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Kraft delignification of energy crops in view of pulp production and lignin valorization

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ABSTRACT

The hardwoods *Acacia dealbata* (mimosa), *Salix* spp. (willow), and the perennial plants *Arundo donax* (giant reed) and *Miscanthus giganteus* (giant Chinese silver grass) are important energy crops, with low requirements and high productivity. The polysaccharide content of these species has drawn attention as source of sugars for biobased products. In this work, biomasses were deconstructed by kraft pulping, evaluating final pulp yields as well as residual lignin (kappa number, KN) as indicators of the pulp quality for conversion to sugars. The black liquors and lignin in the isolated materials were evaluated concerning composition and structural characterization parameters with relevance to further valorizations routes, such as production of vanillin and syringaldehyde. The best trade-off between pulp yield and KN were achieved for 160 °C and pulping time 210 min, with active alkali (AA) 22% for mimosa and willow and AA 18% for giant reed; these three biomasses presented similar pulp yields (45–47%) and KN (13–15). For silver grass a lower AA (16%) and the combination of higher temperature/lower pulping time (170 °C/180 min) were selected. Among the four, silver grass presented the highest pulp yield (51.5%) and the lowest KN (10), which is the first advantage identified for this species. Another advantage is the higher production of lignin by isolation from black liquor (128 g/kg of biomass), compared to the other materials (88–119 g/kg), with the additional benefit of low contamination with inorganic compounds. The isolation of lignins is favorable for the valorization route involving oxidative depolymerization. The structural analysis of lignins and the comparison between the frequency of the main interlinkages and functional groups allowed drawing remarks about their suitability for some applications. The data presented are a tool for decision about the best exploitation route for lignin, contributing for the valorization of the streams generated in biorefining processes of energy crops.

1. Introduction

A shift toward second-generation biofuels and bioproducts is pushing the adaptation of some industrial sectors to assure their competitiveness. This would be made by the development of efficient and cost-effective processing of feedstocks to a range of bio-based products, and integration into existing infrastructure (de Jong et al., 2012), such as kraft pulping industry.

Most of the pulp and paper industries in Portugal, using the facilities provided by the harvesting of *Eucalyptus globulus*, have already established the logistic process for harvest energy crops from marginal plantations, transport for industrial unit, and processing by direct combustion. This is the case of *Acacia dealbata* (silver wattle or mimosa), *Salix* spp. (willow) and *Miscanthus giganteus* (giant Chinese silver grass). *A. dealbata* is considered invasive species in Portugal mainland and the restrictive law in Portugal recommends their control or eradication through large scale plans, being an incentive to their use for energy and / or to bio-products (Carneiro et al., 2014). *Arundo donax* L. (giant reed) is a well-known source of biomass for biofuels/bioenergy (Corno et al., 2014; Scordia et al., 2013), being nowadays the sugar source for the leading industry of cellulosic ethanol in Europe. Besides giant reed, willow and silver grass have been planted for energy crops around the world (Weih, 2010). Willow has been explored in bioenergetic plantations with 4–6 m, in rotation cycles of 3–4 years. Silver grass is a hybrid of two *Miscanthus* species and a fast growing

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perennial crop with productivities of 20–35 t ha^{-1} in Portugal (one of the highest in Europe) (Brosse et al., 2012), close from those reported for Midwestern US locations (Heaton et al., 2010). All of these species have high productivity and favorable energy balance, requiring low maintenance (Angelini et al., 2005; Brosse et al., 2012; Heaton et al., 2004; Lewandowski et al., 2000; Lygin et al., 2011).

The above mentioned factors and the favorable content of polysaccharides (mostly cellulose and hemicelluloses) of mimosa (Yáñez et al., 2009), giant reed (Corno et al., 2014; Shatalov et al., 2001; You et al., 2013), willow (Ferreira et al., 2011; Muñoz et al., 2007) and silver grass biomass (Brosse et al., 2012) are attracting attention for production of sugars and derived bioproducts. However, before enzymatic depolymerization to yield the monomeric sugars, it is necessary to turn the matrix accessible, which encompasses a certain degree of delignification. Several processes for this purpose (often called pretreatments, deconstruction processes or delignification) have been intensively studied in recent years (El Hage et al., 2010a,b,b; Kumar et al., 2009; Zhao et al., 2012), giving also some insights about the effect on cellulose, hemicelluloses and lignin structure (Brodeur et al., 2011; El Hage et al., 2010b; Mosier et al., 2005; Savy and Piccolo, 2014). Some of the lignocellulosic pretreatment technologies studied in recent years are steam explosion (De Bari et al., 2013), organosolv pulping with (El Hage et al., 2010b) or without previous hydrothermal treatment (El Hage et al., 2010a), hydrothermal treatment (Gullón et al., 2012), ammonia fiber explosion (Murnen et al., 2007) acid and alkaline hydrolysis (Scordia et al., 2013; Uppugundla et al., 2014), and processing with ionic liquids (Uppugundla et al., 2014). In most of these processes it is generated a stream containing the lignin of the material, in variable quantities and with different modifications imparted by delignification process and conditions.

It should be highlighted that kraft process has not been considered as deconstruction process for this type of feedstock in the perspective of producing pulps for enzymatic hydrolysis and finally, sugars. Kraft process is known as an efficient delignification process, while preserving the polysaccharide fraction (Llano et al., 2012; Reina et al., 2014). It has been exclusively associated to papergrade pulp. However, this is the immediate and most available technology to be used in biomass deconstruction (first step on biorefining processes) in conventional kraft pulp and paper facilities. In this process, lignin from biomass is partially depolymerized and dissolved in the pulping liquor (Gierer, 1980; Gullichsen and Fogelholm, 2000), being one important side-stream of the process of biomass deconstruction. The aromatic nature and the crosslinked units carrying phenolic and aliphatic hydroxyl groups of lignin has been moving several studies aiming its valorization as renewable source of (i) macromolecule for polymers (Cateto et al., 2009; Hatakeyama and Hatakeyama, 2010) and high performance carbon fibers (Hu et al., 2014; Thunga et al., 2014) (ii) high added-value phenolic compounds, such as vanillin and syringaldehyde, produced by oxidation (Pandey and Kim, 2011; Pinto et al., 2013, 2012; Silva et al., 2009) and other low molecular weight compounds (Pandey and Kim, 2011; Zakzeski et al., 2010) However, the route depends on black liquor composition, including carbohydrates and inorganic content, and strongly governed by lignin characteristics. In recent years, considerable efforts have been made to correlate lignin characteristics with the yield on vanillin and syringaldehyde, since only a fraction of the whole lignin produce these high-added value compounds (Costa et al., 2014; Pinto et al., 2011). Several factors have been identified and correlations have been established, ascertain about the importance of raw material and processing on functionalized monomers production from lignin. Lignins from mimosa, willow, giant reed and silver grass were never analysed in this perspective, in particular resulting from kraft pulping for polysaccharides production.

The main objectives of this study are (i) to evaluate the kraft process to produce pulps from mimosa, willow, giant reed, and silver grass considering the final yield as well as residual lignin (as KN) as indicators of the pulp quality envisaging enzymatic hydrolysis; (ii) to evaluate the lignin in the liquid stream generated in the process, black liquor, as well as the respective isolated lignin, with particular emphasis on structural characteristics in the perspective of further valorization into biobased products such as vanillin and syringaldehyde. The final goal is to provide comparative results about the performance of these species on kraft pulping and characteristics of resulting lignins as a tool for a decision about possible valorization routes for these energy crops/invasive species.

2. Materials and methods

2.1. Biomass origin and composition

A. dealbata (silver wattle or mimosa), *Salix* spp. (willow tree), *A. donax* L. (giant reed), and *M. giganteus* (giant Chinese silver grass) were harvested in the North of Portugal in 2013. The main foliage was removed and the woody materials (mimosa, willow) or stalks (giant reed and silver grass) were air dried and disintegrated to produce standard chips for laboratory kraft pulping. A representative sample was taken, milled, and the fraction 40–60 mesh was separated for analysis. Extractives, ashes and lignin content were quantified according to TAPPI standards. Carbohydrates were quantified after acid hydrolysis by anion-exchange chromatography using a Dionex DX 500 series chromatograph equipped with pulse amperometric detector (Dionex ED 50) and a CarboPac PA-1 column (guard column 4 × 50 mm and analytical column 4 × 250 mm). The eluent was 2 mM sodium hydroxide solution at a flow rate of 1 mL/min and room temperature.

Chemical composition of the mimosa, giant reed, willow and silver grass is presented in Table 1.

Fig. 1 is the schematic diagram of the approach which will be detailed in the following experimental sections. The gray boxes indicate the chemical analysis and characterization performed to each black liquor and respective isolated material (containing lignin), and black arrows the data correlation discussed in Section 3.

2.2. Kraft pulping experiments and resulting streams

Kraft pulping essays for screening of conditions were performed in rotative reactors (VEWERK) equipped with an external electric heating system and temperature control with capacity for 100–200 g of dried biomass and a maximum of 1 L of pulping liquor, using the following conditions: liquor-to-wood ratio 4:1 for mimosa, giant reed and willow and 6:1 for silver grass; active alkali (AA%, as Na_2O) 16%, 18%, 20% and 22%. For each AA, 3 different combinations of temperature and pulping time were conducted: 160 °C for 180 min and 210 min, and 170 °C for 180 min. These two variables can be combined into a single one through the so-called H-factor. H-factor is a kinetic model for the rate of delignification in

Table 1
Chemical composition of lignocellulosic materials.

Parameter	Mimosa	Willow	Giant reed	Silver grass
Ethanol/toluene extractives	4.1	6.3	4.4	4.6
Ashes	1.4	1.1	3.4	3.0
Klason lignin	25.7	21.9	24.3	22.1
Soluble lignin	2.1	1.7	1.8	1.4
Main carbohydrates				
Glucose	47.1	50.2	45.8	47.6
Xylose	15.3	13.8	23.4	25.2