Oxidation of Organosolv Lignins in Acetic Acid

Influence of Oxygen Pressure

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Abstract

The oxidation of four lignins obtained by organosolv pulping of eucalyptus wood (Acetosolv-eucalyptus Acetosolv lignin [EAL]), sugarcane bagasse (Acetosolv-bagasse Acetosolv lignin [BAL] and in acetone/water/$FeCl_3$-bagasse acetone/water lignin [BAWL]), and a softwood mixture (Organocell, Munich, Germany) was performed to obtain vanillin, vanillic acid, and oxidized lignin. Experiments were carried out in acetic acid under oxygen flow using HBr, cobalt(II), and manganese(II) acetates as catalysts. After 10 h the total vanillin and vanillic acid yields were BAL 0.05 mmol, EAL 0.38 mmol, BAWL 0.45 mmol, and Organocell 0.84 mmol. Acetosolv lignins are crosslinked, which explains the lower yields in mononuclear products. The reaction volume (ΔV) of this reaction is –817 cm^3/mol, obtained in experiments performed under oxygen pressure, showing the high influence of pressure on the oxidation. The major part of the lignin stays in solution (oxidized lignin), which was analyzed by infrared spectroscopy, showing an increase in carbonyl and hydroxyl groups in comparison with the original lignin. The oxidized lignin can be used as chelating agent in the treatment of effluents containing heavy metals.

Index Entries: Oxidation of lignins; organosolv lignins; acidic oxidation; utilization of lignins.

Introduction

Oxidation in alkaline medium is an established method for the depolymerization of lignins and lignosulfonates. Vanillin and other aromatic aldehydes and acids are the principal products *(1)*. The industrial yield of vanillin from lignin is between 5 and 10% *(2)*. The industrial production of vanillin by direct oxidation of sulfite-spent liquor began in the United States

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in 1936 but now has been replaced by the eugenol-based route. In other countries (especially Europe) the lignin-based route is still employed *(3)*. The interest in the utilization of pulp byproducts is increasing, especially in Brazil, where pulp production capacity is expected to double in the next 10 yr *(4)*.

In this article we have studied the oxidation in acidic medium because several new pulping processes are performed in which organic acids are used as pulping solvents (Organosolv processes) (*see* ref. *5* for new technologies in the pulp and paper industry). Oxidation is performed in acetic acid using oxygen, cobalt(II), and manganese(II) acetates under conditions developed for the oxidation of p-xylene and other mononuclear aromatic compounds *(6)*. Previous results showed the high efficiency of this catalytic system for the oxidation of lignins *(7)*. The aim of this study is the evaluation of production of vanillin, aromatic acids used in large amounts as coreactants in polyester formulations, and oxidized lignins used as chelating agents *(8)*. The influence of pressure on the yield of these compounds will be also evaluated.

Methods

Organosolv Lignins

Organocell lignin was obtained from the pulping of spruce wood by a methanol/water/NaOH/anthraquinone mixture in a semi-industrial plant in Munich, Germany. Bagasse Acetosolv lignin (BAL) was obtained by pulping depithed sugarcane bagasse with 93% aqueous acetic acid and 0.3% HCl under reflux for 2 h, as described in the literature *(9)*. After evaporation of 80% of the acetic acid from the pulping liquor, the lignin was precipitated with water at 70–80°C, filtered, and dried. Eucalyptus Acetosolv lignin (EAL) was obtained by pulping *Eucalyptus grandis* chips under the same conditions used for BAL. Bagasse acetone/water lignin (BAWL) was obtained by pulping sugarcane bagasse with acetone/water/$FeCl_3$ from a pilot plant in Piracicaba, Brazil.

Oxidation Under Pressure

A mixture of 20 g organosolv lignin, 1 mmol cobalt(II) acetate, 5 mmol NH_4Br, and 200 mL glacial acetic acid was transferred to a 1-L stainless-steel autoclave equipped with a mechanical stirrer. The autoclave was closed, flushed three times, pressurized with 0.5–1.5 MPa O_2, and heated to 210°C, where it was maintained for 15 min under agitation. The heat-up time was 20 min. After the reaction, the autoclave was cooled and the products were removed and filtered. The acetic acid was evaporated from the soluble product. The solid obtained was extracted with diethylether and the insoluble fraction was called oxidized lignin. The ether fraction was silylated with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and analyzed by gas chromatography (GC) for the quantification of vanillin and vanillic acid. The GC-analysis was performed using a Chrompack CP 9000 gas chromatograph with a DB-5 capillary column (30 m × 0.25 mm; 0.25 μm

film thickness). The FID temperature was 280°C and the injector tempera-
ture was 250°C. The column was heated at 45°C for 4 min, and the temperature
was then increased 4°C/min to a final temperature of 280°C. Fluoranthene
was used as internal standard.

Oxidation in an Open System

The oxidations were performed under an oxygen flow and magnetic
stirring in a three-neck round bottom flask, which was connected to a reflux-
condenser and heated in an oil bath. Glacial acetic acid (50 mL), 4.5 mmol
cobalt(II) acetate, 0.5 mmol manganese(II) acetate, and 11.3 mL acetic anhy-
dride were introduced and heated for 30 min. After this time, 0.44 mL HBr
(5.63 mol/L solution in acetic acid) and 11 mL paraldehyde were added
and the O_2 flow was adjusted to 60 mL/min. After 20 min, 5.5 g lignin was
added and the reaction was maintained under reflux (110 ± 5°C) for 10 h.
The mixture was cooled and transferred to a 250-mL round bottom flask,
and 20 mg of fluoranthene was added. The acetic acid was evaporated and
a dark solid was obtained that was extracted twice with diethylether. After
filtration, the solid (oxidized lignin) was dried and analyzed by Fourier-
transformed infrared (FTIR). The extract was concentrated, silylated with
BSTFA, and analyzed by GC as described above.

FTIR Spectroscopy

The FTIR spectra of the original and oxidized lignins were recorded in
a Bio-Rad FTS 40 FTIR spectrometer from KBr pellets (1.5 mg lignin and
350 mg KBr). The spectra were normalized for the absorption at 1510 cm^{-1},
corresponding to the aromatic ring vibration.

Results and Discussion

The catalytic system is based on the oxidation of alkylaromatic compounds
by molecular oxygen *(6)*. The reaction of the cobalt(II) salt with O_2 is the
first step, with the formation of cobalt(III) bromoacetate [$Co(CH_3COO)_2Br$],
which decomposes by homolytic cleavage to regenerate cobalt(II) acetate
and radical bromine. In the sequence, the radical bromine removes one
electron from the aromatic ring of the lignin. This process was confirmed
in the study of simple aromatic compounds *(6)*. Further reactions should be
complexed through the formation of peroxide radicals reaching the cleav-
ages of Cα-Cβ linkages present in the lignin, and giving at the end vanillin
and vanillic acid. Manganese(II) ions also act in the system, avoiding the
decomposition of cobalt(III).

Table 1 shows the total yield of vanillin and vanillic acid for the differ-
ent lignins. Results obtained for oxidation under pressure are also shown.
The open system was not effective for oxidation since the yields in mono-
mers are lower than those obtained under pressure.

Because Acetosolv lignins are crosslinked, they gave the lowest yields
in mononuclear products. Oxidation of the lignins under pressure, with the

Table 1
Yields of Vanillin and Vanillic Acid Under and Without Pressure

Lignin	Open system (A), mmol	Under pressure (B), mmol	Ratio B/A
BAL	0.05	0.27	5.3
EAL	0.38	1.33	3.5
BAWL	0.45	0.67	1.5
Organocell	0.84	5.58	6.6

Table 2
Yields of Oxidized Lignin (Based on Starting Amount of Lignin)
and Total Vanillin and Vanillic Acid
as a Function of Oxygen Pressure for Organocell Lignin

Initial O_2 pressure, MPa	Conversion, %	Oxidized lignin yield, %	Vanillin and vanillic acid yield, mmol
0.5	40.9	33.0	3.34
0.9	46.2	36.0	5.32
1.0	45.9	33.5	5.09
1.5	50.7	37.9	4.17

exception of BAWL, shows an increase in yield of 4–7 times. Pressure influences the thermodynamic and kinetic conditions of the reaction. Mathematical treatment of the variation of rate and equilibrium constants as a function of the pressure shows that they are proportional to the activation and reaction volumes, respectively, as expressed by Eqs. (1) and (2).

$$[\delta \ln(k)]/(\delta P) = (\Delta V^{\#})/(RT) \tag{1}$$

$$[\delta \ln(K)]/(\delta P) = (\Delta V)/(RT) \tag{2}$$

where k = rate constant; K = equilibrium constant; $\Delta V^{\#}$, activation volume; ΔV = reaction volume, P = pressure in MPa; T = temperature in K; and R = gas constant (8.32 MPa cm^3/mol/K).

A negative activation volume means that the formation of the transition state is increased with higher pressure. Kinetic data were not obtained in this set of experiments but the calculation of the reaction volume was performed. The equilibrium is not reached after 15 min of reaction time but an approximation to steady-state was used. Using the conversion for oxidized lignin showed in Table 2 for the Organocell lignin, a reaction volume (ΔV) of –817 cm^3/mol was obtained. This value confirms the high influence of the pressure in the oxidation of the lignin. Because of the crosslinked nature of the lignins, their breakdown is necessary prior to oxidation. Activation and reaction volume studies for lignocellulosics are not often found in the literature; for comparison, the delignification of sugarcane bagasse with acetone has a ΔV = –1533 cm^3/mol *(10)*.
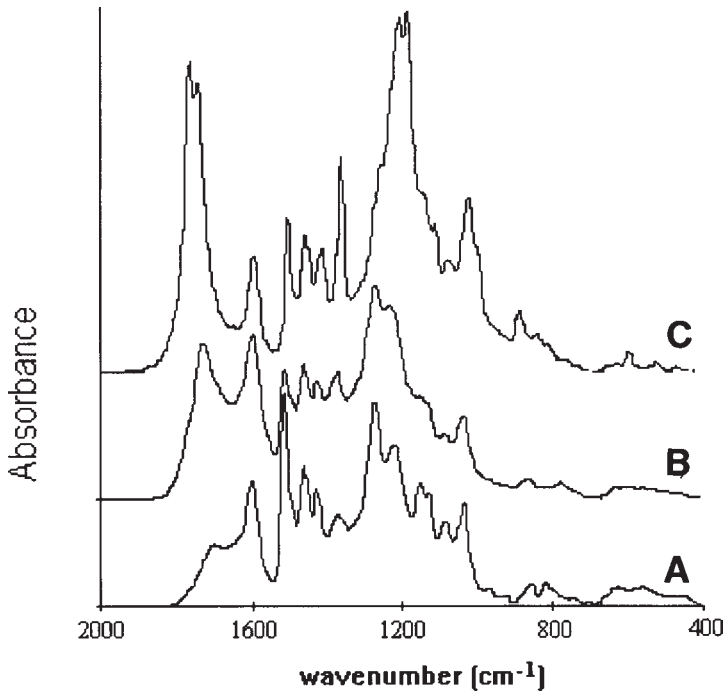
Fig. 1. FTIR spectra of the lignins: **(A)** original Organocell lignin; **(B)** lignin oxidized under pressure (0.9 MPa); **(C)** lignin oxidized in an open system.

Table 3
FTIR Spectra of the Oxidized Organocell Lignins:
Relative Absorbances at 1650 cm^{-1} and 1710 cm^{-1}
Measured with Respect to the Absorbance at 1510 cm^{-1}

Oxidized lignin	A_{1650}/A_{1510}	A_{1710}/A_{1510}
Original Organocell	0.58	0.29
0.1 MPa	0.81	0.69
0.5 MPa	1.06	0.91
0.9 MPa	1.28	1.20
1.0 MPa	1.30	1.25
1.5 MPa	1.45	1.54
In an open system	0.78	1.83

The yields in monomers are not high; however, more than 30% of the lignin is soluble in acetic acid. This fraction, called oxidized lignin, was characterized by FTIR. The spectra of the original and oxidized Organocell lignins (open system and under pressure) are shown in Fig. 1.

Oxygenated groups are most often found in lignin as ether bonds. There are also some nonetherified OH groups, but after oxidation principally an increase in carbonyl bonds is observed. The absorptions at 1650 cm^{-1} and 1710 cm^{-1} correspond to conjugated and nonconjugated carbonyl groups, respectively. Table 3 shows the increase of their intensities for the

oxidized lignins in comparison with the original lignin. The aborbances were measured with respect to the absorption at 1510 cm^{-1}, corresponding to aromatic ring vibrations, which are not influenced by other absorptions.

Conclusions

This work studied the understanding of oxidation as a technique to convert biomass, especially lignin. The concept of obtention of chemicals from lignin in acidic media was evaluated by a new approach, demonstrating that this area was not previously studied in depth. The oxidation of four organosolv lignins was performed both in open and pressurized systems and the overall vanillin and vanillic acid yields were measured. Calculation of reaction volumes gave new information about the system at high pressure. This study, together with the relation of yields in open and pressurized systems, confirms the need of pressure in the procedures to efficiently convert lignocellulosics. In addition, the obtention of macromolecular compounds (oxidized lignin) should be important from a commercial point of view. The increase of polar groups like carbonyls makes the oxidized lignins suitable for their use as chelating agents in the treatment of effluents containing heavy metals.

Acknowledgments

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