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Isolation and characterization of lignin from Moroccan sugar cane bagasse: Production of lignin–phenol-formaldehyde wood adhesive

Amine Moubarik[a,*], Nabil Grimi[b], Nadia Boussetta[b], Antonio Pizzi[c]

[a] MAScIR-NANOTECH, ENSET, Avenue de l'Armée Royale, Madinat El Irfane, 10100 Rabat, Morocco
[b] Université de Technologie de Compiègne, Unité Transformations Intégrées de la Matière Renouvelable (TIMR, EA4297), Centre de Recherche de Royallieu, B.P. 20529-60205, Compiègne Cedex, France
[c] ENSTIB, Université de Nancy 1, Epinal, France

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ABSTRACT

lignin-based materials were isolated from Moroccan sugar cane bagasse after alkaline delignification. Sugar cane bagasse was subjected to hot water (70 °C) and alkaline aqueous solutions (15% of sodium hydroxide (NaOH), 98 °C) treatments. The dissolved lignin macromolecules were separated and purified. The isolated solid was then characterized by different complementary analysis (FT-IR; ^{1}H, ^{13}C NMR; GPC and TGA). In the present work, the possibility of preparing wood adhesives from bagasse lignin has been explored. The results showed that the delignification with 15% NaOH resulted in yields of cellulose and lignin of $42 \pm 2.2\%$ and $13 \pm 1.5\%$, respectively. The extracted lignin scaffolds exhibits high reactivity due to the high content of hydroxyl group. Their higher molecular weight (2781 g/mol) and good thermal stability (180 °C) make them excellent candidates for partial substitution of phenol formaldehyde (PF) resin. A resin formulation in which up to 30% of PF can be substituted by bagasse lignin gave good results and was employed for the elaboration of plywood panels which passed relevant international standard specifications for interior-grade panels.

1. Introduction

One of the most challenging topics in material science today is to convert biomass-derived waste and feedstock to highly added value-materials. For instance, sugar cane bagasse is a fibrous residue of sugar cane stalks left over after crushing and extraction process of the juice from sugar cane. About 54 million dry tons of bagasse are produced annually throughout the world (Mulinari et al., 2009). Most of the bagasse weight is in the form of the so-called fiber and rind particles, which have high length-width ratios (lengths up to a few cm) and correspond mostly to stalk fibro vascular bundles. For the sugar industries, this waste is mainly converted into energy through combustion (Leibbrandt et al., 2011), applications in pulping (Goncalves et al., 2005), activated carbon production (Devnarain, 2003; Qureshi et al., 2008), cellulosic ethanol production (Carrier et al., 2011) and gasification (Mamphweli and Meyer, 2010).

Sugar cane bagasse consists of approximately 50% cellulose, 25% hemicellulose and 25% lignin (Pandey et al., 2000; Ezhumalai and Thangavelu, 2010; Ladeira et al., 2010; Sun and Cheng, 2002). Cellulose is a polydisperse linear homopolymer consisting of regio- and enantioselective β-1,4-glycosidic linked D-glucose units. The polymer contains three reactive hydroxyl groups at the C-2, C-3 and C-6 atoms (Heinze and Liebert, 2001; Sun et al., 2004). Hemicelluloses are composed of xylan, mannan, b-glucan, and xyloglucan polysaccharides (Vibe Scheller and Ulvskov, 2010). Lignin is a complex amorphous polymer composed of phenylpropanoid units consisting primarily of coniferyl, sinapyl, and p-coumaryl alcohols (Hatfield and Vermerris, 2001; Sugimoto et al., 2002). The use of lignin-based materials in various applications requires a proper investigation of its physico-chemical and thermal characteristics to understand the chemical and physical nature and thermal behaviour of this bio-polymer. To obtain different products from sugar cane bagasse, it is necessary to submit the biomass to separation process of its constituents. However, it is a challenge to isolate original lignin from sugar cane bagasse. A variety of methods like organosolv fractionation (Pye and Lora, 1991; Balogh et al., 1992), steam explosion (Rocha et al., 2012; Ibrahim et al., 2010; Glaser and Wright, 1998) and enzymatic hydrolysis (Shevchenko et al., 1999) have been developed in an attempt to isolate and identify cellulose and lignin. One of the most suitable methods for the extraction and separation of lignin is based on the alkaline delignification (Ibrahim et al., 2010; Sun et al., 2004; Fernandez-Bolanos et al., 1999; Käuper, 2004; Mousavioun and Doherty, 2010).

* Corresponding author at: NANOTECH-MAScIR (Moroccan Foundation for Advanced Science, Innovation and Research), ENSET, Avenue de l'Armée Royale, Madinat El Irfane, 10100 Rabat, Morocco. Tel.: +212 6 63 52 81 58.
E-mail address: amine.moubarik@yahoo.fr (A. Moubarik).

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Phenol formaldehyde resins are generally synthesized using petro-chemicals such as phenol and formaldehyde under alkaline catalysts. PF resins provide high strength and are extremely resistant to moisture which prevent delaminating and enable excellent thermal stability and low initial viscosity (Pizzi, 1993). Therefore, reduction of cost and substitution of petroleum-based raw materials are the most important direction of development of PF adhesives. Lignin has been incorporated into wood adhesives due to its similar structure to PF resins (Wang et al., 2009; Turunen et al., 2003; Tejado et al., 2007; Kazayawoko et al., 1992). The suitability of lignin-based materials for manufacturing of lignin–PF resins depends on the polysaccharide composition and total hydroxyl content (phenolic hydroxyl and aliphatic hydroxyl). The low content of polysaccharide was researched for the strength and water resistance of the resins, because the presence of polysaccharide decreased the reactivity of the lignin (Pizzi and Mittal, 1994). In the copolymerization of lignin–PF resins, all of the hydroxyl groups were important to activate the lignin.

In this contribution, lignin fractions isolated from Moroccan sugar cane bagasse was studied using a combination of several techniques TGA, FT-IR, ^{1}H, ^{13}C NMR and GPC. The aim of this study was to get a better understanding on the chemical and thermal properties of the extracted lignin sample and to assess their suitability for partial incorporation into phenol formaldehyde (PF) resin.

2. Experimental methods

2.1. Biological material

Sugar cane bagasse was obtained from a local sugar factory (Doukkala, Morocco). The bagasse was stored indoors during the experiments. The bagasse was air-dried for three days at ambient temperature (up to 8–10% equilibrium moisture content) and then cut into small pieces (1–2 cm). The cut bagasse was ground to pass a 1.0 mm size screen. All chemicals used were of analytical or reagent grade (Sigma–Aldrich, France).

2.2. Isolation of lignin

The procedure for isolation of lignin by delignification with aqueous solution of sodium hydroxide is illustrated in Fig. 1. Twenty grams (oven-dry matter) of sugarcane bagasse were treated with a hot water at 70 °C for 2 h. The solid-to-liquid ratio used was 1:10. The treatments were carried out in a steel reactor with a Parr 4836 temperature controller (Parr Instrument Company, Moline, IL). At the end of the reaction the pre-treated sugarcane bagasse was cooled (25 °C), washed with water (S:L ratio = 1:10; w/w) and centrifuged (2000 rpm, t = 10 min) to separate the solubilized hemicelluloses.

Lignin was then extracted from the pretreated sugar cane bagasse using alkaline treatment. Sugar cane bagasse was placed in a reactor with an aqueous alkaline (15% NaOH (m/v)) solution. The solid-to-liquid ratio was 1:10. The suspension was maintained under agitation (250 rpm) for 90 min at 98 °C. At the end of the reaction the delignified material was filtered to obtain the black liquor without any fibrous materials. Sulfuric acid (5 N H_2SO_4) was added until reaching pH 2 in order to precipitate the acidified lignin, which was then collected and washed by centrifugation and air-dried. The lignin powder, with rather low amount of carbohydrate, was used directly in the preparation of lignin–PF adhesive. No additional purification steps were performed. All the yields of lignins represent the mean of at least triplicate analysis.

Lignin samples were subjected to acetylation in order to enhance their solubility in organic solvent in gel permeation chromatography (GPC) and ^{1}H, ^{13}C NMR analysis. During the acetylation process, all the hydroxyl functional groups are substituted by new acetyl groups. Acetylation was performed using Vázquez et al. (1999) method.

2.3. Lignin characterization

FT-IR measurements were performed in an ABB Bomem FTLA 2000-102 instrument by direct transmittance using KBr pellet technique. Each spectrum was recorded over 20 scans, in the range from 4000 to 200 cm^{-1} with a resolution of 4 cm^{-1}. Background spectra were collected before every sampling. KBr was previously oven-dried to avoid interferences due to the presence of water. The characteristic bands of lignin were assigned according to the literature.

^{1}H and ^{13}C NMR spectra of extracted lignin samples were recorded on a Bruker Avance 500 MHz spectrometer from 80 mg of sample dissolved in DMSO (1.0 mL). Each spectrum was recorded with 32,768 data points, 5.2 μs pulse and pulse delay of 1.547 s (relaxation delay 2.5 μs; 90° pulse). The ^{13}C NMR spectra were recorded at 25 °C after 30,000 scans.

Gel permeation chromatography provides a rapid way to obtain information on the molecular weight of polymers. Samples have been examined through THF-eluted 350A HT-GPC using a MALVERN instrument (TX, USA) equipped with three styrene–divinylbenzene copolymer gel columns of 50, 500, and 104 Å from Polymer Laboratories. The columns were calibrated using polystyrene standards in the 92–66.000 g/mol range. The molecular weight and molecular number were compared to polystyrene standard; the presented results in this work are thus relative values. The flow rate of THF was 1 ml/min and the samples were dissolved in THF at a concentration of 1 mg/ml and stored for 24 h at 5 °C to avoid variations in molecular weight.

Thermogravimetric analysis (TGA) was used to determine the thermal stability and degradation of the lignin samples using a TGA Q50 thermogravimetric apparatus. Ten milligrams of each cured sample were placed on a balance located in the furnace and heat was applied over the temperature range from room temperature to 1000 °C at a heating rate of 5 °C/min in air. Mass losses vs. temperature thermograms were obtained showing the different decomposition processes. Three replicates were used for optimal adhesive mix.

2.4. Preparation of resin formulation

A phenol-formaldehyde resol with a solids content of 46% and a viscosity of about 450 cp was prepared using a 2.2:1 formaldehyde: phenol ratio and 7.3% (w/w) of NaOH. The resols were prepared in a two liters glass reactor with mechanic stirring and temperature control. The necessary amount of the reactive according to the established formulation was fed into the reactor. When the operating temperature was reached (90 °C), the extension of reaction was monitored, measuring resol viscosity at 25 °C. The lignin–PF adhesives were prepared by copolymerisation of lignin (with variable amounts) at room temperature.

2.5. Plywood manufacture and testing

Five ply laboratory plywood panels of dimension 250 mm × 250 mm × 10 mm were prepared from 2 mm thick Maritime pine (*Pinus pinaster*) veneers of 4% moisture content at a glue mix spread of 225 g/m^2 single glue line. Plywood bonded with bagasse lignin–PF resin has been assembled and hot pressed under 12 bar at 160 °C for 6 min. The fixed bonding conditions of 160 °C pressing temperature and 12 bar were selected to reproduce the industrial conditions used to bond plywood panels. The longer pressing time of 6 min was used to assure full reaction.