

Coconut Husk Lignin. III. Reactivity of Alkaline Extracts with Formaldehyde

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SYNOPSIS

In this article we report results of the evaluation of the reactivity of polyphenolic extracts of coconut husk with formaldehyde in both acidic and alkaline media. The objective of this evaluation was to determine if the extracts could be used in the preparation of phenol-formaldehyde-type resins. Extracts were obtained using aqueous solutions of NaOH (with and without anthraquinone) and NH_4OH . Because of their low Stiasny's Number values, these extracts are not suitable for phenol-formaldehyde resin preparation in acidic conditions unless they are mixed with phenol or phenolic derivatives. Nevertheless, extracts obtained with NaOH, especially at 100 and 120°C, showed sufficient reactivity with formaldehyde in basic conditions and may therefore be considered suitable for resin preparation in an alkaline medium. The resins were characterized using infrared spectroscopy (IR), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). A transition temperature prior to decomposition was not detected; their thermal stability was similar to phenol-formaldehyde-type resins. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyphenolic and lignin extracts obtained from bark and plants have been made to react with formaldehyde in order to prepare phenol-formaldehyde-type resins.¹⁻³ The reactivity of these materials depends on factors related to the original source from which they are extracted, as well as on the liquor composition and digestion time and temperature used for the extraction.⁴ A fundamental requirement for achieving a significant degree of reaction between formaldehyde and the extract is that the latter contains sufficient unsubstituted reactive sites on the aromatic rings of its polyphenolic structures.⁵ Thus, the type of lignin expected to show a significant reactivity with formaldehyde would be that obtained

from monocotyledon plants,[‡] since their lignins generally contain a relatively high concentration of *p*-hydroxyphenylpropane groups,⁷ as well as variable quantities of syringyl and guaiacyl groups. The structure of these three backbones of lignin are shown in Figure 1.

Coconut husk, the fibrous outer part of the coconut, is generally discarded during the *copra* extraction process. Coconut husk has recently been shown to form fibrous-agglomerate building materials by application of suitable temperature, pressure, and catalytic conditions, without requiring the addition of other components.⁸ This capability is apparently due to the high lignin contents of coconut husk. High yields of lignin can be extracted from coconut husk using dilute aqueous caustic soda solutions.⁹ These extracts could then be made to react with formaldehyde and used in the preparation of phenol-formaldehyde-type resins.

Only those lignin units having free phenolic hydroxyl groups are capable of nuclear aromatic reaction in alkaline media. Thus, the relative paucity of reactive sites in guaiacyl-syringyl lignins is due to the *para*- and *ortho*-positions being blocked by the alkyl side chains (two sites in syringyl and one in guaiacyl groups, respectively) (Fig. 1). Lignin extracted from coconut husk has approximately

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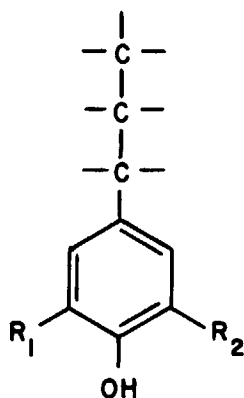
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‡ Monocotyledoneae is one of two subclasses of flowering plants (Anthophyta Division); their embryos have one cotyledon and the flowers parts are mostly in threes. Except for the palms, almost all the monocotyledon plants have herbaceous stems and a cambium is almost always lacking. For more details, see [6].

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- (I) $R_1, R_2 = H$
 (II) $R_1 = H, R_2 = OCH_3$
 (III) $R_1, R_2 = OCH_3$

Figure 1 Schematic structure for the lignin backbones for (I) *p*-hydroxyphenylpropane, (II) guaiacyl, and (III) syringyl groups.

equal amounts of guaiacyl and syringyl groups, with phenolic units having one and no potentially reactive sites with formaldehyde, respectively.^{5,10,11} However, because of its low total methoxyl content, as estimated by nuclear magnetic resonance,¹² this lignin probably contains a significant number of *p*-hydroxyphenylpropane groups containing two potentially reactive sites, each with insignificant steric hindrance.⁵ In this paper, an evaluation of the reactivity of coconut husk lignin with formaldehyde in both alkaline and acidic conditions is presented. The study was carried out using IR spectroscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

EXPERIMENTAL

Materials

All reagents and solutions were reagent grade and purchased from E. Merck (Darmstadt, Germany). Coconut husk was obtained from mature and dried coconuts (*Cocos nucifera* L.), which were collected during winter from 15-year-old coconut palms in Dzilam de Bravo (Peninsula of Yucatán, Mexico). Coconut palms of this region belong to the Typica "Atlantic Tall" variety,¹³ according to the Harries' classification for *Cocos nucifera* L.¹⁴

Sample Preparation

Samples of coconut husk were milled in a Wiley-type Brabender mill and made to pass through a 0.78 mm mesh sieve before application of further treatments.

Lignin Extraction

The polyphenolic extracts were obtained from coconut husk by using alkaline solutions at different temperatures. The procedure was selected over other methods^{15,16} because it is simple and it renders a high yield of lignin containing a high hydroxyl number.⁹ Twenty gram samples of dried coconut husk powder were placed in a 2 L Parr reactor and digested with aqueous 2% (w/w) NaOH solutions (with or without anthraquinone) or with a 5% (w/w) aqueous NH₄OH solution. The process was carried out for 5 h at constant temperature in the range from 100 to 160°C. A Pyrex glass kettle with constant stirring was used in those cases when reflux conditions were selected. In all cases, the sample weight-to-liquor volume ratio was 1 : 20.

EXTRACTS CHARACTERIZATION

All alkaline extracts were concentrated by partial evaporation of water from the samples until 50% total solids was attained in the extracts. The total solids in extracts were determined by drying aliquot parts at 105°C. The reactivity of the extracts was tested in both an acidic (Stiasny's Number determination) and an alkaline medium.

Stiasny's Number Determination¹⁷

A portion of the polyphenolic extract was taken and its pH was adjusted to 11 with some drops of concentrated sulfuric acid. This extract was diluted to 150 mL with distilled water, so that the final solution contained between 1.5 and 0.4% solids. This solution was warmed up to 85°C in a 500 mL flask and then 30 mL of a 34% formaldehyde solution and 15 mL of concentrated HCl were added. The resulting solution was refluxed for 30 min, left to cool, and the precipitate obtained by filtration in a porous glass (40 M) filter, previously dried at 105°C to constant weight. The Stiasny's Number is a useful parameter to evaluate the suitability of polyphenolic extracts and its calculation is simple, as follows:

$$\text{Stiasny's Number} = \left(\frac{Wt_p}{Wt_s} \right) \times 100 \quad (1)$$

where Wt_p is the weight of the precipitate obtained after the reaction of the extract with formaldehyde; and Wt_s , the weight of the total solids contained in a "blank" aliquot part of the extract, which was dried in a constant weight bottle at 105°C. The total solids weight was corrected for the alkali excess, in the case of the extracts obtained with NaOH, subtracting the weight of sodium chloride estimated after titration of NaOH with a HCl 0.5N solution in the corresponding aliquot parts of the extracts.

Reactivity with Formaldehyde (Alkaline Medium)¹⁸

These tests were carried out only on the extracts obtained with the NaOH solution having no anthraquinone. Formaldehyde solution (34%) was placed in a 500 mL glass kettle and phenolic extract slowly added with constant stirring. A molar ratio of formaldehyde to extract (assuming to have an average molecular weight of 180 g/mol) of 3:2 was used. The reaction mixture was warmed up to 85°C for 5 h. Formaldehyde consumption over time was followed by taking 5 mL aliquot parts from the reacting mixture every 30 min, and back titrating with NaOH solution, as follows: The aliquot parts were precipitated by slowly adding 15 mL of 95% ethanol. The precipitate was separated by filtration through a porous glass (40 M) filter and washed with 10 mL of 95% ethanol. The filtrate was acidified to pH 4 with an aqueous 0.5N HCl solution and an aqueous solution of 10% hydroxylamine chlorhydrate was added. The latter solution was in excess with respect to the expected amount of free formaldehyde in the aliquot part. After 10 min, the excess of hydroxylamine chlorhydrate was titrated with 0.5N NaOH solution until pH 4 was again reached.¹⁸ The formaldehyde consumption was determined by the difference between the added formaldehyde (taken as 100 wt %) and the weight percent of nonreacted formaldehyde (*NRF*). The latter was calculated as follows:

$$NRF(\text{wt } \%) = \frac{V \times N \times M_f \times V_t \times 100}{Wt_f \times V_a \times 100} \quad (2)$$

In this equation, V is the volume of NaOH solution consumed during titration and N (0.5) is its normality; M_f , the molecular weight of formaldehyde (30 g/mol); Wt_f , the weight (in grams) of the added formaldehyde; and V_t and V_a , the total volume of reaction mixture and the aliquot part volume, respectively, both in mL. After the reaction of the polyphenolic extracts with formaldehyde was ended,

the product was recovered by precipitation with 95% ethanol and filtration as described above. The resins obtained were characterized by IR spectroscopy, DSC, and TGA.

All IR spectra of resins were obtained from KBr discs containing 0.4% by weight of sample using a spectrophotometer (Perkin-Elmer IR model 683) in a transmittance mode from 4000 to 400 cm^{-1} . The characterization by DSC (Perkin-Elmer DSC-2C) was carried out in a nitrogen atmosphere using 15–20 mg resin samples and scanning from 50 to 300°C with a heating rate of 20°C/min. TGA thermograms between 50 and 750°C were obtained with a thermal gravimetric analyzer (Perkin-Elmer TGS-2) in a nitrogen atmosphere and using a 20°C/min heating rate. Sample size for TGA was 4–7 mg.

RESULTS AND DISCUSSION

Reactivity of Polyphenolic Extracts with Formaldehyde in Acidic Medium (Stiasny's Number)

Results obtained for the Stiasny's Number of the polyphenolic extracts of coconut husk are shown in Table I. Extracts obtained using an aqueous solution of NaOH, both with and without anthraquinone, presented very low Stiasny's Numbers that varied very little with extraction temperature. On the other hand, the extracts obtained with NH_4OH had much higher Stiasny's Numbers that decreased with an increase in extraction temperature. The highest value, 62, was obtained for the 100°C NH_4OH extract and is slightly less than the minimum value of 70 required for polyphenolic extracts to be suitable for preparation of phenol-formaldehyde-type resins.^{10,17} Therefore, these extracts would require the addition of phenol to be of use in resin preparation. In similar studies on extracts of tree bark carried out by Ayla,⁴ high values for the Stiasny's Number (78 and 80, for *P. brutia* and *P. radiata*, respectively) were obtained when extractions were performed at relatively low temperature (70°C) and a short time (2 h) and the extracts concentrated under vacuum at 40°C. These experimental conditions do not favor the extraction of high molecular weight polyphenols, which generally show a low reactivity with formaldehyde in acidic medium.¹⁹ Therefore, it may be postulated that the values for the Stiasny's Number of alkaline extracts of coconut husk would be higher if these experimental conditions were used, because such extracts would contain a lesser amount of high molecular weight polyphenols, although minor val-

Table I Reactivity of Lignin Extracts with Formaldehyde in Acidic Medium (Stiasny's Number)^a

Extraction Conditions			Formaldehyde Reacted (%)	Stiasny's Number
Liquor Composition	Time (h)	Temperature (°C)		
2% NaOH	5	100	34	21 (27)
		120	49	28 (36)
		135	51	25 (32)
		160	58	26 (30)
2% NaOH 0.1% AQ ^b	5	100	44	24 (31)
		120	50	25 (37)
		135	53	25 (31)
		160	57	24 (28)
5% NH ₄ OH	3	100	76	62
		120	76	57
		135	75	53
		160	76	49

^a Values in parentheses correspond to corrected Stiasny's Numbers taking into account the amount of neutralized NaOH.

^b AQ = anthraquinone.

ues for the extracts yield, as a whole, would be expected.^{9,16} In this line of thought, the higher values of Stiasny's Number showed by NH₄OH extracts (Table I) can be explained if it is assumed that there is a smaller content of high molecular weight polyphenols in these extracts than in those of NaOH. Indeed, NH₄OH is a base weaker than is NaOH and, as has been reported,⁹ has rendered medium yield for coconut husk extracts (about of 40 wt %) in comparison with those of NaOH (more than 60 wt %) with a basis on the whole (100 wt %) polyphenols (including lignin) contained in coconut husk.

Reactivity of Extracts with Formaldehyde in Alkaline Conditions

The extracts obtained with 2% NaOH showed a relatively high formaldehyde consumption during reaction in alkaline conditions (Table II), similar in value to that reported for alkaline lignin extracted from wood.²⁰ This reported consumption was con-

sidered as high enough to recommend use of the lignin in preparation of phenol-formaldehyde-type resins.²⁰ Interestingly, the reaction between formaldehyde and the extract obtained at 100°C was practically complete in approximately 1.5 h, whereas those for extracts obtained at higher temperature required almost 5.0 h (Table II). This reduction of reactivity suggests that high extraction temperatures with aqueous NaOH promote structural changes in the polyphenols of coconut husk extracts, as previously reported.⁹ Thus, the extract obtained at 100°C would be more convenient for use in preparation of the resins due to the reduced reaction time.

The degree of reaction of the extracts may be estimated from the data for formaldehyde consumption in alkaline medium (Table II). If an average molecular weight of 180 g/mol for the phenylpropane (C-9) unit of the polyphenolic extracts is assumed, results show that approximately 1 mol of the extract reacts with each mole of formaldehyde. This indicates that there is an average of one reaction

Table II Reactivity of Lignin Extracts with Formaldehyde in Alkaline Medium

Extraction Temperature (°C)	Weight of Solids in the Extract (g)	Formaldehyde		
		Added (g)	Residual (g)	Reacted (%)
100	46.6	6.8	2.5	62.6
120	63.4	9.1	4.0	57.0
135	65.2	9.5	4.1	56.7
160	67.5	10.9	5.0	53.7

Table III Assignment of Infrared Absorption Bands of Resins^a

Resin	Band Position (cm ⁻¹) and Functional Group				
	ν_{OH}	$\nu_{\text{C-H}}$	ν_{ϕ}	$\delta_{\text{C-H}}$	$\nu_{\text{C-O-C}}$
P	3620-3000	2920	1590 1445	1385	1160
S	3680-3000	2925	1600 1420	1350	1145

^a ν = stretching vibration, ϕ = aromatic ring, δ = wagging vibration, P = ethanol-precipitated sample, S = solid sample obtained by drying the aqueous resin solution.

site per C-9 unit of the polyphenolic extracts, which contain a greater amount of lignin in addition to other low molecular weight polyphenols.⁹ This also supports the assumption that the lignin recovered from the extracts contains a high proportion of *p*-hydroxyphenylpropane groups, as indicated by the low methoxyl content determined by NMR and IR spectroscopy.¹²

The results suggest that the coconut husk extracts, which were obtained during the present study, are suitable for use in the preparation of adhesives by their reaction with formaldehyde or by a combination of both with phenol. The preparation of these adhesives would apparently be more convenient using a reaction in alkaline conditions than in acidic. It may also be expected that the extracts obtained with the NaOH-antraquinone system will be more reactive with formaldehyde in alkaline medium since it has been previously reported that antraquinone limits the degree of condensation occurring in coconut husk lignin during extraction.^{9,12}

IR Spectroscopy

Table III shows the assignments of the functional groups to the bands of the IR spectra of the phenol-formaldehyde-type resins obtained in this study. The nomenclature used in the identification of each resin is given in Table IV. Because all the resins contain polyphenols, a band corresponding to the aromatic ring (1600 cm⁻¹) appeared in their IR spectra. This

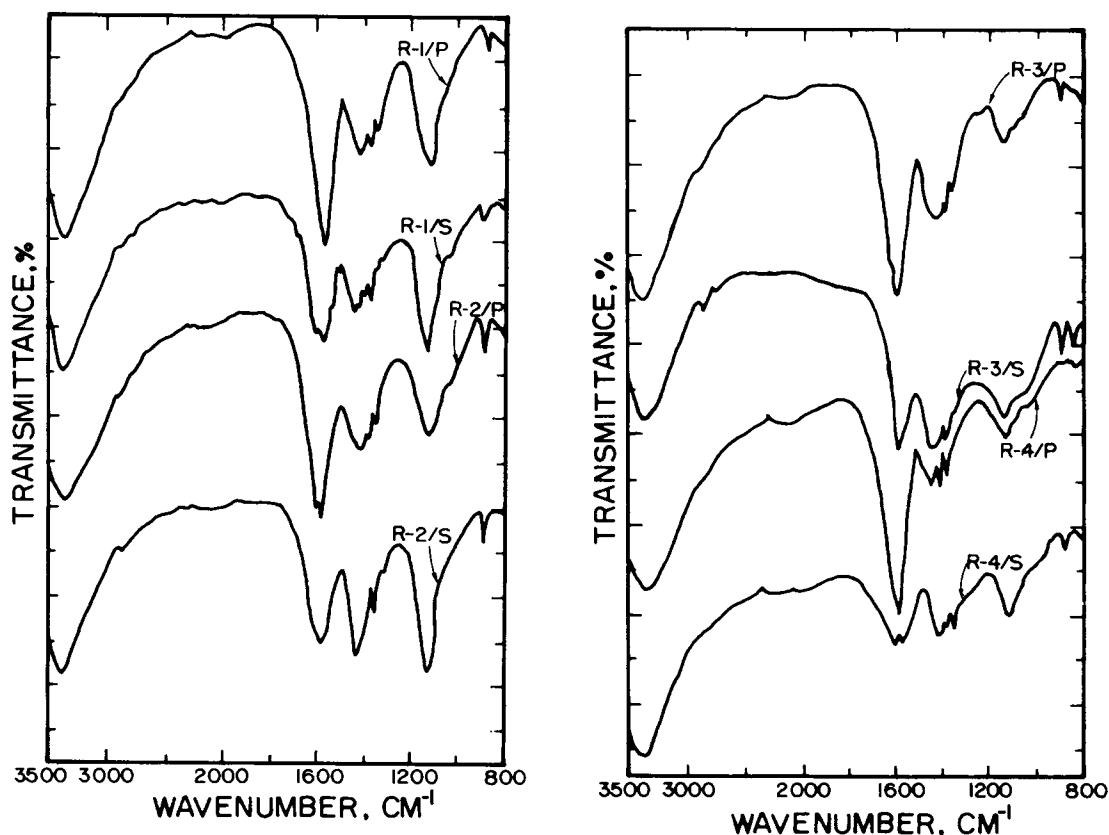


Figure 2 Representative IR spectra of the resins obtained by reaction of coconut husk extracts with formaldehyde in alkaline medium. Nomenclature is explained in Table IV.

band shows a relatively high intensity in the spectra of all the resins (Fig. 2) except those of R-4/S and R-4/P in which the same band was low in intensity. However, the band at 1160 cm^{-1} corresponding to aliphatic ethers is the most important to be analyzed, because these ethers are normally produced by condensation of the hydroxybenzyl alcohol groups, which resulted, in turn, from the reaction of formaldehyde with the aromatic rings. With the basis on the intensity showed by the ether bands, the resins R-1/P, R-1/S, R-2/P, and R-2/S, prepared with extracts obtained at low temperatures (100 and 120°C), contain a higher number of these ether groups than those of the resins R-3/P, R-3/S, R-4/P, and R-4/S, which were prepared with extracts obtained at 140 and 160°C . The most etherified resin was R-1/P, which was recovered by precipitation with ethanol. These results agree with the fact mentioned previously that these extracts (especially that obtained at 100°C) were more reactive with formaldehyde than were those obtained at higher temperatures (Table II). The phenol-formaldehyde-type resins prepared from coconut husk extracts in alkaline conditions were insoluble in solvents such as ethanol, methanol, acetone, dimethylsulfoxide, and dimethylformamide. In contrast, the lignins recovered from similar extracts, which were not subjected to react with formaldehyde, were either completely or partially soluble in these solvents.⁹ This indicates that, for the resins obtained in the present study, the degree of cross-linking that occurred during the final stage of the reaction with formaldehyde was significant.

Thermal Analysis

The DSC thermograms (not shown here) did not show a marked variation in heat capacity increase (ΔC_p) that could be attributed to a glass transition (T_g) or melting (T_m) below their initial decomposition temperature (T_{DI}). This result is expected since the lignins of the polyphenolic extracts used

Table IV Nomenclature Used in Infrared Spectra of Resins

Resin	Conditions Used to Extract Raw Lignin
R-1	2% NaOH, 100°C , 5 h
R-2	2% NaOH, 120°C , 5 h
R-3	2% NaOH, 135°C , 5 h
R-4	2% NaOH, 160°C , 5 h

Table V Thermogravimetric Analysis of the Obtained Resins^a

Resin	T_{DI}^b ($^\circ\text{C}$)	Wt % Mass Loss up to 350°C	Wt % Mass Loss up to 750°C
R-1/P	250	12	18
R-1/S	243	17	41
R-2/P	270	13	25
R-2/S	220	14	37
R-3/P	165	14	31
R-3/S	165	18	43
R-4/P	220	13	31
R-4/S	240	12	42

^a Nomenclature as shown in Tables III and IV.

^b T_{DI} = initial decomposition temperature.

did not present such transitions, under the experimental conditions used here,⁹ and, in addition, cross-linking of the polymeric networks reduces the magnitude of ΔC_p at T_g that the polymer will show in its DSC thermogram. The results of TGA of the resins listed in Table IV are included in Table V and two representative TGA thermograms are shown in Figure 3. In the inset of this figure, it can be seen that resin R-2/P (prepared with the 120°C NaOH extract and precipitated with ethanol) is more heat stable ($T_{DI} = 270^\circ\text{C}$) than is the corresponding lignin recovered from the same extract ($T_{DI} = 220^\circ\text{C}$), which is named lignin-2 in the inset of Figure 3. In general, the thermal stability of these resins is comparable to typical phenol-formaldehyde resins.²¹ Furthermore, several differences in the thermal behavior of the resins obtained can be seen upon a more detailed analysis of Table V:

- A. All the resins began to decompose in the range $250\text{--}270^\circ\text{C}$ and those prepared with the 135°C extract (R-3/P y R-3/S) lost a small amount of mass between 170 to 210°C . This loss of mass could correspond to the fraction of the polyphenolic extract that had not reacted with formaldehyde.
- B. The resins prepared with the 100 and 120°C extracts lost mass more sharply in the range between 270 and 350°C than did the other resins. The resins of the 135 and 160°C extracts lost mass more slowly and to a greater degree and over a greater temperature range ($250\text{--}450^\circ\text{C}$). This result indicates that such resins possess a less uniform chemical structure than do the former resins. It has been reported previously that structural differences of the poly-

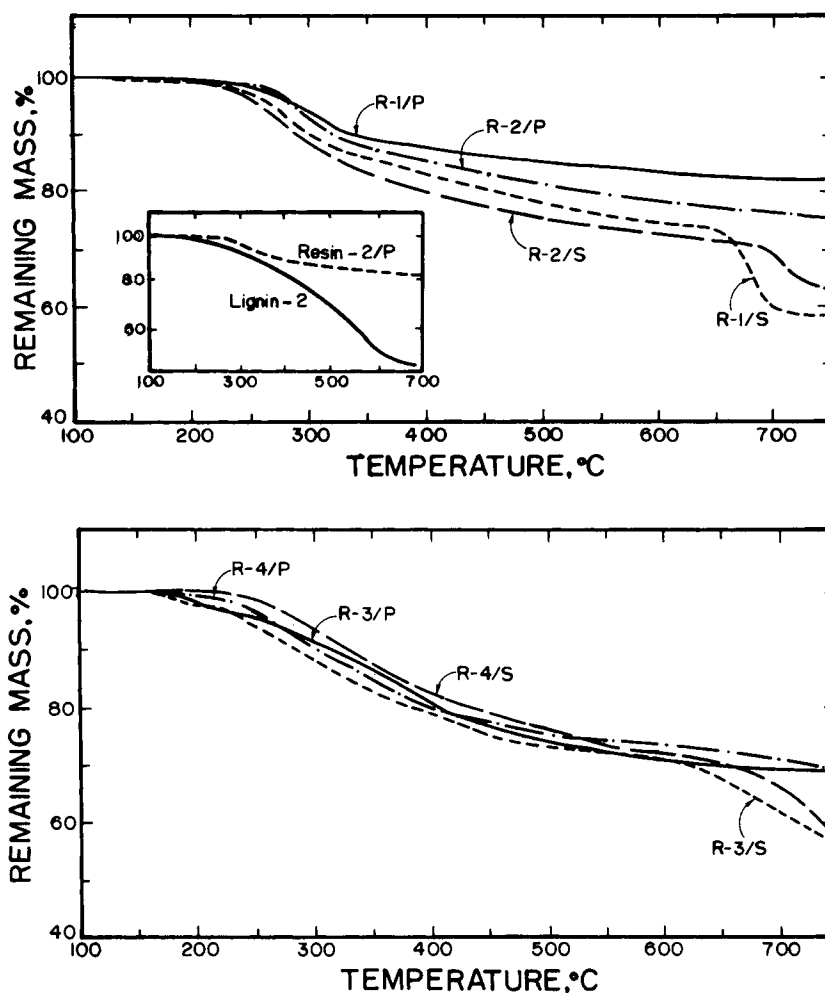


Figure 3 Representative TGA thermograms of the resins of Table IV. A TGA thermogram of lignin-2, which was obtained before the reaction with formaldehyde to obtain the resin-2 (named R-2/P or R-2/S), is included in the inset for comparison.

phenolic components of the extracts are increased with the extraction temperature.^{9,12}

- C. The total loss of mass was less in the resins prepared with extracts obtained at lower temperatures and precipitated with ethanol (Table V). This result agrees with the fact that their IR spectra show a greater relative intensity of the band corresponding to the ether linkages mentioned earlier than in those of the resins of the extracts obtained at a higher temperature. In addition, this confirms the finding that the extracts obtained at lower temperatures (100 and 120°C) are more reactive with formaldehyde than those obtained at 130 and 160°C, as shown in Table II.
- D. Finally, all the resins recovered by evaporation of water (Table V), without precipitation with

ethanol, lost additional mass in the range 620–750°C (R-2/S in Fig. 3). This mass loss could be due to a decomposition of the resins induced by the NaOH still contained. Though this result might not be important in the present study, it suggests an area for additional studies.

CONCLUSIONS

The Stiasny's Numbers of the polyphenolic extracts obtained from coconut husk with aqueous solutions of NaOH (with and without anthraquinone) were significantly less than the minimum of 70 required for the extracts to be used in the preparation of resins by reaction with formaldehyde in acidic conditions. Nevertheless, the low reactivity of the extracts

in such conditions may be compensated for by mixing with phenol, or its derivatives, to provide part of the phenol consumed in the preparation of phenol-formaldehyde resins. In contrast, when the reaction was carried out in alkaline conditions, these NaOH extracts reacted significantly with formaldehyde. This indicates that such extracts can be used to prepare phenol-formaldehyde-type resins in basic conditions more easily than in acidic medium. Stiasny's Numbers for the NH_4OH extracts were higher in value, 49–62, than those of NaOH, and were slightly less minor than the required value of 70.

The IR spectra of the resins show a high extent of etherification reaction between hydroxybenzyl alcohol groups, which were produced by the reaction of formaldehyde with aromatic rings of polyphenolic extracts. This indicates the occurrence of an appreciable degree of cross-linking, primary in the extracts obtained with NaOH at 100 and 120°C. Of the experimental conditions employed in this study, these were the most suitable for obtaining coconut husk extracts with NaOH for use in the preparation of phenol-formaldehyde resins, whereas for the extracts of NH_4OH , the most convenient extraction temperature was 100°C.

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