

Waste Liquors from Cellulosic Industries.

IV.* Lignin as a Component in Phenol Formaldehyde Resol Resin

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Synopsis

The lignin separated from the spent liquor of soda pulping of rice straw can replace a part of phenol in the condensation reaction with formaldehyde in a basic medium to form phenol lignin-formaldehyde (PL-F) resol resin. The production of phenol lignin-formaldehyde resol resin was carried out in two stages: First was the formation of the adduct (lignin phenol) using different lignin percentages; second was the condensation of the adduct with formaldehyde. Reaction variables, i.e., molar ratio of formaldehyde to phenol lignin, polymerization time, amount of sodium hydroxide as a catalyst, and polymerization temperature in the polymerization step were studied. Solubility of the produced resol resin in different solvents, its viscosity, and yield were determined. Lignin could replace up to 40% of phenol in the produced resin. Infrared spectra of the prepared resin were determined. Structural similarity of phenol-formaldehyde to phenol lignin-formaldehyde resin was shown. Also, relative absorbance of characteristic bands of the resins were calculated and claimed too much on the effect of reaction parameters on the prepared resins.

INTRODUCTION

During pulping of lignocellulosic materials, approximately one-half of the raw material is obtained as cellulosic pulp whereas the other half, consisting mainly of lignin, hemicellulose and ash, is dissolved in the spent liquor. Industrial use of this waste liquor is of great environmental and economical importance. Utilization of spent liquors from wood pulping for different purposes has been developed. In most paper mills, alkali and kraft lignins in black liquor are primarily used as fuel during combustion of black liquor for the recovery of pulping chemicals. Lignins are also used as a raw material for the manufacture of technically useful polymers.¹⁻⁴

However, in the case of pulping of rice straw, which is used in many pulp mills in Asia and Africa, black liquor is wasted mostly in water streams. This is mainly due to the high silica content in the black liquor. At Rakta Mill in Egypt, a huge amount of black liquor from soda pulping of rice straw is wasted in water stream. Now, Rakta has made contacts with several international consulting firms regarding the feasibility of recovering the soda from this black liquor. The wasted lignin from this treated spent liquor amounts to about 10,000 tons/year.

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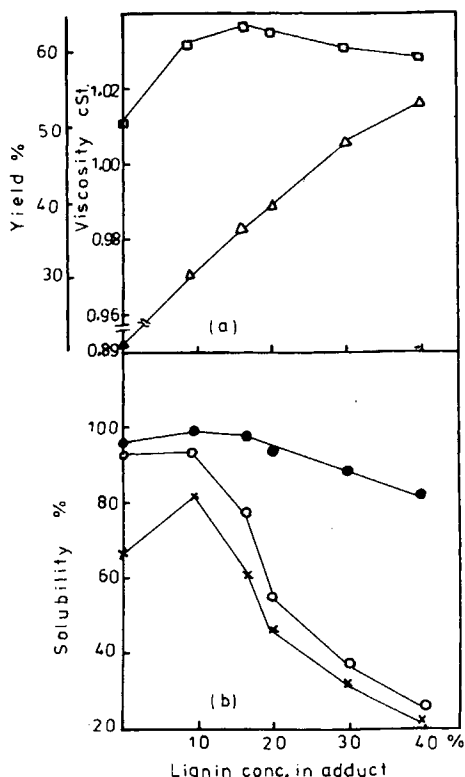


Fig. 1. Effect of lignin content in adduct on yield and physical properties of produced resol. Adduct time 2 h, temperature 160°C, polymerization time 2 h temperature 95°C, 1.5 mol formaldehyde. Solubility: (●) methanol; (○) ethanol; (x) acetone; (□) yield; (Δ) viscosity.

In view of the difference between the black liquor from wood pulping and that from rice straw pulping, the present studies investigate the possibility of using lignin, separated from the spent liquor of soda pulping of rice straw, as a partial replacement of phenol in preparing resol resin. This study is a part of a general investigation⁵⁻⁸ on the waste liquors from cellulosic industries. Phenol lignin-formaldehyde resins are almost prepared in two steps; namely, adduct and polymerization stages. In a previous study⁸ it is shown that the most important factor affecting the yield during adducting is the lignin concentration. This study deals with this factor and its effect on yield and some properties of the prepared phenol lignin-formaldehyde resol resin.

RESULTS AND DISCUSSION

Adduct Stage: Lignin Concentration

The effect of a partial replacement of phenol (P) by lignin (L) in the adduct stage at 160°C for 2 h on the properties of the produced resol is shown in Figure 1. The polymerization stage was carried out using molar ratio 1.5:1 between formaldehyde (F): phenol lignin (PL), 4% sodium hydroxide as catalyst (based on PL) and 2 h polymerization time.

TABLE I
Effect of Some Reaction Variables on the Relative Absorbances (IR Spectra) of Resins

Expt no.	Lignin in adduct ^a (%)	1120 cm ⁻¹ —O— linkage <i>E</i> _{rel}	755 cm ⁻¹ —CH ₂ — group <i>E</i> _{rel}
1	100.0 (lignin)	—	—
2	0.0 (resol)	0.054	0.429
3	9.1	0.108	0.432
4	16.6	0.122	0.523
5	30.0	0.237	0.733
6	40.0	0.299	0.805
7	9.1	0.097	0.079
8	9.1	0.071	1.446
9	9.1	0.062	0.499

^aAdduct time 2 h at 160°C and 2% oxalic acid based on phenol. Polymerization temperature 95°C, polymerization time 2 h and 1.5 mol formaldehyde. Expt 7: polymerization temperature 80°C. Expt. 8: molar ratio of formaldehyde:phenol lignin 1.1:1. Expt. 9: polymerization time 2.5 h.

The increase of lignin concentration to phenol up to 17% increased the resol yield from about 50 to 63%. Further increase in lignin concentration resulted in slight decrease in resol yield. This can be referred to the fact that a part of excess added lignin does not react with phenol during the adduct stage, i.e., this unreacted lignin is lost during resin purification. It was also found that increasing the lignin concentration in adduct up to 9% enhanced the solubility of the prepared resol to 99, 94, and 82% in methanol, ethanol, and acetone respectively [Fig. 1(b)]. Further increasing of replaced phenol by lignin up to 40% resulted in a drastic reduction in the solubility of the resol. This is due to the increase in the total molecular weight of adduct product (PL) by increasing of lignin concentration. Thus, the viscosity of phenol lignin-formaldehyde (PL-F) resol resin is increased by increasing lignin concentration during adduct, and it ranged from 0.890 cSt for blank resol resin, i.e., resol without replacement of phenol with lignin to 1.016 cSt at lignin concentration of 40%. Also, increasing the lignin concentration during adduct stage enhanced the crosslinking between phenol lignin and formaldehyde. This can be indicated by the increase of the relative absorbances of the methylene group (*E*_{rel} at 755 cm⁻¹) from 0.429 to 0.809 on changing lignin concentration from 0 to 40%, respectively. The same trend was noticed for etheric linkages, as shown in Table I.

On the other hand, solubility of the prepared resol resin (PL-F) in different solvents has the following order: methanol > ethanol > acetone. This can be attributed to the lower molecular weight and higher polarity of methanol than those of the other solvents.

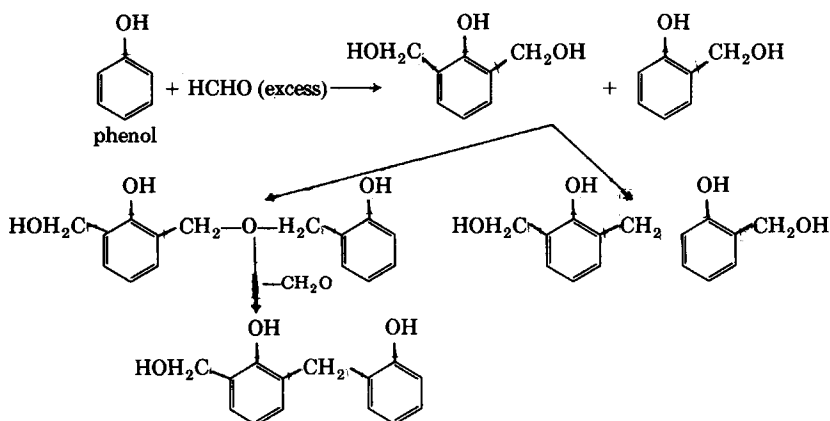
Polymerization Stage

The different reaction variables during the polymerization stage, i.e., molar ratio of formaldehyde (F) to phenol lignin (PL), polymerization time, polymerization temperature, and amount of added sodium hydroxide as a catalyst, were investigated.

The phenol lignin (PL) which was used to study the polymerization variables was prepared by reacting 10 g phenol and 1 g lignin, i.e., about 9% lignin concentration, at 160°C for 2 h in the presence of 0.2 g oxalic acid.⁹

Formaldehyde : Phenol Lignin Ratio

Resol resin (PL-F) is formed by the reaction of excess formaldehyde (F) with phenol lignin (PL), at about 1.5:1 molar ratio, in the presence of 4% sodium hydroxide based on (PL). The methylol phenol can condense either through methylene linkages or through ether linkages. In the latter case, subsequent loss of formaldehyde may occur with methylene bridge formation, as shown in the following equations:



Products of these types are soluble and fusible and contain alcoholic groups. If the reactions leading to their formation are carried further, large numbers of phenolic nuclei can condense to give an insoluble network formation. In this study, the molar ratio of formaldehyde to phenol lignin was changed in the range of 1.1–1.7:1. At formaldehyde to phenol lignin molar ratio of 1.5:1, a maximum yield and viscosity were obtained [Fig. 2(a)]. Solubility of (PL-F) in common organic solvents, began to decrease sharply after that ratio, as shown in Fig. 2(b).

Lowering the molar ratio of formaldehyde:phenol lignin from 1.5 to 1.1 gave a resin with more similarity to novalac as characterized by the high relative absorbance of $-\text{CH}_2-$ group in the latter case (Expts 3 and 8, Table I).

Polymerization Time

The effect of polymerization time, using 4% sodium hydroxide based on (PL) as a catalyst, on the yield and viscosity of the resin is represented in Figure 3(a). Thus, yield and viscosity increased from 56 to 67.5% and from 0.942 to 1.080 cSt, respectively, by increasing the reaction time from 1.5 to 2.5 h. In the latter case, subsequent loss of formaldehyde may occur with methylene bridge formation, as indicated from the former equations and comparison of the relative absorbances of ether linkages and methylene $-\text{CH}_2-$ groups (Expts 3, 9 in Table I). The solubility of the produced resins

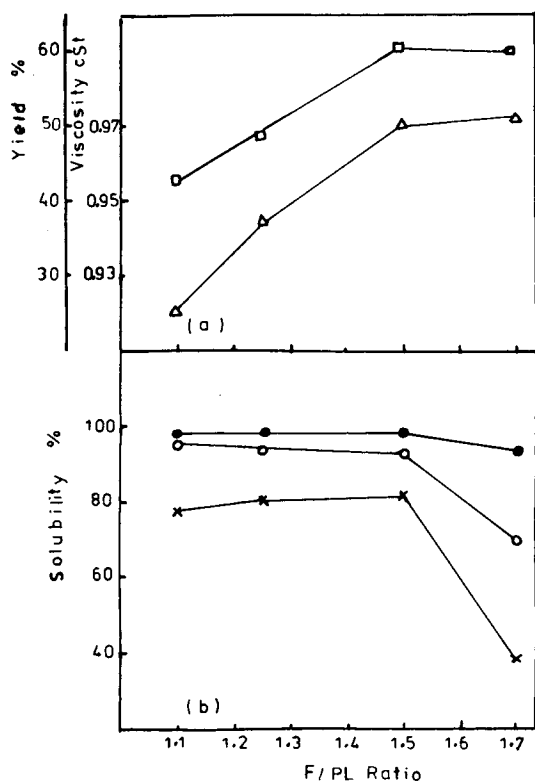


Fig. 2. Effect of F/PL ratio on yield and physical properties of produced resol. Adduct time 2 h temperature 160°C, 9.1% lignin. Polymerization time 2 h, temperature 95°C. Solubility: (●) methanol; (○) ethanol; (x) acetone, (□) yield; (Δ) viscosity.

in the organic solvents was nearly not affected by increasing the polymerization time from 1.5 to 2 h [Fig. 3(b)]. Further increase in the reaction time up to 2.5 h decreased its solubility, i.e., gave resin with high molecular weight.

Polymerization Catalyst

In this work, sodium hydroxide with different amounts was used as a base catalyst during polymerization stage. The effect of this catalyst on the yield and some physical properties of the produced resin is shown in Figures 4(a) and 4(b). It was found that the yield of resin increased by increasing sodium hydroxide concentration up to 4% based on PL, while the viscosity increased progressively by increasing the amount of catalyst within the range used (1–6%). However, the change in the solubility of resins in some organic solvents was slightly influenced by increasing the sodium hydroxide concentration, as shown in Figure 4(b).

Polymerization Temperature

Increasing the polymerization temperature from 80 to 95°C at reaction time of 2 h, formaldehyde : phenol lignin 1.5 : 1 and 4% sodium hydroxide showed slight effect on the solubility of resin in methanol and ethanol. The solubility

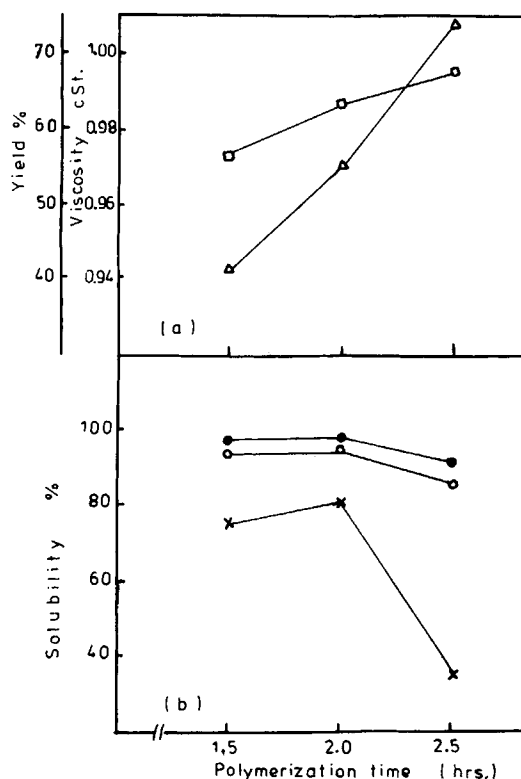


Fig. 3. Effect of polymerization time on yield and physical properties of produced resol. Adduct time 2 h, temperature 160°C, 9.1% lignin. Polymerization temperature 95°C, 1.5 mol formaldehyde. Solubility: (●) methanol; (○) ethanol; (x) acetone; (□) yield; (Δ) viscosity.

in acetone has remarkably influenced and attained 91 to 81% for polymerization temperatures of 80 and 95°C.

The calculation of infrared spectra, represented by Expts 3 and 7, Table I, indicated that resin which was prepared at a low polymerization temperature (80°C) has highly etheric linkages relative to methylene group.

Infrared Spectra

The infrared (IR) spectra of alkali lignin isolated from soda black liquor produced from pulping of rice straw, phenol-formaldehyde resin (resol) and some phenol lignin-formaldehyde resol resins are shown in Figure 5. All the spectra are characterized by the presence of broad band of hydroxyl group at 3300 cm^{-1} , weak aromatic bands close to 1600 and 1500 cm^{-1} , and substituted benzene bands in the range of 870 and 670 cm^{-1} . A strong band was found at $2850\text{--}2860\text{ cm}^{-1}$ for the pure lignin sample, which indicates the methoxyl groups. This band was not found in pure phenol-formaldehyde resol resin (Expt no. 2, Table I). On the other hand, intensity of this band became weak or nearly disappeared in the phenol lignin-formaldehyde resol resins (Expts nos. 3-9, Table I). This is due to the hydrolysis of the methoxyl groups of the pure lignin, at high temperature during the adduct stage and/or the high pH

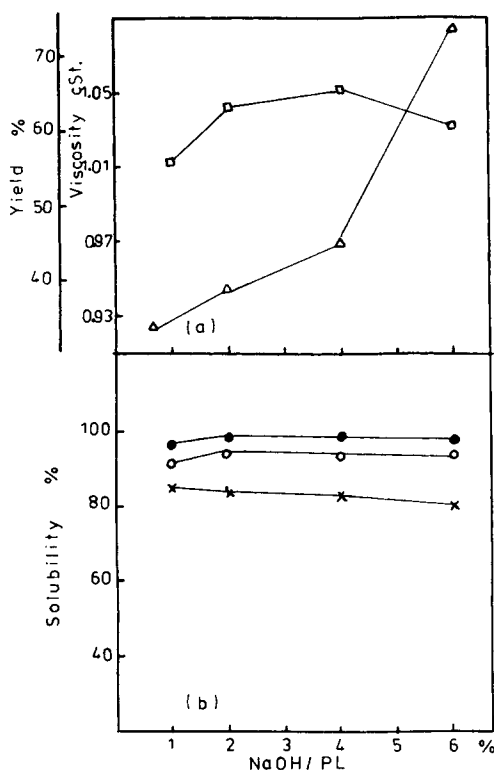


Fig. 4. Effect of NaOH/PL on yield and physical properties of produced resol. Adduct time 2 h, temperature 160°C, 9.1% lignin. Polymerization temperature 95°C, time 2 h. Solubility: (●) methanol, (○) ethanol; (x) acetone; (□) yield; (Δ) viscosity.

during the polymerization stage, which was carried in alkaline medium, to form hydroxyl groups,¹⁰ which react with formaldehyde. All resol resins are characterized by the appearance of strong band of methylol groups at about 1050 cm^{-1} and a weak band of ether linkages at 1120 cm^{-1} . Figure 5 shows also a strong band due to aromatic C—H (most probably 1,2 disubstituted) at 755 cm^{-1} , but with less absorbance than in case of novalac. On the other hand, this band (755 cm^{-1}) does not appear in the pure lignin sample. This is due to the reaction of phenol in ortho or para position, to its phenolic hydroxyl group, with the α -hydroxyl groups of the propane side chains of lignin.

The relative absorbances (E_{rel}) of both ether linkages band (1120 cm^{-1}) and methylene groups (755 cm^{-1}), referring to aromatic bands at about 1505 cm^{-1} , were calculated and represented in Table I. It is clear that the relative absorbances of etheric and methylene groups were increased by increasing the concentration of lignin content in the produced phenol lignin-formaldehyde resol resin. On the other hand, these relative absorbances decreased with decreasing the polymerization temperature from 95 to 80°C (Expts nos. 3 and 7). Relative absorbance of methylene group band at 755 cm^{-1} not only increases with decreasing the mole of formaldehyde (Expt no. 8), but also with increasing of the polymerization time (Expt no. 9).

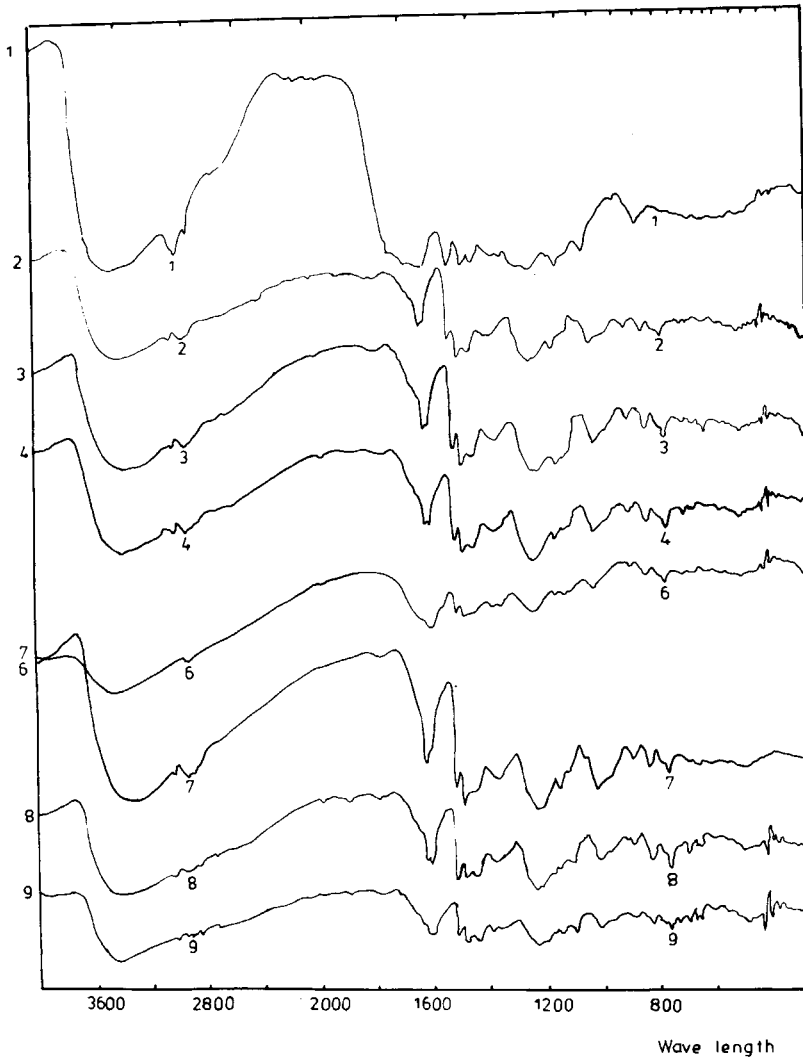


Fig. 5. IR spectra of lignin and resins: (1) lignin; (2) PF resin; (3, 4, 6, 7, 8, 9) PL-F.

EXPERIMENTAL

Materials

Black liquor was obtained as a byproduct from industrial pressure soda cooking of rice straw at Rakta Pulp and Paper Mill, Alexandria, Egypt. Lignin (L) was separated from desilicated soda black liquor, by acidifying with sulfuric acid.⁵ It has the following chemical analysis: lignin 86.8%, ash 1.5%, and hemicellulose and carbohydrate 11.8% (by difference). Reagent grade formaldehyde (F) of 37% concentration, phenol (P), oxalic acid, and sodium hydroxide were used.

Preparation of Resin

Phenol lignin-formaldehyde (PL-F) resol resin was prepared through two stages, namely, adduct and polymerization stages.

Adduct Stage

Phenol lignin (PL) is obtained by acidolysis of soda lignin and condensation of phenol in the ortho or para position to its phenolic OH groups with the α -hydroxy groups of the propane side chain of the lignin.⁹ In the present work, phenol was mixed with different percentages of separated soda lignin, ranged from 9 to 40% of the total weight of phenol and lignin and 2% oxalic acid based on phenol was used as a catalyst. The reaction was carried out in a small stainless steel autoclave (50 mL) heated in a controlled electric oven at a temperature which was 5°C above the stated reaction temperature.^{8,9}

Polymerization Stage

Phenol lignin (PL), unreacted phenol (P) or lignin (L), formaldehyde (F) in the required ratio and sodium hydroxide catalyst were charged into a resin kettle. The reactants were stirred and heated in a water bath at 95°C for 1.5–2.5 h. Two layers were formed after stirring was stopped.⁸ At the end of the required polymerization time, the resin was separated and purified by adding distilled water to complete the separation of rubby resin. The resol resin was washed with warm distilled water till free from formaldehyde odor, and then dehydrated by using vacuum at about 50–60°C. This step should be stopped when the produced resin is brittle and nontacky at room temperature. The yield and physical properties of the prepared resins were determined.

Testing of Resins

Solubility of resol powder in different organic solvents, e.g., methanol, ethanol, and acetone was determined.¹¹ Viscosity was determined in methanol (1% resin) using an Ostwald viscometer no. 2 at 25°C.¹²

Infrared spectra were recorded on a Beckman 4250 spectrophotometer using potassium bromide disc. The relative absorbances of etheric linkage and methylene group were calculated¹³ referring to absorbance of aromatic skeletal vibrations at about 1505 cm⁻¹.

CONCLUSIONS

1. Phenol can be replaced by lignin, separated from soda spent liquor of rice straw pulping, to 40% of the phenol lignin amount. The produced resins have good properties. Further increasing of lignin up to 50% does not produce a comparable resin.
2. The different polymerization variables during the resol preparation play an important role on the resol properties.
3. The best conditions for resol preparation, by using lignin as a partial component, are as follows: 1.5:1 molar ratio of formaldehyde (F):phenol

lignin (PL), 2% sodium hydroxide as a base catalyst and polymerization time 2–2.5 h at 95°C.

4. The solubilities of the produced resins in the different solvents have the following order: methanol > ethanol > acetone.

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