Hydrogenolysis of Lignins

Influence of the Pretreatment Using Microwave and Ultrasound Irradiations

ADILSON R. GONÇALVES*,1 AND ULF SCHUCHARDT2

*1Department of Biotechnology—FAENQUIL,
CP 116, 12.600-000 Lorena, SP, Brazil,
E-mail: adilson@debiq.faenquil.br;
and 2Instituto de Química—UNICAMP,
CP 6154, 13081-970 Campinas, SP, Brazil*

Abstract

Hydrolytic eucalyptus lignin was converted to oils by hydrogenolysis. The lignin was obtained by acid hydrolysis of eucalyptus chips from two semi-industrial sources in Brazil: FTI and Coalbra. Hydrogenolysis was performed in an 1-L reactor using lignin/water ratio 1/4 (w/v), pH 9 (adjusted with NaOH), 0.1 g sodium formate/g lignin, 20 MPa (argon pressure) at 280°C for 15 min. After reaction, the products were filtered and the solids extracted with chloroform/ethanol 3/1 (v/v). The solvent was evaporated from the organic phase and a dark oil was obtained. The solid remaining after extraction was weighed to calculate the conversion. Without pretreatment conversions were 41.3 and 47.9% for Coalbra and FTI, respectively. The oil yields were 22.7–27.6% for Coalbra and FTI, respectively. Using microwave pretreatment (30 min of irradiation at 490 W) the conversions were 41.6–50.5% and the oil yields increased slightly to 25.2–31.4%. The polymeric chains in the lignin breakdown due to the action of water near the boiling point under microwave irradiation. On the other hand, by using ultrasound (30 min at 50°C in a ultrasound bath of 25 kHz and 0.8 W/cm^2) the conversions were 35.2–46.9% and oil yields were 22.0–27.1%. Ultrasound favors the formation of radicals that probably caused the reticulation of lignins, decreasing the conversion and yield. Oils analyzed by infrared spectroscopy showed an increase in C=O bond intensities, compared with the original lignins.

Index Entries: Hydrogenolysis of lignins; oils from biomass; microwave; ultrasound.

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*Author to whom all correspondence and reprint requests should be addressed.

Introduction

Acid hydrolysis of eucalyptus wood results in fermentable sugars and hydrolytic eucalyptus lignin as the main by-product *(1)*. This lignin is reticulated due to the cross-linking reactions promoted by the acidic conditions. Depolymerization of the lignin macromolecule to mononuclear aromatics requires intensive energy use and the yields in pure compounds are therefore typically low. In 1981, Goheen *(2)* reviewed the main techniques used to obtain low-molecular weight products from lignins. Such processes are performed at high pressures and temperatures: gasification, hydrogenolysis, pyrolysis, hydrolysis, and oxidation.

Schuchardt and Matos *(3)* developed hydrogenolysis of sugarcane bagasse under pressure (inert gas) using sodium formate as reducing agent. This system successfully liquefied hydrolytic eucalyptus lignin using batch and continuous-flow reactors with oil yields reaching 44.8% at 270°C, 13 MPa for 30 min *(4,5)*. These oils are mainly phenols which can be used to obtain pharmaceutical feedstocks—guaiacol, syringol, etc. *(6)*. In the present work, we performed this reaction using two different sources of lignin and under milder conditions to study the pre-treatment with microwave or ultrasound.

Materials and Methods

Hydrolytic Eucalyptus Lignins

Hydrolytic eucalyptus lignins (HEL) were obtained from two sources: (a) **FTI:** by cooking of wood chips with 3% H_2SO_4 (wt% in respect to lignin) at 170°C for 3 h in a pilot plant at the FTI in Lorena-SP (Brazil), (b) **Coalbra:** by cooking of wood chips with 1 % H_2SO_4 (wt% in respect to lignin) at 190°C for 4 h in a commercial plant purchased from Russia and operated in Uberlândia, MG, Brazil, during 1983–1987.

The lignins were ground in a mortar and analyzed by standard methods to determine Klason lignin, moisture, ash, and carbohydrate contents *(7,8)*. Elemental analysis (carbon and hydrogen) was performed in a Perkin-Elmer PE2400. Because nitrogen was not present in the samples, oxygen was assumed to be the remaining material. Thermogravimetric analysis of FTI lignin was performed in a Dupont 1090, from 25°C to 800°C at 10 K min^{-1} under argon flow of 25 mL min^{-1}.

Hydrogenolysis and Analysis of the Products

The hydrogenolysis reactions were performed in a 1-L high-pressure rocking autoclave described earlier *(9)*. Fifty or 100 g of lignin was suspended in water. A 30% NaOH solution was added until pH reached 9.0. Sodium formate was added (4.5 or 9.0 g) and the final pH was measured. The mixture was stored for 24 h at 25°C and then, in some experiments, was irradiated with microwaves or ultrasound, as described later. The mixture was introduced into the autoclave, that was pressurized with

Table 1
Chemical and Elemental Analysis
of Both Eucalyptus Hydrolytic Lignins

	FTI (%)	Coalbra (%)
Klason content (%)	71.0	77.9
Soluble lignin (%)	0.9	1.2
Moisture (%)	11.0	12.6
Ash (%)	1.3	3.3
Carbohydrates (%)	15.8	5.0
C (%)	57.4	62.0
H (%)	5.0	5.6
O (%)	37.6	32.4

argon at 6 MPa, shaken horizontally at 1.8 Hz, and heated with a 1500-W external heating device, reaching 200°C after 27 min and 280°C after additional 20 min (total heating time 47 min). This temperature was maintained for 15 min. The pressure at the reaction temperature was 20 MPa. The heating was turned off and the autoclave cooled to room temperature, while still being shaken.

After opening the autoclave, the products were transfered to a beaker and the pH was measured. The mixture was filtered and the heavy-dark solids were extracted with a chloroform/ethanol 3:1 (v:v) mixture in a 600-mL Soxhlet extractor for 20–40 h (end point determined by the absence of coloration in the extract). After evaporating of the solvents (1 mm Hg at 40°C), a dark-brown and viscous oil was obtained, which was weighed and characterized in a Perkin-Elmer 1430 infrared spectrometer. The residue of the extractions was dried for 12 h at 110°C and weighed to determine the conversion rate.

Irradiation Pretreatment

1. Microwave: The beaker with the mixture was introduced in a microwave oven, with a rotate-plate, and irradiated at 490 W for 15 min. After irradiation, the water that evaporated due to heating was replaced.
2. Ultrasound: The beaker with the mixture was introduced in a ultrasound-bath of 25 kHz with power of 0.8 W cm^{-2}, at 50°C. After thermal equilibrium, irradiation was started and maintained for 30 min.

Results and Discussion

Lignins Analysis

Table 1 shows the analysis of FTI and Coalbra lignins. Because of the milder hydrolysis conditions of FTI process, FTI-lignin has a higher carbohydrate content when compared with Coalbra lignin.
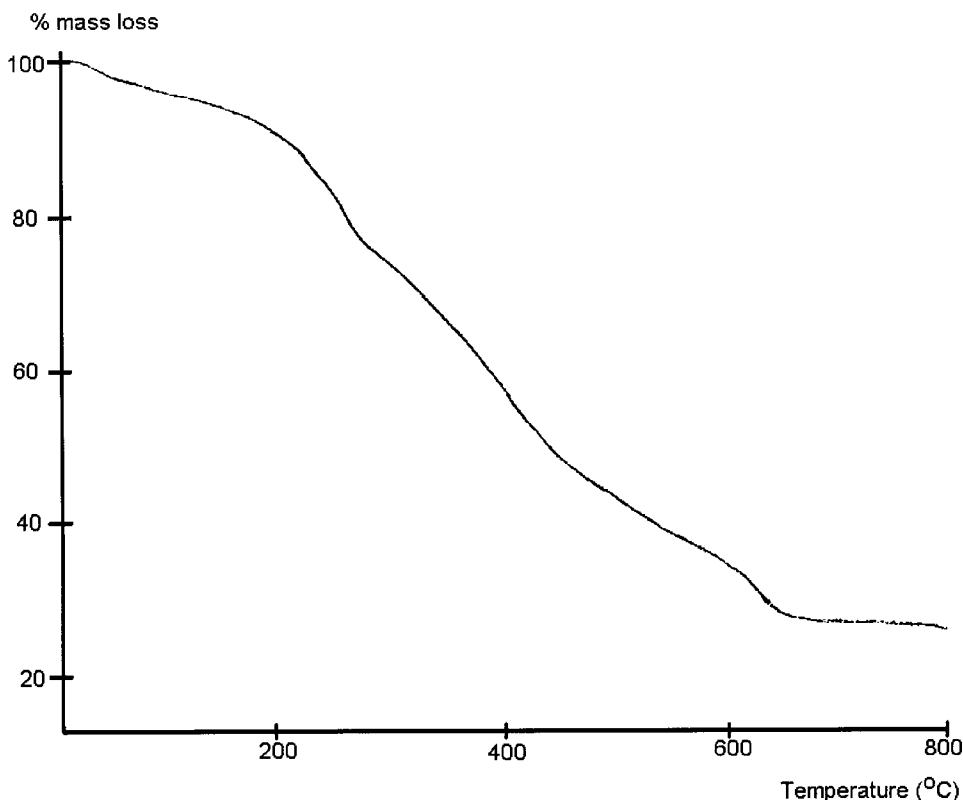
Fig. 1. Thermogram of hydrolytic eucalyptus lignin obtained from FTI.

Figure 1 shows the thermogram of FTI-lignin. Below 200°C, low-molecular-weight compounds adsorbed on lignin (mainly water) is lost. In the range 200–350°C, carbon monoxide and carbon dioxide are lost, coming from carbonylic and carboxylic groups of lignin and residual carbohydrates. Dehydratation can also occur, and above 240°C lignin cross-linking increases. Near 270°C, ether linkages are cleaved, and between 350–500°C, homolytic cleavages of carbon-carbon bonds occur. Above 500°C, lignin is transformed into coke. Reactions aiming to obtain low-molecular-products should be performed from 240–350°C, where cleavages occur, but not total decomposition of the aromatic rings (carbon-carbon homolytic cleavages).

Hydrogenolysis

Swelling of lignin is very important to effectively contact reagents with the entire sample. The reaction system was previously studied for this kind of reaction *(4)*; here we introduce pretreatment with irradiations. Alkaline formate at high pressure and temperature breaks C–C and C–O linkages, at the α-position of aromatic rings, forming low-molecular-weight compounds *(3)*. Temperatures higher than 300°C should be avoided due to the decomposition of formate to CO_2 and H_2 *(3)*. Alkaline conditions favor

Table 2
Conversion and Oil Yield of Hydrogenolysis as
a Function of the Pretreatment and Lignin Source[a]

Experiment number	Lignin source	Lignin mass (g)[b]	Pretreatment	Conversion (%)	Oil yield (%)
1	Coalbra	84.16	none	41.3	27.6
2	Coalbra	84.13	microwave	41.6	31.4
3	Coalbra	84.16	ultrasound	35.2	22.0
4	FTI	43.86	none	47.9	22.7
5	FTI	43.88	microwave	50.5	25.2
6	FTI	87.72	microwave	50.2	28.0
7	FTI	87.75	ultrasound	46.9	27.1

[a]Lignin-water ratio 1:4 (w/v), 0.1 g sodium formate/g lignin, 6.0 MPa initial pressure of argon, 15 min at 280°C.

[b]Water and ash free.

the solubilization of the products, mainly phenols and carboxylic acids. Table 2 shows the conversions and oil yields obtained for the hydrogenolysis of FTI and Coalbra lignins.

Hydrogenolysis works well with sugarcane bagasse with conversions near 100% and oil yields higher than 60% *(3)*, but is not very adequate for lignin. Without pretreatment, conversions ranged from 41.3 to 47.9% and oils yields from 22.7 to 27.6%, which is similar to previous results of lignin conversion *(4,5)*. Using microwave pretreatment, conversions were 41.6 to 50.5% and the oil yields were 25.2 to 31.4%. The polymeric chains in lignin break down due to the action of water near the boiling point under microwave irradiation. Using ultrasound, the conversion was 35.2–46.9% and oil yields were 22.0–27.1%. Because ultrasound favored the decrystalization of celluose before its hydrolysis *(10)*, we tested this irradiation to favor cleavages of C–C bonds at the α-position in the aromatic rings of lignin. Inversely, ultrasound favored the formation of radicals that probably caused the reticulation of lignins, changing slightly the values of conversion and yield.

FTI lignin has a smaller effect from ultrasound pre-treatment probably due to its lower reticulation in comparison with Coalbra lignin. The high reticulation of Coalbra lignin was also evidenced in other works *(4)*.

Infrared Spectroscopy of Oils

The oils obtained in some experiments and the original FTI lignin were analyzed by infrared spectroscopy (Fig. 2). Significant differences were observed, especially in the 1660 and 1700 cm^{-1} regions, corresponding to the conjugated and nonconjugated carbonyl groups. Table 3 shows the relative absorbance (normalized by the absorption at 1510 cm^{-1}) of selected bands in the infrared spectra of oils and lignin.
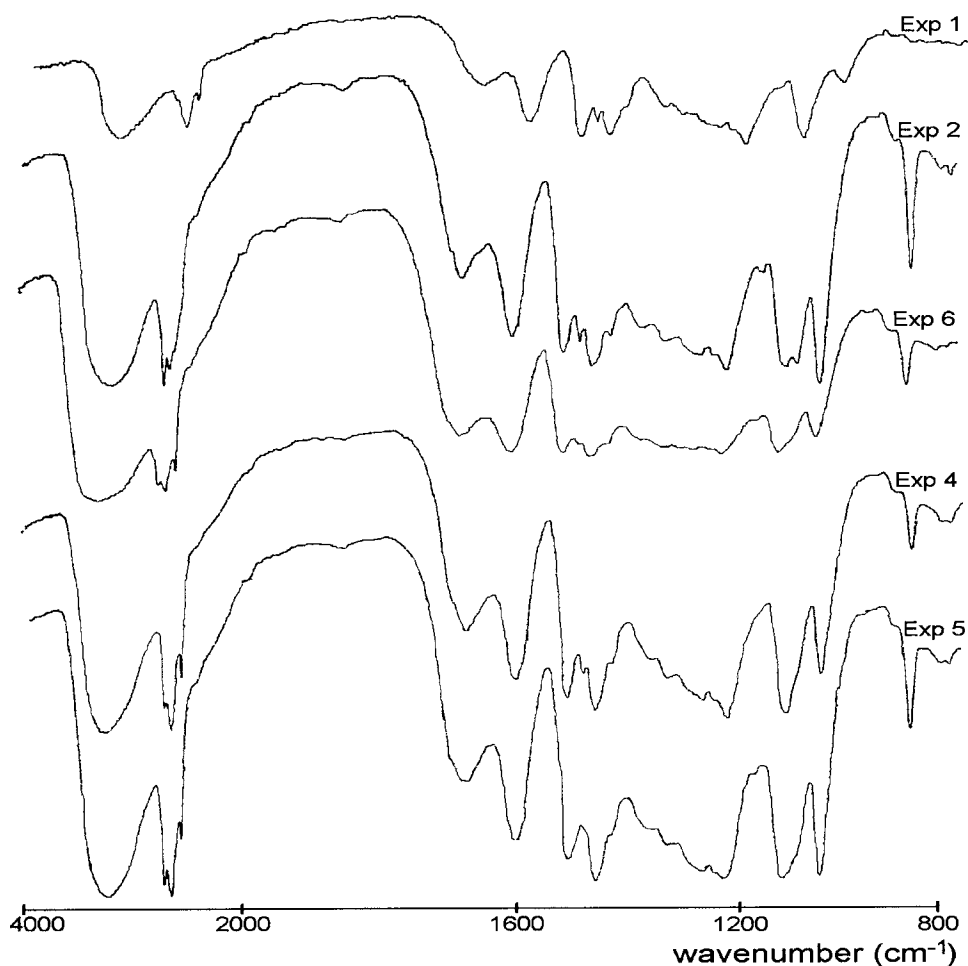
Fig. 2. Infrared spectra of oils and FTI lignin.

Table 3
Infrared Spectra of Oils and Lignin[a]

	A_{1700}/A_{1510}	A_{1660}/A_{1510}	A_{1480}/A_{1510}	A_{1460}/A_{1510}	A_{1100}/A_{1510}
FTI lignin	0.78	1.21	1.17	0.97	1.86
Exp.1	0.52	0.85	0.84	0.98	0.99
Exp.2	0.54	0.87	0.90	1.14	1.13
Exp.4	0.65	0.90	0.86	1.08	1.06
Exp.5	0.61	0.88	0.90	1.15	1.09
Exp.6	0.93	1.04	0.93	1.26	0.85

[a]Relative absorbances at selected wavenumbers measured in respect to the absorbance at 1510 cm^{-1}.

Oils from FTI lignin (Experiments 4–6) have higher carbonyl contents and lower ether contents than oils from Coalbra lignin (Experiments 1 and 2), as evidenced by absorptions at 1700 cm^{-1} and 1100 cm^{-1}, respectively. The absorbance at 1700 cm^{-1} of the oil obtained in Exp. 6 was higher than the other oils, and also the original lignin. This experiment was performed with 100 g FTI lignin using microwave pretreatment resulted in increased C=O absorptions (1700 cm^{-1}) and decreased C–O absorption (1100 cm^{-1}). There is no evidence for changes in other absorptions with experimental conditions. Absorptions of OH groups (3400 cm^{-1}) were not measured due to the high interference of moisture in this region.

Conclusions

Hydrogenolysis can convert up to 31% of hydrolytic eucalyptus lignin into oils. Microwave irradiation is a useful pretreatment for the reaction, increasing the oil yield by 11–14%. FTI lignin is less cross-linked than Coalbra and was more susceptible to the action of formate in the hydrogenolysis and suffered no influence of ultrasound.

Acknowledgments

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