Coconut Husk Lignin. I. Extraction and Characterization

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SYNOPSIS

Recently lignin has been the object of a renewed interest because of the need to use raw materials from renewable resources. One such resource is coconut husk, a material usually discarded during the copra extraction process. Due to its high lignin content, coconut husk has been recognized as having a variety of applications. Therefore, it is important to know the approximate structure of coconut husk lignin and those variations introduced by different isolation methods. This work reports a general characterization of coconut husk lignin. Results are given of the contents of hydroxyl and noncondensed guaiacyl units, the extractability of the lignin in alkaline and "organosolv" media along with thermal properties of the extracted lignins. The extraction system of NaOH–anthraquinone at 150°C was most conveniently based on the relatively low amount of condensed lignin generated.

INTRODUCTION

Lignocellulosic materials have lately been the object of renewed interest.[1-3] The main reason for this activity is the necessity of exploring alternative raw materials from renewable resources.[1,2] Lignin is one of the most abundant naturally occurring polymers, usually obtained as a by-product generated throughout all pulping processes and burned on site to generate heat due to its high energetic content. A number of practical uses for lignin wastes have been described in the literature.[4-7] Recently, the number of potential applications for reprocessed or modified lignins has been steadily growing.[7-9]

One of the main drawbacks of lignin, from a practical standpoint, is the variability observed in its composition, molecular structure, and molecular weight. These three factors depend on the type of plant from which it is obtained and have motivated a large number of investigations devoted to the study of lignin structure. Most of these investigations have been carried out in forest products laboratories and some date back to the last century.[10] Coconut husk, the fibrous external portion of the fruit of coconut palms, is a by-product of the copra extraction process and is generally considered as a waste. A variety of uses have been proposed for coconut husk lignin, which is present at levels of up to 33% by weight of the husk.[11] The applications range from the fabrication of particle board agglomerated by "its own resin"[12] to the hydrogen chloride extraction of lignin to be used as an additive in the formulation of reinforced plastics.[11] One important aspect that, in our view, has been omitted in these efforts is the knowledge of the approximate structure and characteristics of the lignin involved. Also overlooked have been the general extractability features of the polymer, which are of the utmost importance since its physicochemical properties depend highly on the method of isolation used.[13,14] Since chemical reactivity and potential applications of the material are intimately connected to these properties, it would be desirable to know them in order to devise further studies in this area.

In this study we present the extractability characteristics of coconut husk lignin, as well as a general characterization of the products obtained. The extractions were carried out using different alkaline solutions and aqueous organic or "organosolv" combinations.[13,14] The infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic characterization of these lignins together with studies on their

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reactivity toward formaldehyde will be reported in future papers.

EXPERIMENTAL

Sample Preparation

Coconuts used in this study were collected during winter from 15-year old coconut palms in the east coast of the Peninsula of Yucatan (Dzilam de Bravo, Yucatan, Mexico). According to the Harries's classification for *Cocos nucifera L.*,[15] the coconut palms of this region belong to the Typica "Atlantic Tall" variety.[16]

The husk samples came from mature coconuts, dried and defibered. The samples were milled in a Wiley-type mill (G. W. Brabender) and the resulting powder was separated into coarse and fine fractions by means of a 0.78-mm sieve. The fine powder was dried in a forced air oven at 105°C for further treatment.

Lignin Extraction

To carry out the lignin extraction the technique described by Lai and Sarkanen[14] was used. In a typical procedure, 10 g of coconut husk powder were subjected to a digestion process in a 2-L Parr reactor using various time and temperature combinations. A glass reactor was used when reflux conditions were necessary. All tests were carried out by keeping a sample–liquor ratio, in parts per volume (p/v), of 1 : 20. The different liquor formulations used are listed in Table I.

Following the digestion, the resulting product was left to cool in the reactor, then filtered through filter paper (Whatman No. 1). The cellulosic residues were washed off with distilled water. The aqueous filtrate was acidified to pH 1 with concentrated sulfuric acid and allowed to boil for one hour. The precipitate obtained in this operation was separated by filtration through coarse-porosity filter paper (Shriver S-936) and washed with distilled water until a pH 7 was reached. The resulting lignin samples were dried in a forced air oven at 105°C.

"Dioxane lignin" was extracted according to the procedure described by Pepper et al.[17] Coconut husk powder (25 g) was refluxed with 300 mL of a 9 : 1 dioxane–water mixture in 0.025 *N* hydrochloric acid. The process was carried out in a 1-L glass kettle for 10 h, maintaining a small but constant nitrogen flow. The material was isolated following the procedure recommended for hardwoods whose lignin is termed "B-lignin."[17] The liquor, which had previously been neutralized with sodium bicarbonate, was concentrated to small volume and slowly poured into a 1% sodium sulfate solution. The precipitated lignin removed by centrifugation was diluted with water and acidified to pH 3 with dilute hydrochloric acid. The precipitate obtained was washed and dried in the manner described above for the other lignins.

LIGNIN CHARACTERIZATION

Acetylation

Lignin samples (1 g) obtained from the previous digestion procedures were refluxed for 3 h in 20 mL of an acetylating mixture of pyridine and acetic anhydride.[18] The samples were left to cool, and 50 mL of water were added through the condenser. After

Table I Composition of Liquors Used for Coconut Husk Lignin Extraction[a]

Nomenclature	System	Concentration by wt or Ratio	Temperature (°C)	Time (h)	Other Additives
L-1	Aq. NaOH	2%	100	5	None
L-2	Aq. NaOH	2%	100	5	0.1% AQ
L-3	Aq. NaOH	2%	160	5	None
L-4	Aq. NaOH	2%	150	5	0.1% AQ
L-5	Dioxane–water	9:1 (v/v)	100	8	0.025*N* HCl
L-6	Aq. NH_4OH	5%	100	3	None
L-7	Aq. NH_4OH	5%	150	3	None
L-8	Butanol–water	1:1 (v/v)	170	5	1% HCl
L-9	Aq. Na_2SO_3 and $NaHSO_3$	12.5 and 3%, respect.	180	5	None
L-10	Ethylene glycol–water	4:1 (v/v)	120	7	1% HCl
L-11	Ethanol–water	1:1 (v/v)	80	7	1% HCl

[a] Aq. = aqueous; AQ = anthraquinone.

further cooling, an additional 100 mL of cold water were added. The resulting precipitate was filtered and washed with cold water, then dried at 105°C to constant weight. One-gram samples of this product were treated with reagent-grade chloroform and the resulting soluble and nonsoluble fractions separated by filtration (Whatman No. 1). Drying was carried out at 105°C in weighing bottles and the weight difference recorded when constant weight conditions had been attained.

Determination of Phenolic Hydroxyls

Ultraviolet (UV) spectra of alkaline (pH 12) lignin solutions, as well as of the pH 6 lignin solutions, were obtained using a UV–visible spectrophotometer (Spectronic 2000, Bausch and Lomb) scanning between 200 and 400 nm. Phenolic hydroxyls were determined by the method of Goldschmid,[19] measuring the absorbance difference of lignin when dissolved in pH 6 and in alkaline media.

The following expressions were used to obtain the concentration of phenolic hydroxyls in the sample:

$$\%OH_{ph} = \Delta\alpha_{max} \frac{17}{41} \quad (1)$$

where $\Delta\alpha_{max}$ is the absorption maximum of lignin solution in the 280–300 nm region and is defined as follows:

$$\Delta\alpha_{max} = \frac{A_{max}}{C_L} \quad (2)$$

A_{max} is the absorbance maximum between 280 and 300 nm in the UV spectrum obtained when the lignin solution at pH 12 and that at pH 6 were used as sample and reference, respectively, and C_L is the lignin concentration (g/L) in the solution. The phenolic hydroxyl content in moles per gram of lignin was calculated as follows:

$$C_{OH} = \frac{\Delta\alpha_{max}}{4100} \quad (3)$$

Total Hydroxyl Determination

This analysis was carried out by initial acetylation of 1-g samples of lignins and a control solution, containing only the acetylating mixture, following the procedure already described. The acetic acid formed was titrated with an excess of 0.1 *N* KOH solution in the cell of a potentiometer (Conductronic pH model 20). From the titration curve obtained, the neutralization point was determined. The percentage of total hydroxyls in the sample was calculated by applying the expression:

$$\%OH_{tot} = \frac{(V_0 - V) \times N \times M \times 100}{W_s \times 1000} \quad (4)$$

where V_0 and V are the volumes, in mL, of KOH solution required to neutralize the control and sample specimens, respectively, N is the normality of titrating solutions, M the hydroxyl group molecular weight (17 g/mol), and W_s the weight of the lignin sample in grams.

Solubility Tests

Samples of dry, powderous lignin (50 mg) were placed in test tubes and 0.5 mL of solvent added. These mixtures were shaken at room temperature for 24 h. After, these mixtures, solutions, or suspensions were left at rest for 6 h. Solubility of these lignins was qualitatively assigned with basis on visual observations as follows: (a) mixtures rendering slightly colored or colorless solutions were considered as insoluble (I); (b) mixtures having a intense brown reddish color, but showing a precipitate, were taken as partially soluble (Ps); (c) finally, mixtures showing no precipitate and a very dark brown color were considered to be soluble (S).

Purity

The amount of Klason lignin present in the samples was determined by analysis with 72% H_2SO_4 (TAPPI standard method T13m-54). Reducing sugars were detected in the filtrate of hydrolyzed (6 *N* HCl) lignin samples using Fehling's reagent.[18]

Reduction with Sodium Hydroboride

Samples of lignin (1 g), previously extracted with sodium hydroxide solution, with or without anthraquinone, were dissolved in 10 mL of isopropanol. The solution was treated with 1.2 g of sodium hydroboride and the mixture heated at 60°C for 4 h. Water (10 mL) was then added and the mixture refluxed for 30 min. The isopropanol was eliminated *in vacuo* using a rotary evaporator. The treated lignin was precipitated by adding an aqueous solution of hydrochloric acid until a pH 2 was reached. The precipitate obtained was washed and centrifuged until the pH of the liquid was neutral. The reduced lignin was recovered and vacuum dried at 105°C.

Estimation of Noncondensed Phenolic Units

The colorimetric method of Adler and Lundquist was followed.[20] Samples of the extracted lignins (1 g) were first reduced with sodium hydroboride, then treated with 10 mL of a 0.5 *N* HCl solution in methanol–dioxane (1 : 1, v/v) for 48 h at 25°C. The samples were washed, recovered by centrifugation, and dried at 105°C. To transform guaiacylic phenols into quinones, two 300-mg samples of reduced lignin were placed in 10 mL of a mixture of methylcellosolve–water (3 : 2, v/v) and treated with 500 mg of sodium nitrodisulfonate (Fremy's salt) added under a nitrogen atmosphere. The solutions were left for 3 h and then diluted with the methylcellosolve–water mixture to 25 mL. The absorbance of these solutions was determined at 365 and 486 nm (Bausch and Lomb Spectronic 2000 spectrophotometer). In all cases, except for dioxane lignin, a further 1 to 5 dilution was required since the initial concentration was too high for the working range of the instrument.

Thermal Characterization

A differential scanning calorimeter (DSC) (Perkin-Elmer DSC 2C) was used to obtain the thermograms of the extracted lignins. About 20–25 mg of the powderous, dried sample lignin was pelletized by pressing it, at room temperature, under 3000 psi of pressure for 5 min. All samples were kept in a dessicator with P_2O_5 before the measurements were taken. DSC runs were performed under a constant flow (20 mL/min) of nitrogen at a heating rate of 20°C/min. Two runs from 50 to 200°C, and a third from 50 to 300°C, were performed on each one of the samples. The glass transition temperature (T_g) was defined as the onset of the major change in heat capacity (C_p) in DSC traces. Thermal gravimetric analysis (TGA) (Perkin-Elmer TGS-2) was carried out using a nitrogen flux of 20 mL/min and a heating rate of 20°C/min. The mass loss suffered by the lignins tested (4–7 mg) was recorded as a function of temperature between 50 and 750°C. Data accumulation and handling of DSC and TGA runs were performed on a Perkin-Elmer 3600 Data Station.

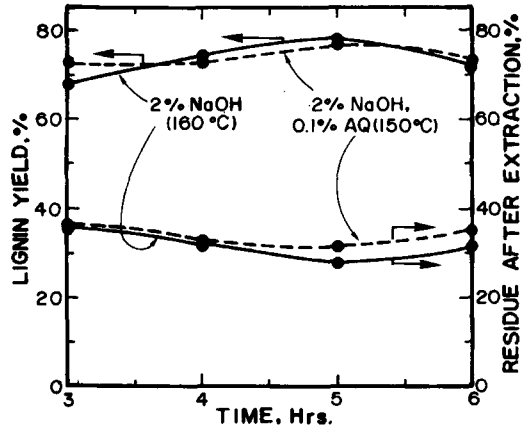


Figure 1 Lignin yield and residue after extraction of coconut husk with alkaline and sulfite systems for different lengths of times.

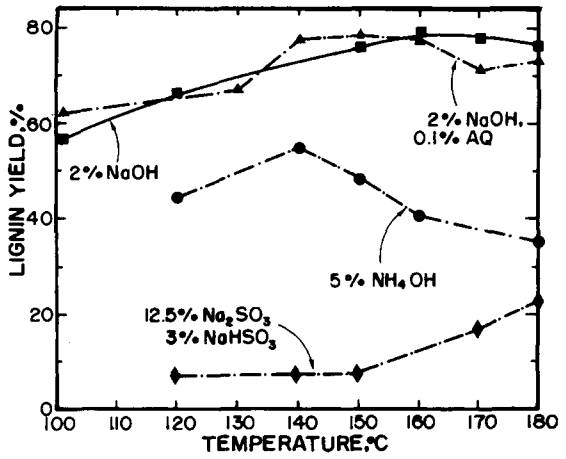


Figure 2 Lignin yield after coconut husk extraction at different temperatures with alkaline and sulfite systems.

RESULTS AND DISCUSSION

Lignin Yield

Lignin yield was calculated by comparing the amount of lignin precipitated by treatment of the extraction liquors with H_2SO_4 with the total amount of lignin present in the coconut husk (about 33% by weight).

Figure 1 shows that high temperatures tended to favor the lignin extraction yield, particularly between 140 and 160°C. Above 160°C a slight decrease was observed for the NaOH and NaOH–anthraquinone (NaOH–AQ) systems. Extractions with NH_4OH produced medium yields that decreased markedly as digestion temperature increased above 140°C (Fig. 2). Very low yields were obtained with the sulfite system. However, these yields increased at temperatures above 150°C. It must be pointed out that the yields obtained were calculated on the basis of the amount of lignin recovered by acid precipitation and that, as seen in Figure 3, the cellulosic residue determined was lower for higher digestion temperatures. This means that an important fraction of the ammonia- and sulfite-extracted lignin

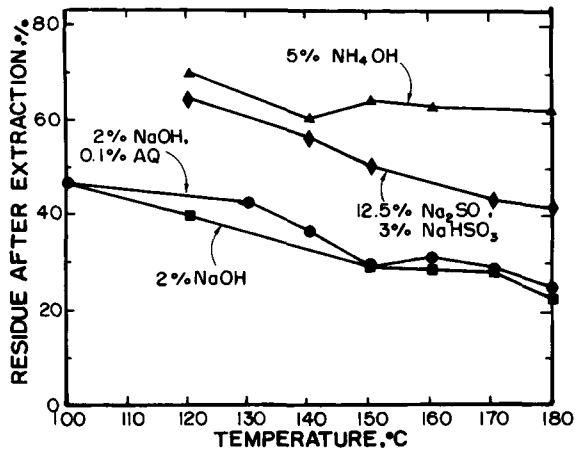


Figure 3 Residue after coconut husk extraction at different temperatures with alkaline and sulfite systems.

does not precipitate with the addition of acid under the conditions used. It is possible that under such conditions at temperatures above 140°C lignin suffers chemical modifications that render it partially soluble in acidic solutions.[13,14]

For systems in which NaOH was used, with or without anthraquinone, no significant differences in their yields were observed, except that maximum yield (78%) was obtained at a lower temperature when anthraquinone was used. However, this result might be influenced by the length of the experiment. In order to determine the role of the digestion time in the process, experiments were carried out using different digestion periods for the extraction temperatures where maximum yield had been observed: 150°C for NaOH–AQ and 160°C for NaOH (Fig. 2). Taking into consideration the results obtained, it was decided to apply a two-level factorial experimental design to evaluate the relative importance of time (t, in hours) and temperature (T, in °C) on the final lignin yield ($R\%$). Temperatures used were 120 and 160°C for NaOH extractions, 130 and 150°C for NaOH–AQ extractions, and 3 and 5 h of digestion time were used in both cases (Table II).

Assuming a linear behavior, and since the time–temperature interaction was insignificant in both cases, the following equations were obtained by applying Yates' algorithm:[21]

$$R\%(\text{NaOH}) = 8.77 + 0.29T + 4.55t \quad (5)$$

$$R\%(\text{NaOH} - \text{AQ}) = 9.16 + 0.52T + 1.63t \quad (6)$$

From these expressions it is observed that digestion time has a greater effect on the NaOH system, while the NaOH–AQ system is more affected by the

Table II Yields of Lignin after Extraction under Conditions with NaOH and NaOH–AQ Systems

System	Temperature (°C)	Time (h)	Yield (wt %)
2% NaOH	120	3	57.6
	160	3	68.0
	120	5	65.6
	160	5	78.2
2% NaOH, 0.1% AQ[a]	130	3	64.2
	150	3	73.4
	130	5	66.2
	150	5	77.9

[a] AQ = anthraquinone.

temperature. This difference can be explained if one takes into consideration that anthraquinone acts as a "redox" catalyst in the delignification process[22] and, as reported for alkali pulping of wood shavings,[23] significantly increases the rate of delignification during the initial phase (up to 1.45 h at 170°C).

The yields of 45 and 47% obtained for ethylene glycol–water (under reflux conditions) and n-butanol–water (at 110 and 170°C) systems, respectively, do not differ significantly from each other (Table III) and are comparable to the 44% yield of the NH_4OH system (Fig. 1). The yield of lignin extracted with dioxane–water mixtures was 16%. This is an expected value because this system does not significantly modify the chemical structure of lignin.[13,14]

Noncondensed Guaiacyl Units

The results shown in Table IV were obtained using a molar absorptivity of 800 for the band at 486 nm. This is because the highest absorbance band at 365–

Table III Yield of Lignin Extracted with Organosolv Systems

System	Temperature (°C)	Time (h)	Yield (wt %)
Ethylene glycol–water, 4:1 (v/v), 1% HCl	120	7	59.7
Butanol–water 1:1 (v/v), 1% HCl	95	7	45.1
	170	5	47.0
Ethanol–water 1:1 (v/v), 1% HCl	80	7	11.0

Table IV Percentage of Noncondensed Guaiacyl Units in Extracted Lignins

Noncondensed Phenolic Units	Lignin				
	L-1	L-2	L-3	L-4	L-5
%	0.3	2.2	1.9	4.2	5.1

367 nm[20] was not well defined in the UV spectra. The values obtained for NaOH–AQ lignin at 150°C and dioxane–water (Table IV) are comparable with those reported for lignin extracted with dioxane–water mixtures from hardwoods[24] and fall between 4 and 10% of noncondensed guaiacyl units. It must be pointed out that the values in Table IV represent the noncondensed guaiacyl units having their phenolic group in the free form.[20] Noncondensed guaiacyl units having their phenolic group alkylated were not quantified. Furthermore, since the relative quantities of syringyl and *p*-hydroxyphenyl groups are not known, only a qualitative evaluation can be made of the effect of anthraquinone on lignin as a whole. On this basis the lower values of noncondensed phenolic units in lignins extracted without anthraquinone can be attributed to the occurrence of further condensation of polymeric fragments of lignins, as pointed out during batch delignification studies.[25] It can be concluded that anthraquinone minimizes such condensation by deactivating the reactive groups of lignin fragments, perhaps as the quinonemethide species.[22]

Purity and Solubility

Reducing sugars were detected in all lignin samples. The obtained values of Klason lignins varied from 82.8% for NaOH-extracted lignin at 160°C to 93.7% for NH_4OH lignin at 150°C (Table V). Taking into account that a small fraction of lignin might have been dissolved in 72% H_2SO_4,[26] the true Klason lignin values will be slightly lower than those obtained.

Results in Table VI show, as expected, that the solubility characteristics of the lignins extracted depend on the system and conditions used. The data indicate that the best solvents for lignin are pyridine, ethylcellosolve, dimethylformamide, and dimethylsulfoxide. Solubility parameters of these solvents, as listed in Table VII, range from 21.9 to 26.5 $J^{1/2}/cm^{3/2}$ and are comparable to the values of 21.0–25.0 $J^{1/2}/cm^{3/2}$ reported as optimum from studies with binary solvent mixtures.[27] However, it may be noted that although acetonitrile and ethanol possess solubility parameters within the optimum range (24.1 and 26.1 $J^{1/2}/cm^{3/2}$, respectively), they are not efficient solvents for lignin (Table VI). This discrepancy may be explained on the basis of the contribution of hydrogen bond values (δ_h) to the solubility parameter of each solvent (Table VII). Ethanol, for example, possesses a higher capacity for hydrogen bond formation (δ_h = 19.5 $J^{1/2}/cm^{3/2}$) than do the lignin solvents. These results are in agreement with those obtained previously using the measure of hydrogen bond capacity, determined by observing the infrared shift of the O-D band when the solvent was mixed with CH_3OD.[28] As already discussed, lignins are soluble in solvents having solubility parameters within the range of 21.0–25.0 $J^{1/2}/cm^{3/2}$ and a moderate hydrogen bond contribution (approximately 6.0–15.0 $J^{1/2}/cm^{3/2}$). However, it must be noted that, according to the previous criteria, pyridine behaves abnormally since it is a good lignin solvent in spite of having a δ_h value lower than that of acetonitrile (5.9 vs. 6.1 $J^{1/2}/cm^{3/2}$, Table VII from Ref. 29). This behavior could be due to the fact that acetonitrile has a higher polar contribution (δ_p = 18.0 $J^{1/2}/cm^{3/2}$) to its solubility parameter or, alternatively, to an acid–base interaction between pyridine

Table V Phenolic and Total Hydroxyls and Klason Lignin in Extracted Lignin

Lignin	Phenolic OH's		Total OH's		Klason Lignin
	(wt %)	(OH/C-9)[a]	(wt %)	(OH/C-9)	(wt %)
L-1	1.3	0.14	10.9	1.15	91.9
L-2	1.3	0.14	7.3	0.78	82.8
L-3	1.6	0.17	8.7	0.91	88.3
L-4	2.0	0.21	6.6	0.70	92.2
L-5	1.8	0.19	5.0	0.52	95.0
L-6	1.1	0.12	3.7	0.39	86.5
L-7	1.7	0.18	9.5	1.01	93.7

[a] (OH/C-9) = the number of hydroxyls per phenylpropane unit.

Table VI Solubility of Coconut Husk Lignins[a]

Solvent	Lignin								
	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	L-9
Diethyl ether	I	I	I	I	I	I	I	Ps	Ps
Ethyl acetate	I	I	I	I	I	I	I	I	I
Chloroform	I	I	I	I	I	I	I	I	I
Acetone	Ps	Ps	Ps	Ps	Ps	Ps	Ps	Ps	Ps
Dioxane	Ps	Ps	Ps	Ps	Ps	I	I	Ps	I
Pyridine	Ps	Ps	S	S	S	Ps	Ps	Ps	Ps
Acetonitrile	I	I	Ps	Ps	I	I	I	I	I
EC	Ps	Ps	S	S	S	Ps	Ps	I	Ps
DMF	S	S	Ps	S	S	Ps	Ps	Ps	Ps
Ethanol	Ps	Ps	Ps	Ps	Ps	Ps	Ps	Ps	Ps
DMSO	S	Ps	S	S	S	Ps	Ps	Ps	Ps
Methanol	Ps	Ps	Ps	Ps	Ps	Ps	S	Ps	Ps
Water	I	I	I	I	I	I	I	I	I

[a] I = insoluble; Ps = partially soluble; S = soluble; EC = ethylcellosolve; DMF = dimethylformamide; DMSO = dimethylsulfoxide.

and the phenolic groups of lignin. This latter possibility appears to be the most probable cause for the anomalous solubility of lignin in pyridine.

It is evident that further studies, both quantitative and systematic in nature, on the solubility of lignin are required. Initial fractionation will prevent masking of the results due to the chemical heterogeneity of lignin. The results obtained should be correlated with the parameters in Table VII, keeping in mind the possibility of specific interactions between lignin and some solvents.

Hydroxyl Contents

Table V shows that lignins with higher numbers of phenolic hydroxyls are obtained when the NaOH–AQ system at 150°C is used while lower hydroxyl contents are produced with the boiling NH_4OH sys-

Table VII Three-Component Solubility Parameters[a] of Solvents Used in the Test of Lignin Solubility

Solvent	Solubility Parameter,[b] $J^{1/2}$ $cm^{-3/2}$				Hydrogen Bonding Capability
	δ_t	δ_d	δ_p	δ_h	
Diethyl ether	15.4	14.4	2.9	5.1	Poor
Ethyl acetate	18.6	15.2	5.3	9.2	Moderate
Chloroform	18.9	17.7	3.1	5.7	Poor
Acetone	20.0	15.5	10.4	7.0	Moderate
Dioxane	19.9	17.5	1.8	7.4	Moderate
Pyridine	21.9	18.9	8.8	5.9	Moderate
Acetonitrile	24.1	15.4	18.0	6.1	Moderate
EC	24.3	16.1	9.2	14.3	Moderate
DMF	24.9	17.4	13.7	11.3	Moderate
Ethanol	26.1	15.8	8.8	19.5	Strong
DMSO	26.5	18.8	15.4	10.2	Moderate
Methanol	29.7	15.2	12.3	22.3	Strong
Water	47.9	12.3	31.3	34.2	Strong

[a] Data from Ref. 29.

[b] δ_t = total parameter of solubility; δ_d = dispersion, δ_p = polar, and δ_h = hydrogen bond contributions to the total parameter of solubility.

tem. The number of total hydroxyls found is a minimum for the NH_4OH system, maximum for the lignin extracted with NaOH under boiling conditions, and intermediate for the NH_4OH system at 150°C. However, it should be kept in mind that the carbonyl groups in the sample interfere with the method for phenolic hydroxyl determination.[30] This interference does appear to have occurred and it is evident when the region at 330–370 nm of the UV spectra is analyzed. The UV spectra show a shoulder for pH 6 solution spectra (Fig. 4) and a broad band for differential alkaline spectra (Fig. 5).

It is also important to note that the acetylation of lignins invariably produced a chloroform-soluble and a chloroform-insoluble portion (Table VIII) having higher and lower acetylation degrees, respectively. In fact, a major portion of the acetylated NaOH–AQ lignin and sample of acetylated dioxane–water lignin was completely soluble in chloroform. This result concurs with the higher value of noncondensed phenolic units determined on these lignins. In addition to the different hydroxyl contents (Table V), there are three other possible explanations for the varying solubility behavior found: the difference in molecular weights of the extracted lignins, the nonuniform distribution of reactive sites, and the resulting differences in accessibility to the acetylating mixture.[31]

Thermal Analysis

Differential scanning calorimetry tests showed that the obtained lignins have a glass transition temperature, T_g, ranging from 147 to 172°C (Fig. 6 and Table IX). These results, together with the fact that their DSC runs did not show any endothermic peaks below the degradation temperatures, are in accord

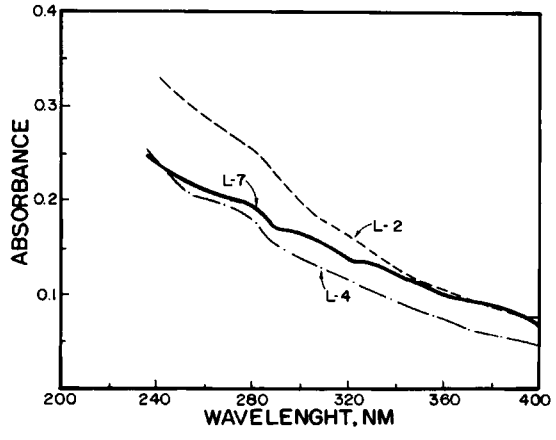


Figure 4 Typical UV spectra of coconut husk lignins.

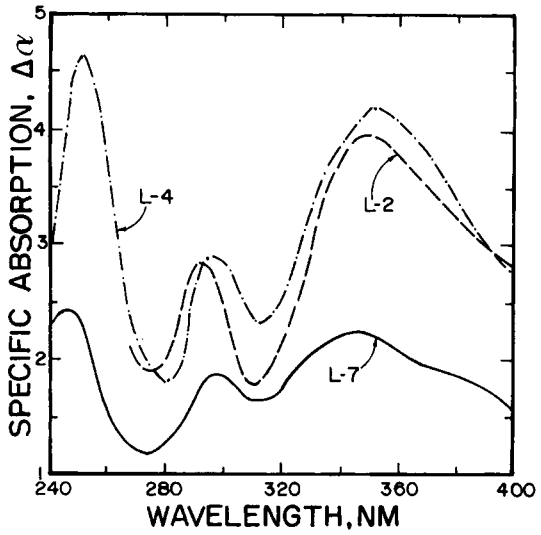


Figure 5 Typical differential UV spectra between neutral and alkaline solutions of lignins.

with the finding that lignin is amorphous in nature.[32–34] The T_g's of the tested lignins are in the range of values reported for other lignins.[35,36] There are several features worthy to mention about the DSC thermograms in Figure 6. Lignins extracted with aqueous NaOH having no anthraquinone (L-1 and L-3), as well as those extracted with NH_4OH (L-6 and L-7), show a small value of ΔC_p at the T_g than those extracted with aqueous NaOH–AQ (L-2 and L-4), dioxane (L-5), bisulfite (L-9), or with organosolv systems (L-8, L-10, and L-11). This may indicate that the first two systems induced a higher extent of condensation in the extracted lignins than the other ones. Furthermore, the DSC trace of lignin obtained with NaOH–AQ at 150°C (L-4) is very similar in shape and in its T_g value to that of dioxane lignin (L-5). This is a expected result in light of the observations that, during the delignification process of lignocellulosic materials, AQ significantly reduces the extent of lignin condensation.[22] These results

Table VIII Soluble and Insoluble Weight Percentages of Acetylated Lignins in Chloroform

	wt % of Acetylated Lignin	
Lignin	Soluble Fraction	Insoluble Fraction
L-1	25	75
L-2	63	27
L-3	57	43
L-4	100	0
L-5	88	12

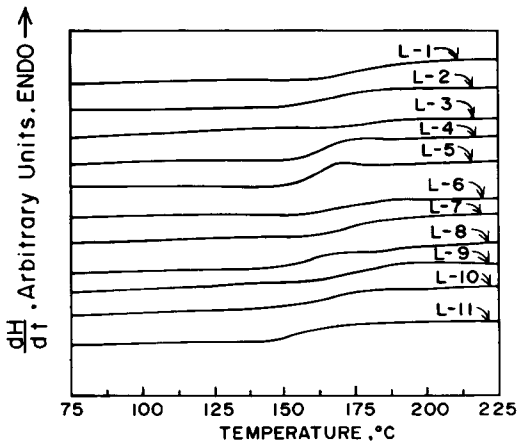


Figure 6 DSC thermograms of lignin samples extracted from coconut husk.

are in accord with those obtained from the quantification of noncondensed guaiacyl units, and of hydroxyl contents, in alkaline and dioxane lignins, as well as with the behavior of the acetylated lignins. In general, it can be noted that the T_g's of the lignins extracted with NaOH–AQ and with organosolv systems are very similar in value, whereas those of lignins extracted with NaOH having no AQ as an additive (L-1 and L-3), as well as those obtained with NH_4OH (L-6 and L-7) and with bisulfite (L-9) are higher in value. An ample discussion on the T_g results requires additional information about structural details of these lignins, as may be the extent and type of rupture, and condensation, suffered by the lignins, as well as the degree of combination that might be taking place between these lignins and the reactives or the solvents (in the case of the organosolv systems) used in the delignification process.

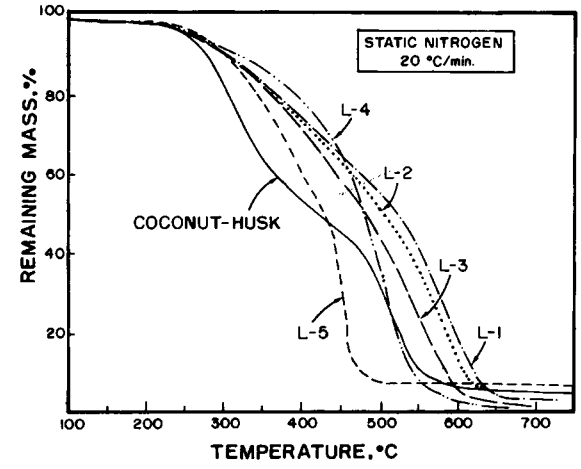
The decomposition characteristics yielded some relevant information and were thus followed by thermal gravimetric analysis (TGA). Figure 7 shows that the extracted lignins start to decompose between 200 and 250°C. However, their thermogravimetric curves are sufficiently different so as to allow their classification into three groups. Lignins L-4, L-8, and L-11 belong to the first group; their mass loss ratio increases gradually with temperature, then more rapidly once approximately 50% of the initial mass has been lost. The thermal stability of this group, with respect to the temperature of initial decomposition (T_{DI}), follows the order L-8 (250°C) > L-4 (240°C) > L-11 (200°C). While there are no notable differences in the thermal stability of these lignins, clear differences are observed in their final decomposition temperature (Table IX): L-8 (605°C), L-4 (560°C), L-11 (470°C). These results are expected since, unlike typical alkaline systems, the extracting organosolv systems do not cause significant modifications in the structure of the lignins.

The fact that the thermal stability of the NaOH–AQ extracted lignin (L-4) is similar to that of the organosolv extracted lignins (L-8 and L-11) can be explained by assuming that anthraquinone limits structural modification of the lignin during its extraction, which has already been mentioned. The higher thermal stability observed for lignins L-1 and L-3 (extracted with NaOH without AQ, Tables I and IX) lends support to the assumption made above. All lignins from L-1 to L-10, with the exception of L-4 and L-8, form the second group. The thermogravimetric curves of these lignins show two decomposition stages that are difficult to differentiate. The range for the first decomposition stage of this group is rather wide (190–267°C) and the lowest

Table IX TGA and DSC Analysis of the Extracted Lignins[a]

Lignin	T_g, (°C)	T_{DI}, (°C)	T_{DF}, (°C)	Wt % Mass Loss
L-1	165	235	660	97
L-2	152	245	615	95
L-3	172	210	600	98
L-4	152	240	560	98
L-5	150	190	500	96
L-6	161	240	665	98
L-7	162	255	670	99
L-8	148	250	605	98
L-9	161	220	570	98
L-10	154	267	660	99
L-11	147	200	470	98

[a] T_g = glass transition temperature; T_{DI} = initial decomposition temperature; T_{DF} = final decomposition temperature.



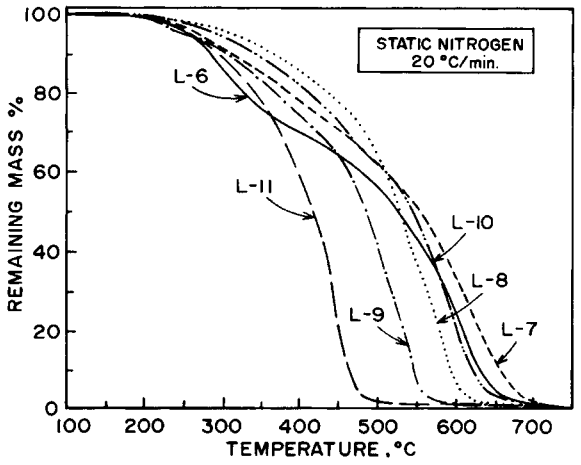


Figure 7(a) TGA thermograms of lignin samples extracted from coconut husk. A thermogram of powdered coconut husk is given for comparison.

Figure 7(b) TGA thermograms of ammonia, sulfite, and organosolv lignins extracted from coconut husk.

T_{DI} values correspond to the lignins extracted with butanol–water (L-3, 210°C) and dioxane–water (L-5, 190°C). The highest T_{DI} value (267°C) corresponds to the lignin extracted with ethylene glycol–water (L-9), suggesting that this, in spite of being an organosolv system, does cause modifications in the lignin structure.

The following sequence was observed for the final decomposition temperatures (T_{DF}) of the lignins of the second group: L-7 (670°C) > L-1 (660°C) = L-10 (660°C) > L-2 (615°C) > L-3 (600°C) > L-9 (570°C) > L-5 (500°C). These results do not show a clear correlation with either the type of system or the extraction temperature used (Fig. 7 and Tables I and IX). However, it may be noted that L-5 (dioxane–water) and L-11 (ethanol–water) have comparable T_{DF} values and were both extracted with organosolv systems.

The third group includes lignin L-6 and the coconut husk, both clearly showing two decomposition stages. The first decomposition stage of both L-6 and the coconut husk occurs in the range of 240–350°C, while the second stage of L-6 takes place at a slightly higher range (450–650°C) than that of the coconut husk (470–550°C). These results appear to indicate that when the extraction is carried out with NH_4OH at 100°C (L-6 conditions) significant amounts of coconut husk components are extracted. These components, probably low molecular weight polyphenols, decompose during the first stage but do not suffer changes in their thermal lability during the extraction process.

On the basis of the results already discussed and assuming that the chemical heterogeneity of lignin is directly related to its thermal stability, general conclusions may be made. The lignins of the first group (L-4, L-8, and L-11) have fractions that are less chemically differentiated. Thus lignin L-11, with the narrowest decomposition range (220–470°C), apparently has a less diverse composition than the other lignins. The decomposition range of L-11 is very similar to that of L-5 (190–500°C), the "dioxane lignin," considered to be the least modified extracted lignin.[13] This is in agreement with the fact that L-5 showed the highest percentage of noncondensed guaiacylic phenolic units (5.1%, Table IV) and yielded a large chloroform-soluble fraction when acetylated (Table VIII). Similarly, it should be noted that lignin L-4, with a percentage of noncondensed guaiacylic units comparable to that of L-5 (Table IV), dissolved completely in chloroform after being acetylated (Table VIII). These results indicate that anthraquinone favors the extraction of slightly modified lignins that are comparable, in general terms, with lignins obtained using dioxane–water.

Finally, lignins L-4, L-5, and L-9 show a moderate stability compared to coconut husk, while the rest of the lignins present a notably wider decomposition range. This fact suggests that during the extraction of the latter lignins rearrangements and structural changes may have occurred[25] that resulted in the expression of chemical heterogeneity.

CONCLUSIONS

High yields of lignin are obtained from coconut husk when alkaline extraction systems are used: up to 77% with extraction temperatures of 150°C (NaOH–

AQ) and 160°C (NaOH without anthraquinone). When organosolv systems are used, lower yields are obtained.

The NaOH–AQ system was found to be the most adequate for the extraction of coconut husk lignin. Due to the low degree of chemical modification of the lignin obtained with this system, it has the potential to be used in those instances where further chemical reactions on the lignin are required. Larger soluble acetylated fractions are generated from lignins extracted with NaOH at high temperatures and in the presence of anthraquinone.

Based on the percentages of noncondensed guaiacylic units, the yields of chloroform-soluble acetylated lignin fractions, and the results of the thermal gravimetric analysis, it can be concluded that the lignins extracted with the NaOH–AQ and dioxane–water systems do not experience significant structural modifications during the extraction process. This indicates that anthraquinone effectively limits condensation reactions in the lignin when aqueous NaOH is used as the extracting medium.

All the obtained lignins showed a glass transition temperature (T_g) ranging from 147°C, for that extracted with ethanol–water, to 172°C for that obtained by using aqueous NaOH having no anthraquinone as an additive at 160°C. The DSC traces, as well as the T_g values, of the lignin extracted with dioxane–water were very similar with that obtained with aqueous NaOH–AQ, which reinforces the above finding that these lignins are similar in structure. These results qualitatively agree with the solubility properties of the studied lignins. All the lignins obtained in this work lose practically all of their mass when heated over 500°C and did not show fusion temperatures (T_m) before decomposing.

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