



Investigation of oil palm based Kraft and auto-catalyzed organosolv lignin susceptibility as a green wood adhesives



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ABSTRACT

The aim of this study is to highlight the application and potentiality of oil palm based lignins in the synthesis of green phenolic resins. The delignification processes were conducted using Kraft and auto-catalyzed ethanol–water pulping processes. The extracted lignins were characterized using elemental analysis, Fourier transform-infrared, ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, molecular weight distribution (M_n , M_w and polydispersity), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The obtained FTIR results revealed that the Kraft lignin contained substantial amounts of guaiacyl units with smaller amounts of syringyl units. The molecular weight of Kraft lignin was 1564 g mol^{-1} which is higher than organosolv lignin at 1231 g mol^{-1} . The activated free ring position (2.99%) of Kraft lignin was comparatively higher than that of organosolv lignin (2.06%) which was measured using Mannich reactivity analysis. Thermal analysis of Kraft lignin showed higher thermal stability compared to organosolv lignin. The structural and thermal characteristics implied that Kraft lignin had higher potential for the production of green phenolic resins when compared with organosolv lignin.

1. Introduction

Biomass is a promising source of energy that can replace fossil fuels. Thus, it is important in sustainable production. Biomass resources are cheaper compared with other resources, such as crude oil and natural gas [1]. Moreover, the acquisition of products from biomass does not add carbon dioxide to the atmosphere. Plant biomass mainly consists of cellulose, hemicellulose, and lignin, which together form a complex and rigid structure [1,2]. It is also called lignocellulosic biomass [2]. Malaysia has more than four million hectares of oil palm plantations that generate an estimated 15 million tons of empty fruit bunches (EFB) from the mechanical processes of palm oil production, unfortunately, still treated as waste [3]. An important compound extracted from EFBs is lignin [4]. Lignin is the most complex natural phenolic polymer, and is defined as an amorphous, cross-linked, and three-dimensional network polymer. The presence of a variety of functional groups such as aliphatic and phenolic hydroxyl groups, as well as on the carbonyl groups in the lignin structure, enables this polymer to undergo a multitude of modifications. Many studies have

been conducted on the production of environment-friendly products from biomass polymers, with a primary focus on lignin for the production of polymeric compounds, especially phenolic and epoxy resins [5–9]. According to some studies, some parts of the lignin structure are similar to those of phenol, making this material an attractive potential replacement for phenol in wood adhesive resins [10]. Environmental and health concerns, as well as fears of scarcity of petroleum-based materials, may affect the production of the most dominant wood adhesive [11]. This situation has prompted researchers to focus on the development of green wood adhesives, which seem appropriate to reduce dependence on petroleum-based materials. To optimally use lignin in the synthesis of phenolic resins that are free of formaldehyde, their suitability should be determined through a study of their chemical and thermal properties [12,13]. Some previous studies have reported that lignin obtained from the Kraft and organosolv processes differ in physical and chemical characteristics [13]. Kraft pulping is the most commonly used process in the world, despite the many processes required in producing chemical pulp [14]. Organosolv fractionation is one of the most promising pretreatment technologies.

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Compared with the Kraft pulping process, the organosolv process results in higher purity retrieved lignin; in addition, the absence of sulfonates in the process makes it more environmentally friendly [1,15,16]. From organosolv lignin, production of some valuable products like resins and phenol is possible [17,18]. The aims of this work were to characterize the different types of lignin extracted from oil palm empty fruit bunch (OPEFB) using Kraft and auto-catalyzed ethanol–water pulping processes and to examine their suitability for the preparation of green phenolic resin. Interestingly, in this work, strong acids were not used in the delignification process when preparing organosolv lignin unlike most previous studies [19,20] that focused on strong acids as catalysts, which has led to an uneconomically process due to high corrosion of the equipment resulting from the presence of strong acids.

2. Experimental

2.1. Materials

The oil palm empty fruit bunch (OPEFB) long fiber that was used for delignification processes was supplied by Sabutek Sdn. Bhd., Malaysia. Sodium hydroxide (NaOH), sodium sulfide (Na₂S), and ethanol (EtOH, 96%) were obtained from QREC (ASIA), Malaysia. All the chemicals that were used in this study were of analytical grade and were used without further purification.

2.2. Kraft pulping

Kraft pulping process was carried out in a 10-L digester. Solutions were prepared by dissolving 190 g of NaOH in 1.5 L distilled water (19% based on raw material) and 250 g Na₂S in 1.5 L of distilled water (25% based on raw material), with a solvent-to-fiber ratio of 8:1. The cooking temperature was set from room temperature to 170 °C for 3 h. The contents in the digester were stirred by rotating the digester, which was controlled by a motor. The pressure of Kraft pulping was around 12 bar to 15 bar. After cooking, the pulp was washed and separated by screening through a sieve and then the black liquor was collected.

2.3. Kraft lignin extraction

The Kraft black liquor has a pH of 12.5. Kraft lignin (KL) was precipitated from the concentrated black liquor by acidification using 20% (v/v) sulfuric acid (pH 2) [21]. Precipitated lignin was filtered and washed with distilled water at pH 2 and then dried in a vacuum oven at 45 °C for 48 h [22]. The lignin was purified by extraction in a Soxhlet apparatus for 6 h with *n*-pentane to remove the lipophilic non-lignin matters, such as wax and lipids. This step was followed by filtration and washing of the product using distilled water (normalized at pH=2) to remove the excess amount of *n*-pentane and non-lignin phenolic compounds that may have remained after the pulping process. The purified KL was dried in a vacuum oven at 45 °C for 48 h. KL was treated with hot water to dissolve the residual sugars [23]. Finally, the obtained lignin was dried in a vacuum oven at 45 °C for 48 h.

2.4. Organosolv lignin extraction

Organosolv lignin (AEL) was recovered as a byproduct from OPEFB using an autocatalyzed ethanol–water pulping process. The air-dried OPEFB was ground from 20–60 wire mesh using a ball mill. The OPEFB was dried overnight at 105 °C in an oven prior to the pulping process. The mass ratio between dried OPEFB and the used solvent was 1:10. A 0.5 L stainless steel reactor was loaded with the raw material (22 g) and 80% aqueous ethanol, and then heated to 210 °C for 2 h (cooking process). After cooking, the reactor was quenched rapidly to room temperature in an ice-water bath to terminate the reaction. The solid and solvent fractions were separated using a filter paper and

washed with warm (60 °C) aqueous ethanol (8:2, 3×50 ml). The filtrates and original liquid fractions were combined and poured into distilled water with continuous stirring for 30 min to precipitate lignin. AEL was then collected by centrifugation at 3500 rpm for 15 min. AEL was obtained by freeze drying for further analysis.

2.5. Characterization of lignin

The ash content was identified using the proposed method by Mohamad Ibrahim et al. [21]. The lignin powder was obtained by drying the lignin samples at 105 °C in a vacuum oven until constant weight was obtained. Thereafter, approximately 0.5 g lignin samples were weighed and placed in crucibles and calcined at 900 °C for 4 h. The ash content of the lignin samples was calculated by measuring the weight percentage of lignin samples in the crucible after the burning process. The content of carbon, hydrogen, nitrogen and sulfur were analyzed using a Thermo Finnigan model Eager 300 analyzer. The percentage of oxygen was calculated by subtracting the contents of C, H, N and S from 100%. The percentage of proteins was calculated as N (%)×6.25 [21,24]. Based on the elemental composition C_aH_bO_cS_d, the average of double bond equivalent (DBE) was calculated according to Eq. (1) [24]:

$$DBE = \frac{(2a + 2) - b}{2} \quad (1)$$

where

a=Molar ratio of carbon

b=Molar ratio of hydrogen

Fourier transform infrared (FTIR) spectroscopy of KL and AEL was performed in a direct transmittance mode using a Perkin Elmer model System spotlight 200 instrument. Each spectrum was recorded over a frequency range of 600 cm⁻¹ to 4000 cm⁻¹ with resolution of 4 cm⁻¹ and 20 scans.

The lignin samples underwent an acetylation process to improve their solubility in the organic solvent for the gel permeation chromatography (GPC) and nuclear magnetic resonance NMR analyses. All hydroxyl functional groups were substituted into acetyl groups during the acetylation process. The acetylation was conducted using the method proposed by Thring et al. [25]. Briefly, 30 ml of 1:1 (v/v) mixture of pyridine and acetic anhydride were added into 2 g of lignin in a 100 ml conical flask. After stirring for 48 h at room temperature, the mixture was treated with 10 volumes of 1% (v/v) HCl at 0 °C. The resulting precipitate was filtered, washed with deionized water to a neutral pH, and dried at room temperature.

Weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (M_w/M_n) were determined by GPC. Tetrahydrofuran (HPLC grade) was used as a mobile phase with a flow rate of 1.0 mL min⁻¹ using a Water 1525 Binary HPLC Pump. Water Styragel columns, HR 5E THF, and HR 4E THF, as well as a Water 2414 Refractive Index detector, were used. The columns were calibrated using a narrow molecular weight monodispersed polystyrene standard ranging from 580 g mol⁻¹ to 8,500,000 g mol⁻¹ in the eluent. Briefly, acetylated lignin samples were dissolved in the eluent at a concentration of 10 mg mL⁻¹. The solution was filtered using a 0.45 μm filter. Then, 20 μL of the filtered solution was injected into the HPLC system.

Liquid-state ¹H and ¹³C NMR spectra were obtained with a Bruker Avance 500 NMR spectrometer operating at a frequency of 100–59 Mhz. Both acetylated lignins (150 mg) were dissolved in DMSO-d₆ (0.40 mL). Spectral analyses were performed using XW in Bruker software.

The thermal behaviors of the lignin samples were studied by thermogravimetric analysis (TGA) using a Perkin Elmer TGA 7 thermogravimetric analyzer. About 10 mg of sample was put into a

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