophotometric methods are not adequate for kraft lignins, after alkaline oxidation lignin become more soluble in acid medium, thus sulfuric acid precipitation is not useful to carry out the analysis. On the other hand, the spectrophotometric procedure can not discriminate between lignin and its oxidation products. To overcome this problem, lignin reaction expressed by the difference LIG_o - LIG is assumed equal to the sum of analyzed products (ΣP_i) and conversion can be expressed by Eq. [1].

$$X = \frac{LIG_o - LIG}{LIG_o} = \frac{\sum P_i}{LIG_o} \qquad [1]$$

Yield and selectivity of a product are calculated by Equations [2] and [3] respectively. Both parameters, express the absolute and relative importance of a product in the oxidation reaction. Subscript j refers to V, S, VA and SA, while subscript i is also extended to the rest of the products found in the oxidation, so AGC and ASG were also considered when they appear among the products.

$$Y_j = \frac{P_j}{LIG_o} \cdot 100 \qquad [2]$$

$$S_j = \frac{P_j}{\sum P_i} \qquad [3]$$

Lignin conversion varies among the oxidants and showed little variation with temperature or oxidant concentration. Lignin conversion versus reaction time is shown in Figure 3 at 180°C as an example. As can be seen, the lignin is converted in the first hour of reaction and at 90 minutes the conversion reaches about 90% of its final value. At this time nitrobenzene converts around 23% of the original lignin and copper(II) oxide around 13%. Compared with nitrobenzene, lignin conversion with copper(II) oxide is significantly less and less affected by temperature. The observation is consequent with the higher oxidant power of nitrobenzene.

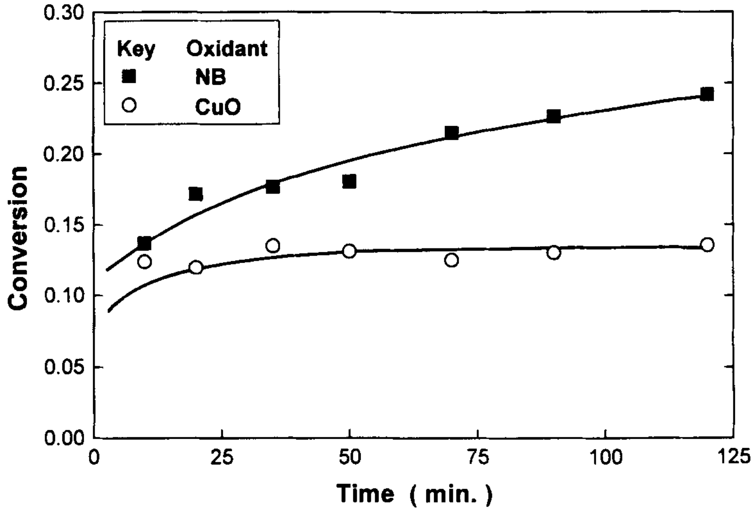
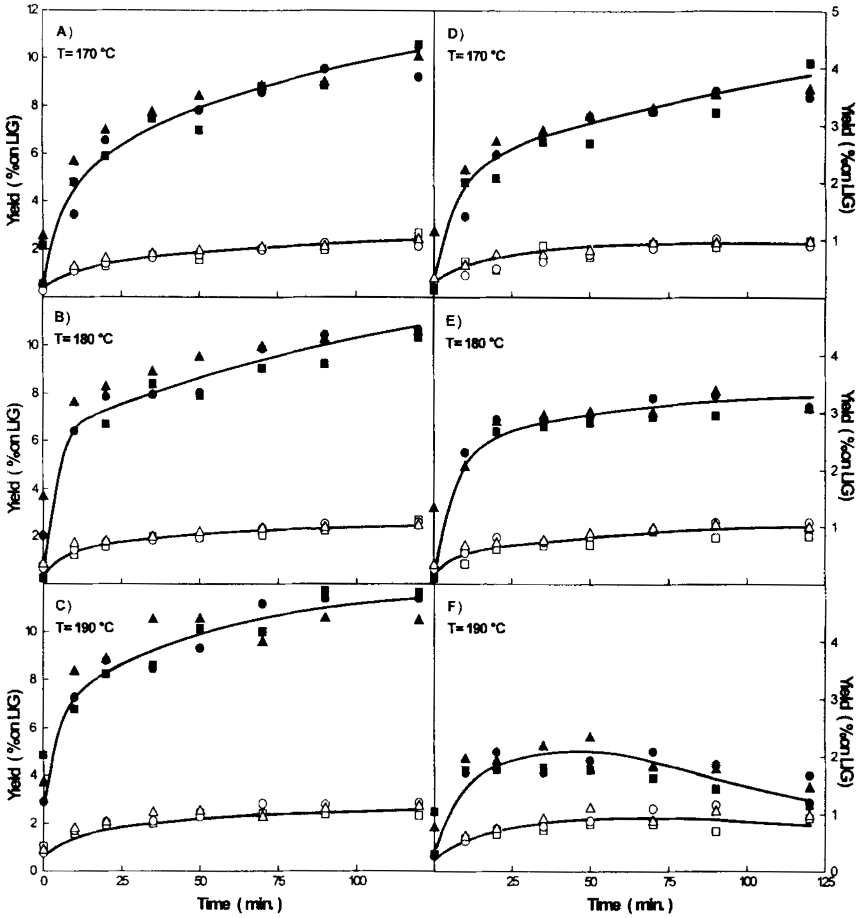


FIGURE 3. Lignin conversion at 180 °C, NB=9 mL/gLIG, CuO=2.7 mol/molLIG

Other experiences in which the lignin was oxidized with nitrobenzene employed similar conditions and a great variety of lignin preparations. Leopold[42] oxidized spruce protolignin with nitrobenzene (2 hours, 180 °C, 2N NaOH and 4 g NB/1 g LIG/40 g alkali) obtaining 27% of V. Kavanagh and Pepper[24] oxidized a *Populus tremuloides* protolignin (2.5 hours, 170-180 °C) with yields of 36% in S and 15% in V. Kagawa[29] extended the oxidation (4 hours, 160 °C, 6 g NB/g LIG, 2N KOH) to other lignin preparations: protolignin, hydrochloric acid lignin, soda lignin and acid precipitated soda lignin. Differences in yield showed that protolignin is the most favorable raw material for vanillin production, while the acid precipitate lignin showed the poorest result (6% V). Kraft black liquor oxidation has not been studied as much as other lignin preparations; Salomon[30], in the oxidation of an acid precipitated hardwood kraft lignin (1.5-5 mL NB/g LIG), obtained low aldehyde yield (2% V, 4% S) comparable to that obtained by Kagawa[29] from hydrochloric acid lignin.

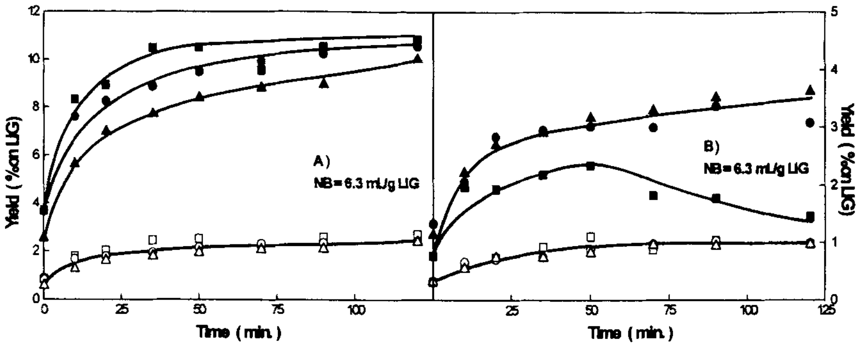
Four products, identified as S, V, SA and VA, were obtained in nitrobenzene oxidation. The results of aldehyde and acid yield versus reaction time are presented in Figure 4 (a to f) for different temperatures and oxidant concentrations. These curves show that yield does not depend on the nitrobenzene concentration used, however temperature has a significant effect on the aldehydes and syringic acid yields. Figure 5 (a and b) show the variation in yield with the temperature for a fixed nitrobenzene concentration (6.3 mL NB/g LIG), vanillin or syringaldehyde concentration increases with temperature, while the syringic acid concentration is smaller at higher temperatures. Although aldehyde yield is affected by temperature, at the end of the reaction (120 minutes), the concentration is similar at different temperatures, as can be seen in Figure 5 a. This behavior could be explained by considering that only a fraction of kraft lignin is able to produce phenolic aldehydes. If at the end of the oxidation (120 minutes) all of this lignin is converted, the aldehyde yield will be similar at any temperature, but the reaction rate will be higher as the temperature increases. Syringic acid reduction is explained by the instability of this compound at high temperature[44], which results in the maximum yield with time found at 190 °C. Although yields increase with reaction time, except for SA at 190 °C, the main increase in yield takes place in the first hour of reaction.

As lignin oxidant, CuO was first used by Pearl[32], in his experiences with softwood lignosulfonates he established the oxidation conditions to reach the maximum vanillin production (2 hours, 170-190 °C, 13 mol/mol alkali/LIG, 14 mol/mol $Cu(OH)_2$/LIG). Pepper and Karapally[39] oxidized softwood and dioxan lignin, obtaining a higher yield when wood is used instead dioxan lignin (14.7 % V versus 9.4 % V). In the lignin oxidation with copper compounds there is little information on kraft lignin oxidation; Salomon[30], based on the Pearl and Beyer[45] conditions, oxidized an acid precipitated hardwood kraft lignin; in this work[30], the maximum yield (2.3 % aldehydes) was observed for 2 hours and a 10 mol CuO/mol LIG.



Key	NB (mL/g LIG)	Products Aldehydes	 Acids
□	12		
○	9	V on A, B, C	VA on D, E, F
△	6		
■	12		
●	9	S on A, B, C	SA on D, E, F
▲	6		

FIGURE 4. Effect of NB concentration on aldehyde (A, B and C) and acid (D, E and F) yields at different temperatures of reaction.

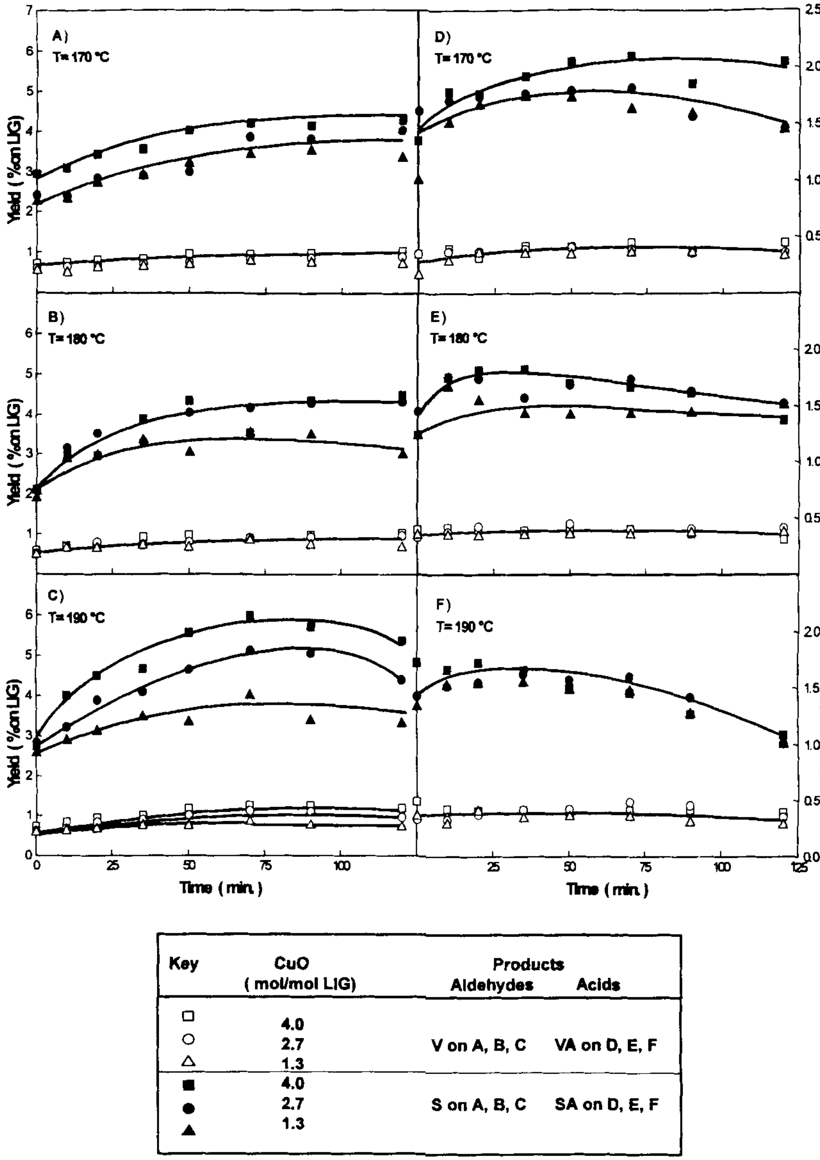


Key	T (°C)	Products Aldehydes	Acids
□	190		
○	180	V on A	VA on B
△	170		
■	190		
●	180	S on A	SA on B
▲	170		

FIGURE 5. Effect of reaction temperature on aldehyde (A) and acid (B) yields employing NB as oxidant with a concentration of 6.3 mL NB/g LIG

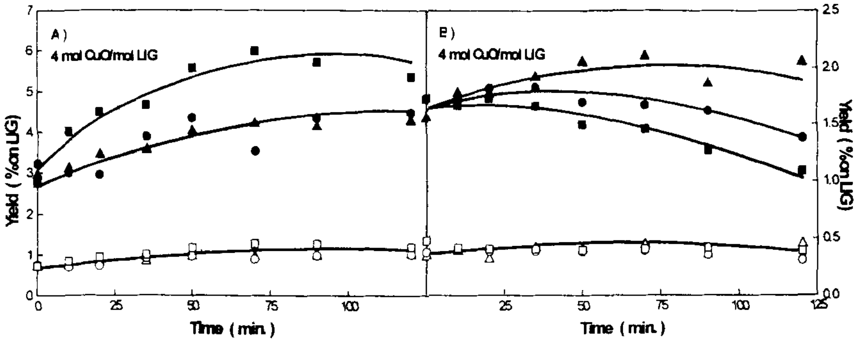
In CuO oxidation two new products were identified in addition to aldehydes and acids, the products identified in nitrobenzene oxidation. These products were identified in previous works as acetoguaiacone and acetosyringone[9,12,39], steady in the conditions of CuO oxidation.

Figure 6 (a to f) shows aldehyde and acid yield versus reaction time at different temperatures and CuO concentrations. Figure 6 (a to c) shows the effect of oxidant concentration on aldehyde yield, while the effect on the acid yield is less pronounced (Figure 6 d to f). Reaction temperature has, as in nitrobenzene oxidation, a different effect on each product. The highest temperature increases the aldehyde yield and reduces the syringic acid yield; moreover, the CuO concentration also improves yields and a combined temperature-CuO effect is



Key	CuO (mol/mol LIG)	Products Aldehydes	Acids
□	4.0	V on A, B, C	VA on D, E, F
○	2.7		
△	1.3		
■	4.0	S on A, B, C	SA on D, E, F
●	2.7		
▲	1.3		

FIGURE 6. Effect of CuO concentration on aldehyde (A, B and C) and acid (D, E and F) yields at different temperatures of reaction.



Key	T (°C)	Products Aldehydes	Products Acids
□	190	V on A	VA on B
○	180		
△	170		
■	190	S on A	SA on B
●	180		
▲	170		

FIGURE 7. Effect of reaction temperature on aldehyde (A) and acid (B) yields with CuO as oxidant at a concentration of 4 mol CuO/mol LIG

observed. A clear maximum for aldehyde concentration is found at about 80 minutes of reaction for the higest temperature (4 mol CuO/mol LIG), which represents 6% of S and only 1.3% of V (Figure 7). The low aldehyde yield, with respect to the nitrobezene oxidation, is explained by taking into account the two new products formed in the CuO oxidation, acetoguaiacone and acetosyringone (the ketones corresponding to V and S, respectively). Nitrobenzene oxidizes the ketones to give the aldehydes, while copper oxide stops the oxidation in the ketones, as a result, aldehyde yield decreases with respect to nitrobenzene oxidation.

Product selectivity was the third parameter studied, as a measurement of the relative importance of a product. Figure 8 shows the product selectivity, for each

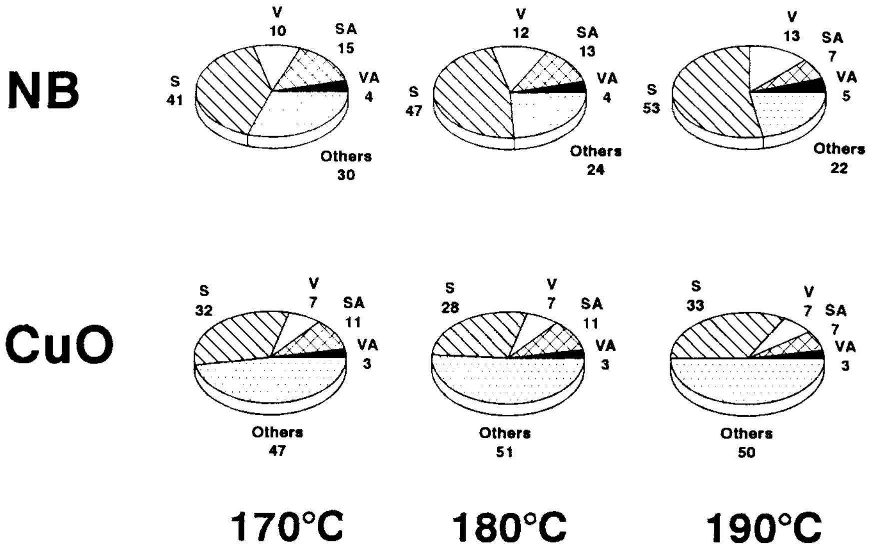


FIGURE 8. Comparation of the product selectivity for NB and CuO oxidations. Average values 120 minutes of reaction time.

oxidant, at the end of reaction, temperature is the variable in the diagram. As expected from yield data, S has the highest value and, in the case of nitrobenzene oxidation, represents about 50% of the total phenolic products. The presence of AGC and ASG reduced the selectivity for the rest of products while an increase in reaction temperature caused the aldehyde selectivity to increase due to the syringic acid decomposition and a slight increase in aldehyde yield.

Sample Effect

Figure 9 shows the aldehyde yield (V plus S) at 120 minutes for different oxidant concentration and temperature. To compare oxidant concentrations the numbers +1, 0 and -1 represent respectively the maximum, medium and minimum values for each oxidant concentration employed (it does not mean that the oxidant has a similar oxidant capacity at the same level). Nitrobenzene is the

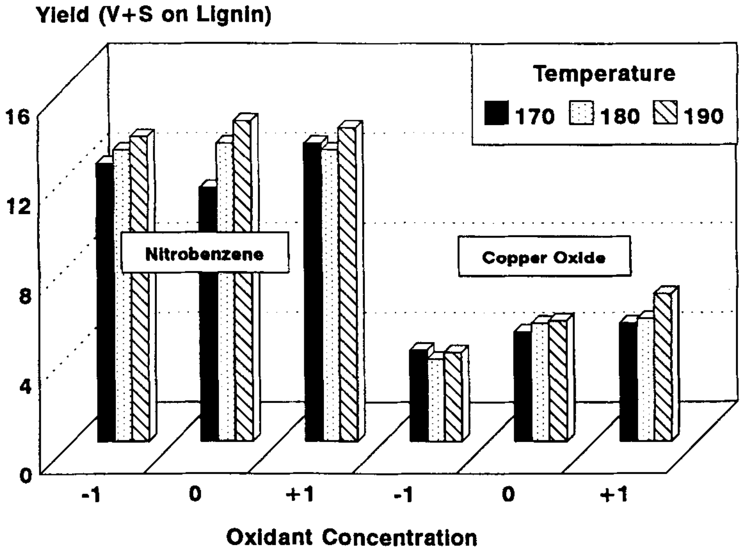


FIGURE 9. Comparation of the total aldehyde yield for NB and CuO oxidations (120 minutes of reaction time).

most effective oxidant to produce aldehydes while with copper oxyde a moderate yield is obtained. Nitrobenzene and its reduction products are harmful and must be removed from the reaction products; however, copper(II) oxide and the reduced form copper(I) oxide could be easily separated from the alkaline solution. In addition most of the copper(II) oxide is regenerated from the reduced form, which makes this oxidant more attractive than nitrobenzene.

The aldehyde yield shown in Figure 9 is clearly decreased with respect to other lignin oxidation experiments, those employing non modified lignin (see Tables 1 and 2), but is higher than others obtained from alkali-lignins. Thus it is clear that the aldehyde yield depends on the lignin sample used. Chemically isolated lignins (soda or kraft lignin) were not suitable materials to produce phenolic aldehydes, however, the isolated eucalyptus kraft lignin employed in our

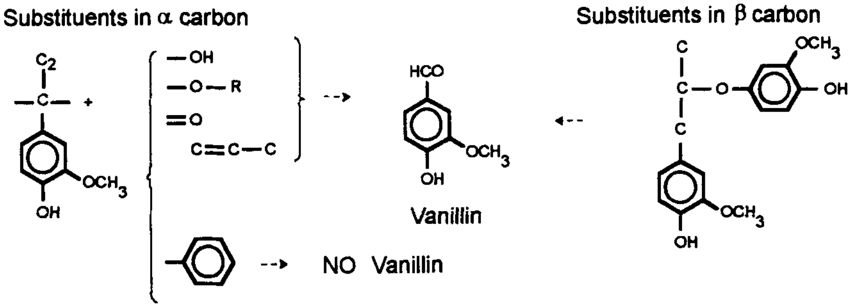


FIGURE 10. Vainillin yield from lignin in the NB oxidation. Effect of the side-chain substituent.

oxidations have produced more aldehyde than other oxidations made on similar lignin samples[29,30], both with nitrobenzene and with CuO as oxidant agent. The oxidations were made with a calcium precipitated kraft lignin, which suggests that the isolation procedure could modify chemically the lignin and change its behaviour under oxidation conditions.

The study of model compound oxidations[10,46] have contributed to the knowledge of lignin oxidation. As shown in Figure 10, guaiacyl propane structures under the nitrobenzene oxidation conditions show a different behaviour, depending on the side-chain substituents: α-hydroxyl, α-carbonyl or α-ether can produce vanillin, α-β double bonds and β-O-4 ether also yields vanillin, but α-aromatic substituents are stable under these conditions of oxidation with nitrobenzene. Other guaiacyl structures (not involving side chain bonds), such as 5-alkyl, can also produce vanillin, but β-β pineresinol and 5-5 diphenyl, or the 5-O-4 and 1-O-4 ether type are resistant to oxidation under the conditions quoted above. Figure 11 shows these lignin dimers.

When kraft cooking lignin is employed, the lignin not only is depolymerised but is also condensed. Some authors, quoted by Chiang and Funaoka[47], have

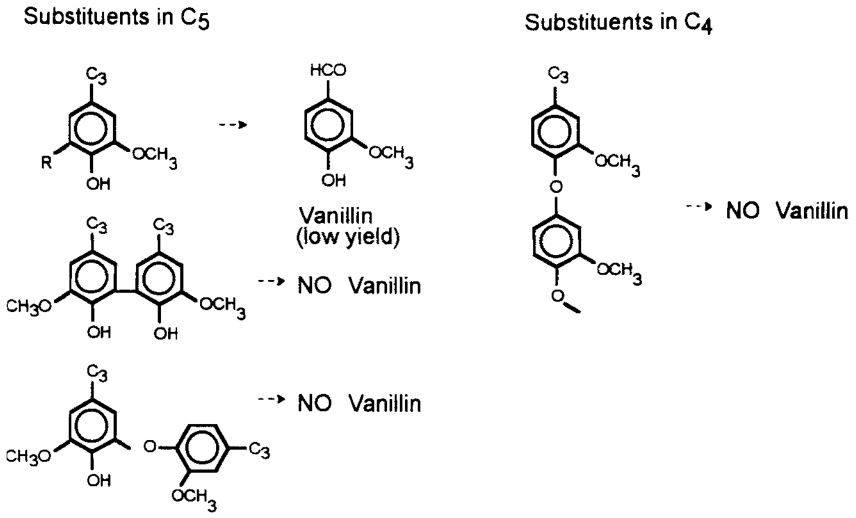


FIGURE 11. Vainillin yield from lignin in the NB oxidation. Guaiacyl structures not involving side-chain bonds.

sugested that α-5, α-1 or 5-5 structures are obtained under kraft pulping conditions. Other lignin structures (β-β, 5-5 diphenyl and 5-O-4 ether) have also been reported to be in the protolignin[47]. As it is mentioned above, some of the previous protolignin and kraft lignin structures were identified as not producing vanillin.

If separation of kraft lignin from black liquor is made by acid precipitation, filtration of the acid suspension is difficult and must be made at 80 °C to accelerate it. Under these conditions, kraft lignin condenses and so, the subsequent nitrobenzene oxidation will show a reduced aldehyde yield. In the nitrobenzene oxidation of a hydrolizated acid sulfuric lignin Funaoka et al.[48] obtained a reduced yield in guaiacyl derivatives (5% in V + VA) and a 35-40% from protolignin. They supossed that condensation reactions were the cause of the poor yield. In a recent work[49], Chang et al. studied the contribution of lignin structures to nitrobenzene oxidation products. They obtained vanillin when condensed structures were oxidized, however the vanillin yield remained low in all the cases.

When kraft lignin is removed by calcium-alcohol precipitation[8] most of the lignin is precipitated as a solid, easy to filter, the subsequent lignin oxidation giving a higher aldehyde yield than acid precipitated lignin. Differences in yield have been related to the isolation method that produces non-reactive derivatives.

CONCLUSIONS

Calcium-alcohol precipitation is an adequate method to isolate kraft lignin from black liquors and also to improve the phenolic aldehyde yield in lignin oxidation. Syringaldehyde and vanillin could be obtained from kraft lignin with short reaction times, which means 14% from nitrobenzene (40 min.,190°C, 6 mL NB/g LIG), and 8% from copper oxide (70 min., 190°C, 4 mol CuO/mol LIG). The improvement in aldehyde yield has been related to the precipitation procedure, which avoids the lignin condensation and thus favours aldehyde formation.

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NOMENCLATURE

ald.	Aldehyde.

comp.	Compound.
LIG	Lignin. In Equation [1] lignin concentration in g/L.
LIG_o	In Equation [1] initial lignin concentration in g/L.
HW	Hardwood.
NaMNB	Sodium m-nitrobenzoate.
NB	Nitrobenzene.
ph.	Phenolic.
P_i	Concentration of product i, in g/L.
S	Syrinaldehyde.
SA	Syringic acid.
S_j	Selectivity of product j.
sol.	soluble.
SW	Softwood.
V	Vanillin.
VA	Vanillic acid.
X	Lignin conversion.
Y_j	Yield of product j.

Subscripts

i	Refers to each oxidation product identified in the analysis.
j	Refers to each oxidation product of interest (S, V, SA, VA).

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