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# Preparing phenolic resins using pulping spent liquor

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## ABSTRACT

The method of using spent liquor (SL) obtained from the chemical pretreatment stage of wheat straw semi-chemical pulping to prepare spent liquor phenolic resins (SLPR) was investigated in the present work. In this work spent liquor was modified with phenol, and then the modified spent liquor was further synthesized with phenol and formaldehyde under appropriate conditions. Experimental data shows that the substitution mass fraction of spent liquor for phenol, the mole ratios of formaldehyde and sodium hydroxide to phenol, temperature and duration time of addition and condensation reaction all show significant influence on the properties of SLPR. SLPR and pure phenolic resins (PR) exhibited almost the same macromolecular structures characterized by FT-IR, and the main properties of the SLPR such as free formaldehyde content, gel time and bonding strength demonstrated superiority to that of PR.

## 1. Introduction

Phenolic resins were first synthesized using phenol and formaldehyde by the German chemist Bayer in 1872, and are commonly used in various fields because of their superior bonding strength, excellent water resistance and electrical insulation and so on [1]. Aiming to reduce the cost of raw materials and improve the eco-friendliness of the products, considerable efforts have been undertaken in the past decade to replace phenol partially with biomass such as lignin and its derivatives [2–14]. Agricultural residues such as wheat straw offer a promising alternative to hardwood and softwood for papermaking in countries such as China, where forest resources are limited. In the chemical pretreatment stage of wheat straw semi-chemical pulping, a certain amount of lignin, hemi-celluloses and cellulose may undergo degradation and end up in spent liquor. The spent liquor could be used as a promising substitute for phenol in the preparation of phenolic resins, but research in this area has been limited. The aim of our research in this area has been to explore the feasibility of using pulping spent liquor as an effective substitute for phenol in the preparation of phenolic resins. In the present work, a method for preparing SLPR has been investigated and related technology parameters which affect the properties of SLPR discussed. Mechanisms responsible for the formation of the SLPR are also considered.

## 2. Experimental

### 2.1. Chemicals and materials

Phenol, sodium hydroxide, and a formaldehyde solution with an effective concentration of 37% were all analytically pure and procured from a local chemicals store. Cotton cloth with basis weight of 80 g/m$^2$ used to test bonding strength of adhesives was procured from a local merchandiser. Wheat straw, which was kept in storage more than 3 months, was obtained from a local paper mill having a moisture content less than 10%.

### 2.2. Methods

#### 2.2.1. The preparation of spent liquor

Wheat straw was cut into pieces varying from 3.0 to 5.0 cm long and cooked with sodium hydroxide solution in a 15 L rotary electric heated digester. Prior to cooking, the raw material, sodium hydroxide of 6.0% based on oven dry straw and makeup water, was placed into the digester. The ratio of liquor (volume, mL) to wheat straw (weight, g) was 5:1. The temperature of the mixture was increased from room temperature to 110 °C over a period of 90 minutes and then maintained at this temperature for a further 60 min. Following this process, the contents of the digester were transferred into a plastic container, diluted with a certain amount of cold water and agitated vigorously for approximately 10 min to diffuse spent liquid from the straw pieces.

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The mixture was then transferred into a nylon bag of 100 mesh, and spent liquor was obtained by pressing the mixture manually. The spent liquor was then evaporated under conditions of 100 °C and atmospheric pressure to yield a higher concentration of 28.0% (solids content). Pulp obtained from the above process was then enclosed in a sealed polyethylene bag and stored for further use.

#### *2.2.2. Modification of spent liquor with phenol*

90.0 g of spent liquor with a solids content of 28%, 25.0 g of phenol and 4.0 g of sodium hydroxide were added into a 500 mL four-neck flask. The mixture was then heated to 45–50 °C and stirred for 20 min. The temperature was then raised to 105 °C and maintained at this temperature for 150 min. The modified product was then allowed to cool to room temperature.

#### *2.2.3. Synthesis of SLPR*

A predetermined amount of spent liquor modified with phenol and sodium hydroxide was added into a 500 mL four-neck flask. The reaction mixture was then stirred for 20 min at 45–50 °C, followed by the addition of an appropriate quantity of formaldehyde solution into the reaction system. The reaction system was heated to a temperature of 60–65 °C and maintained at this temperature for 1.0 h to allow completion of addition reactions. The mixture was then heated to 80 °C and maintained at this temperature for 2.0 h to allow completion of condensation reactions. Finally, the end product i.e. SLPR was cooled in a water bath to room temperature. Meanwhile, pure PR was prepared in accordance with the similar procedures to SLPR.

### *2.3. Testing methods*

The solids content of the spent liquor was determined in accordance with TAPPI Standard (TAPPI T 650 OM 2005.01.01, solids content of black liquor). The lignin content of the spent liquor was determined in accordance with Chinese state Testing Standard (GB/T 2677.8-1994). The ash content of the spent liquor was determined by referring to Chinese state Testing Standard (GB/T 742–2008). Other organic components of the spent liquor can be considered as degraded carbohydrates originating from the wheat straw, and their content can be calculated by deducting lignin and ash from the solid content of the spent liquor. The pH, free formaldehyde content, gelation time and viscosity of the synthesized adhesives were all determined in accordance with Chinese state Testing Standard (GB/T 14074-2006).

The bonding strengths of the prepared adhesives were determined using a method based on Chinese State Testing Standards (GB/T 12914-2008 and GB/T 2791-1995). The testing procedure can be described as follows: Cotton cloth was cut into pieces with the size of 170 mm × 120 mm. Adhesives were coated evenly on one surface of the cloth, with coating weight~~s~~ (oven dry) controlled at 5.0 g/m$^2$. Coating area was controlled at a size of 170 mm × 80 mm by retaining a 40 mm blank space on one side of the cloth in the width direction. One piece of coated cloth and another piece of uncoated cloth were laminated together. The resulting assembly was then pressed at 0.2 MPa and room temperature for 5.0 min in a laboratory hydraulic press. The pressed assembly was then treated for 5.0 h under constant temperature and humidity conditions (23 ± 1 °C and 50 ± 2% respectively), and then cured for 30 min at 150 °C in an oven. The cured assembly was then treated for 24 h under the previously mentioned condition. Sample with dimensions of 150 mm × 100 mm was prepared by removing approximately 10 mm of material from each side of the pressed materials. The samples were then cut into ten testing specimens with dimensions of 15 mm × 100 mm. The specimens were tested by clamping two blank ends in a tensile testing machine. The remaining coating length of the specimen was controlled at 60 mm when it was stripped in testing machine, the bonding strengths was tested at room temperature, and the stripping rate was controlled at 90 ± 10 mm/min.

Bond strengths were calculated using Eq. (1):

**Table 1**
Basic properties of spent liquor.

| pH | Solids content (%) | Lignin content (%) | Ash content (%) | Other organics content (%) |
|---|---|---|---|---|
| 9.9 | 28.0 | 5.91 | 8.57 | 13.52 |

$$\delta_T = \frac{F}{B} \tag{1}$$

where $\delta_T$ is the bonding strength in kN/m. $F$ is data recorded from the tensile tests, N. $B$ is the width of the specimens in mm.

FT-IR spectra of spent liquor and adhesives were obtained using a Bruker VECTOR22 infrared spectrometer. The binding ability of the adhesives was tested using a Lorentzen & Wettre 062 tensile strength tester.

## 3. Results and discussion~~s~~

### *3.1. Basic properties of the spent liquor*

The basic properties of the spent liquor are presented in Table 1. The FT-IR spectrum of spent liquor is shown in Fig. 1.

As presented in Table 1, the spent liquor contains a certain amount of lignin, ash and other organics. Lignin molecular structure contains substantial benzene rings, so it can be used as a substitute for phenol in the preparation of phenolic resins [15]. Ash mainly consists of silicates which originate from the wheat straw, which can serve as a filler in phenolic resin formulations. The other organics which can include polysaccharides usually have a definite stickiness, which may improve the bonding ability of phenolic resins.

As shown in Fig. 1, the FT-IR spectrum of the spent liquor exhibits obvious molecular characteristics of lignin. Absorption peaks located at 3285 cm$^{-1}$ and 2936 cm$^{-1}$ can be attributed to the stretching vibration of O-H in carbonyl and -CH in methyl and methylene respectively. Absorption peaks located at 1564 cm$^{-1}$ can be assigned to the vibration of the aromatic ring and C = O, absorption peaks located at 1404 cm$^{-1}$ can be attributed to the plane deformation of C-H in the aromatic skeleton. The absorption peaks at 1116 cm$^{-1}$ can be attributed to the stretching of secondary alcohols and C = O, whilst absorption peaks located at 1041 cm$^{-1}$ may originate from the plane deformation of C-H in aryl and C-O in primary alcohol.

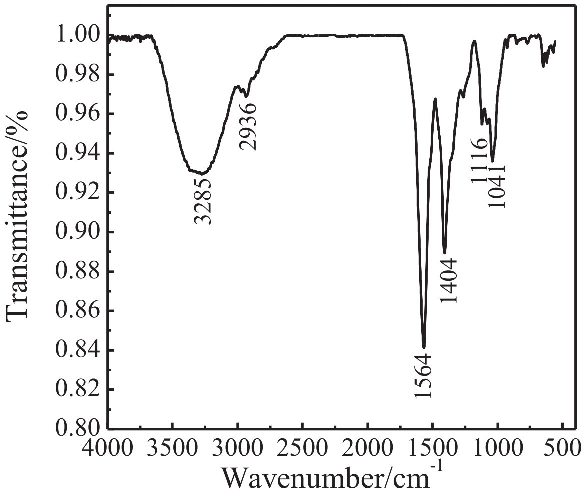

**Fig. 1.** FT-IR spectrum of spent liquor.