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Effect of different organosolv treatments on the structure and properties of olive tree pruning lignin

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ABSTRACT

Different organosolv processes (acetosolv, formosolv and acetosolv/formosolv) were applied to extract lignin from olive tree pruning. Obtained lignins were characterized by several methods to determine their composition, structure and functional groups with the aim of evaluating their potential to be used for obtaining added value compounds. All lignins had very high purity and low sugar and inorganic contamination, especially in the case of lignin obtained from formosolv treatment. Hydroxyl groups were the main functional groups in all lignin samples while the carbonyl groups were the lowest. Finally, the main difference between the lignins was the average molecular weight.

1. Introduction

Biomass is considered an appropriate raw material to replace fossil sources to produce chemical products or energy. Among the different types of biomass, lignocellulosic biomass is the most abundant one with 200 billion metric tons available worldwide [1]. Conversion of lignocellulosic biomass into fuels or chemical products is a rapidly growing research area. This type of biomass is primarily composed of three polymers: cellulose, hemicellulose and lignin.

Lignin is a phenolic biopolymer composed by combination of three phenylpropanoid units: p-coumaryl alcohol, guaiacyl alcohol and syringyl alcohol. Several interunit linkages including β-O-4, α-O-4, β-5, β-β, 4-O-5, 5-5 are formed by dehydrogenation, cross-coupling, and dehydrodimerization reactions during the biosynthesis process of macromolecular lignin. In plant cell walls, lignin fills the spaces between cellulose and hemicellulose, and it acts like a resin that holds the lignocellulose matrix together. About 25–35% of the organic matrix of wood is composed by lignin, moreover, it is a major component of grasses, leaves, and needles [2]. Depending on its origin lignin structure presents differences concerning its monolignol composition. In softwood lignin, usually referred to guaiacyl lignin, the structural elements are derived principally from coniferyl alcohol (G) and trace amounts of synapyl alcohol-derived units (S). On the other hand, normal hardwood lignin, termed guaiacyl-syringyl lignins, is comprised of coniferyl alcohol and sinapyl alcohol-derived units in varying ratios. Nowadays, lignin is used as low heating fuel to generate energy in the pulp and paper industry. However, the aromatic chemical structure of lignin makes it unique and very promising source of renewable products and commodity chemicals [3].

Several different lignin sources, derived from a specific form of biomass pretreatment, could be potentially used as feedstocks for lignin valorization in a biorefinery. These sources could originate either from pretreatments in the pulp and paper industries (i.e., kraft or lignosulfonate) or new feedstocks specific to the biorefinery scheme (i.e., organosolv). The organosolv treatment is an alternative to conventional pulping processes due to many advantages such as; low boiling points, process simplicity, non-sulfur formulas, and easy recycling possibilities with some organic chemicals [4]. Among organosolvents, acetic acid and formic acid have received considerable attention and many studies have been done employing these two organic acids as delignification agents [5–8].

The extraction of lignin from lignocellulosic materials is conducted under conditions where lignin is progressively broken down to lower molecular weight fragments, resulting in changes to its physicochemical properties. Thus, apart from the source of the lignin, the method of extraction will have a significant influence on composition and properties of lignin.

Among lignocellulosic materials olive tree pruning is a lignocellulosic residue obtained from an operation realized to eliminate old branches and prepare trees for the next crop. This agricultural residue is usually left on the cropland (with the consequent risk of plagues) or used as firewood, representing both activities and economic misuse or devaluation of their potential

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exploitation. In Spain, the current annual production is more than 7×10^9 kg with an estimation per year of 3000 kg/ha [9].

The aim of this study is to characterize olive tree pruning lignin obtained by different organosolv treatments in order to assess the possible changes occurred in lignin structure and properties. Acetosolv, formosolv and combination of acetosolv and formosolv treatments were used to obtain different types of lignin from olive tree pruning. The obtained lignins were deeply characterized employing several analytical techniques. Thus, the possibility of using these lignins for further applications is evaluated as an integral part of future biorefineries.

2. Experimental

2.1. Conditioning and analysis of the raw material

Olive tree pruning (Olea europaea, Arroniz variety) used in this work was obtained from a private cultivation in Estella (Navarra, Spain). Olive tree pruning (branches and wood) was acconditioned up to constant moisture and was milled in a Retsch 2000 hammer mill to obtain 4–6 cm size fraction chips free of impurities such as small stones, sand and dust. Characterization of olive tree pruning chips was done according to standard methods [10]. Moisture content (6.50 ± 0.2 wt.%) was determined after drying the samples at 105 °C for 24 h (TAPPI T264 cm-97). Chemical composition, given on dry weight basis, was the following: 3.54 ± 0.32% ash (TAPPI T211 om-93), 15.53 ± 0.12% hot water soluble matter (TAPPI T207 om-93), 31.26 ± 0.46% aqueous NaOH soluble matter (TAPPI T212 om-98), 11.72 ± 0.66% ethanol–toluene extractives (TAPPI T204 cm-97), 22.84 ± 0.67% lignin (TAPPI T222 om-98), 64.63 ± 1.32% holocellulose [11] and 51.16 ± 0.83% α-cellulose [12].

2.2. Lignin obtaining by different organosolv pulping

Acetosolv treatment was carried out based on the conditions used in previous works [13,14]. The olive tree pruning was treated with 90 wt.% acetic acid solution with 0.2% of HCl as catalyst. The pulping reaction was carried out at 130 °C for 90 min and solid:liquid ratio of 1:10 in a 4 L pressure stainless steel batch reactor (EL0723 Iberfluid) controlled by Adkir software. The black liquor, where the lignin was dissolved, was treated with 5 volumes of water and the precipitated lignin (AL) was isolated by centrifugation (5500 rpm, 15 min).

Formosolv treatment was carried out varying only the acid nature and concentration from acetosolv treatment and based on the conditions used in a previous work [6]. Thus, the olive tree pruning was treated with 80 wt.% formic acid solution with 0.2% of HCl as catalyst. All the other parameters were the same as in the acetosolv pulping. The obtained lignin will be named FL from now on.

Acetosolv and formosolv treatments were carried out together. The concentration and nature of pulping media was chosen from a previous work [15]. The olive tree pruning was treated with a solution of formic acid–acetic acid–water (30/60/10, v/v/v) and 0.2% of HCl as catalyst. The other parameters of the treatment and separation of lignin (AFL) were the same as in the previous pulping.

2.3. Lignin characterization

The chemical structure of the different lignins was characterized by attenuated-total reflection infrared spectroscopy (ATR-IR) by direct transmittance in a single-reflection ATR System (ATR top plate fixed to an optical beam condensing unit with ZnSe lens) with an MKII Golden Gate SPECAC instrument. Transmittance spectra were recorded over 32 scans in the wave number range from 4000 to 600 cm^{-1}, with a resolution of 4 cm^{-1}.

NMR spectra were recorded at 30 °C on a Bruker Avance 500 MHz equipped with a z-gradient BBI probe. Typically, 40 mg of sample were dissolved in DMSO-d6. The spectral widths were 25,000 Hz for the ^{13}C dimensions.

The chemical phenolic compositions were determined by alkaline nitrobenzene oxidation. 50 mg of lignin were placed in a tube with sodium hydroxide solution and nitrobenzene and left at 175 °C for 2.5 h. The oxidation products were analyzed by HPLC JASCO instrument equipped with an interface (LC-NetII/ADC) and a photodiode array detector (MD-2018). A Teknokroma Mediterranean sea TR-010006 column (25 cm × 0.46 cm) was used for the experiments and a solution of acetonitrile:water in a ratio of 1:8 with 1% of acetic acid was used as mobile phase. The flow rate was 0.5 mL/min and the analyses were carried out at 40 °C. Calibration was made using compounds standards (Sigma–Aldrich) – vanillic acid, syringic acid, p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillin, syringaldehyde, acetovanillone and ferulic acid.

Lignins were subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin average molecular weight (M_w) and molecular weight distribution (MWD) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a reflex index detector (RI-2031Plus). Two PolarGel-M columns (300 mm × 7.5 mm) and PolarGel-M guard (50 mm × 7.5 mm) were employed. Dimethylformamide with 0.1% lithium bromide was the eluent. The flow rate was 0.7 mL/min and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma–Aldrich) ranging from 70,000 to 266 g/mol.

Acid insoluble lignin (AIL) was determined by subjecting lignin to an acid hydrolysis process consisting in two stages. The first acidic hydrolysis was carried out adding 3.75 mL of sulphuric acid 72% to 0.375 g of lignin. The mixture was left for 1 h at 30 °C. Then, it was diluted with 36.25 mL of deionized water for 3 h at 100 °C. After this time, the solution was cooled for 15 min and then filtered using filters over G4 glass filter crucible. The remaining solid is the acid insoluble lignin. Acid soluble lignin (ASL) was determined by spectrophotometry (UV absorption at 205 nm). Filtrate samples had to be diluted with 1 M H_2SO_4 until absorption was between 0.1 and 0.8 (TAPPI UM250 um-83).

Sugars content was determined injecting the obtained filtrate from AIL analysis into a high performance liquid chromatography (Jasco LC Net II/ADC with a ROA Organic Acid (00H-0138-K0) column (Phenomenex) equipped with a refractive index detector (RI-2031Plus) and a photodiode array detector (MD-2018Plus)). 0.005 N H_2SO_4 prepared with 100% deionized and degassed water was used as mobile phase (0.35 mL/min flow, 40 °C and injection volume 20 μL). High purity standards of D-(+)-glucose, D-(+)-xylose and D-(−)-arabinose (provided by Fluka, with ≥99% of purity) were used for calibration.

A thermogravimetric analysis (TGA) was carried out in a TGA/SDTA RSI analyzer of Mettler Toledo to determine the ash content. Samples of approximately 7 mg were heated from 25 °C to 800 °C at a rate of 10 °C/min in air atmosphere.

Carboxyl groups were studied by aqueous titration. A lignin sample of 0.25 g was suspended in 12.5 mL of sodium hydroxide 0.05 M. After stirring for approximately 3 h until complete dissolution of the lignin sample, the solution was potentiometrically titrated with 0.1 M hydrochloride acid until reaching a pH 7. Carboxyl groups were calculated as the difference between the added NaOH and the consumed.

Oximation reaction was used to determine lignin carbonyl content. Lignin was dissolved in 2 mL of DMSO. Once dissolved, 5 mL of oximating mixture were added to the solution and the mixture was heated at 80 °C for two hours. After that time, the solution was potentiometrically titrated with hydrochloric acid.

The total phenolic content in the analyzed lignin samples was determined by the Folin–Ciocalteau spectrophotometric method