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Multistage treatment of almonds waste biomass: Characterization and assessment of the potential applications of raw material and products

Pedro L. de Hoyos-Martínez [a,b], Xabier Erdocia [a], Fatima Charrier-El Bouhtoury [b], Raquel Prado [c], Jalel Labidi [a,*]

[a] Chemical and Environmental Engineering Department, University of the Basque Country UPV/EHU, Plaza Europa, 1, 20018 San Sebastián, Spain
[b] CNRS/ UNIV PAU & PAYS ADOUR/ E2S UPPA, Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials (IPREM) – IUT des Pays de l'Adour, 371 Rue de Ruisseau, 40004 Mont de Marsan, France
[c] Department of Chemistry, Imperial College London, Exhibition Road, SW7 2AZ London, UK

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ABSTRACT

Almond shells are waste biomass generated in agro-industrial activities, which represent a resource that can be further valorized upon treatment. The purpose of this work was to assess new value-added products obtained through a novel multi-stage delignification process of almond shells. A comprehensive chemical characterization of the raw materials and products involved in each stage of the process was carried out. Moreover, an extensive mass balance was developed, providing a full understanding of the extraction process. The pulps produced did not display a significant cellulose loss and hence they could be exploited as cellulose-rich materials. On the other hand, the obtained lignins presented high purity values (≈90%) and a high reactivity, and their structures became more condensed and homogeneous after each extraction cycle. These features would allow their utilization as feedstock of renewable materials such bio-sourced phenolic resins.

1. Introduction

In the current context, the depletion of the fossil fuels claims for a severe shift in the management and utilization of the sources of energy and materials towards a more green and sustainable path. Thus in the last years, there have been a growing tendency in the study and utilization of different types of renewable sources, especially biomass. This growing interest on biomass has been motivated by several factors (Bilgili and Ozturk, 2015): (i) it is an abundant and renewable source, which can be produced anywhere and that represents an option to decrease the dependency to oil; (ii) it provides a solution to poverty in under developed and developing countries, promoting the rural employment and (iii) it contributes to the reduction of the carbon dioxide (CO_2) emissions. Hence, the utilization of biomass as energy source currently is undergoing a great boost worldwide (Ahmad and Tahar, 2014).

Between the different types, the lignocellulosic biomass counts as the most abundant group representing almost 70% of the total plant biomass (Duchesne and Larson, 1989). Lignocellulosic biomass can be originated from diverse sources such as agricultural and forestry residues, municipal wastes (organic and paper) and several crops (Brandt et al., 2013). In this regard, agroforestry activities are said to generate a huge amount of lignocellulosic residues (Zheng et al., 2014). Nevertheless, the overexploitation of forests (especially in developing countries) are jeopardizing this source, which is descending at an alarming rate. Consequently, agricultural wastes are said to be playing a considerable role in the future of forest industry, aiding to the preservation of this natural resource (Guler et al., 2008).

Almonds are an important crop, especially all over the world's temperate regions. Thus, the global world's almond production in 2016 was reported to be around 3.21 million tons distributed in 1.7 million ha (Food and Agriculture Organization of the United Nations Statistics Division (FAOSTAT), 2014). In this sense, Spain is the second world's major producer of almonds (0.2 million tons) after the USA according to FAOSTAT. Almond shells, which are the lignocellulosic material forming the husk of the almond tree fruit, are ranging 35–75% of the total fruit weight (Ebringerová et al., 2007). Hence, between 70 and 150 million kg of this waste are remaining annually in Spain and accordingly, almond shells valorization as a potential source of energy and materials is of great interest. Normally almond shells are burned owing to their higher heating value (HHV) which is comparable to that of forest residues

* Corresponding author.
E-mail address: jalel.labidi@ehu.eus (J. Labidi).

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(Chen et al., 2016). Nevertheless, this generates problems such as air pollution, soil erosion and decrease of soil biological activity (Çöpür et al., 2007). Consequently, the valorization of almond shells through their lignocellulosic components (cellulose, hemicellulose and lignin), e.g. for nanopaper manufacturing (Urruzola et al., 2014), bio-oil production (Önal et al., 2014) or as bioadsorbent (Ben Arfi et al., 2017), appears as a more environmentally friendly solution.

On the other hand, lignocellulosic biomass is generally considered as a composite material with a recalcitrant structure composed of three biopolymers namely cellulose, hemicellulose and lignin (Zhao et al., 2012). Lignin which accounts for 10–30 wt% of lignocellulosic biomass (Maity, 2015), is a natural amorphous aromatic complex macromolecule highly crosslinked. It is composed of several subunits i.e. p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, derived from the coumaryl, coniferyl and sinaphyl alcohols respectively (De Wild et al., 2014).

Concerning lignin uses, it is said to be a promising renewable source in several fields due to its aromatic nature (Lora and Glasser, 2002). Accordingly, several potential applications have been reported such as the production of chemicals (Shen et al., 2015), its utilization in materials (Faruk et al., 2016) or its employment as antioxidant (Pouteau et al., 2003). All these potential applications confront with its current situation in the industry, where only the 2% of the lignin industrially produced is used for commercial purposes (Laskar et al., 2013).

Regarding lignin valorization, a key point is the extraction process. Traditionally lignin is produced as a by-product (waste) of the pulp and paper industry. Thus, the most industrially used processes for isolating lignin are sulfate (Kraft) and sulfite (Fernández-Rodríguez et al., 2017). However, they exhibited several disadvantages derived from environmental aspects of the process and the heterogeneity of the lignins. This has triggered a growing interest on the sulfur-free delignification processes such as organosolv, alkaline and ionic liquid pretreatments (Vishtal and Kraslawski, 2011). Organosolv pretreatment is able to isolate high purity lignins, avoiding the significant salt amount formed in alkali process. Thus, the high water consumption required in this pretreatment (Chaturvedi and Verma, 2013) can be avoided reducing the downstream costs. Nevertheless, higher temperatures are needed in organosolv pretreatment compared to the alkali one, which can be performed at ambient temperature (Brodeur et al., 2011).

Regarding the pretreatment with ionic liquids, it allows the fractionation of lignin and hemicellulose without the utilization of volatile organic solvents (as in the case of organosolv pretreatment). However in organosolv pretreatment, the solvent can be readily recovered by distillation with high yields and low energy consumption, whereas the ionic liquids are difficult to be recycled and reuse (Kumar and Sharma, 2017). Among these sulfur-free extraction methods, organosolv method has drawn considerable attention in the last decades. Organosolv extraction method is an efficient technique for delignification based on the employment of a mixture formed by an organic solvent (mainly alcohols) and water (Wild et al., 2015). The lignin is solubilized into this solvent and the washing liquor and from here, it can be precipitated by lowering the pH.

Several reactions are generally occurring during this pretreatment. The most relevant for lignin extraction, is the hydrolysis of the lignin-hemicellulose linkages and internal lignin bonds via cleavage of the 4-O-methylglucuronic acid ester bonds and α and β-O-aryl ether linkages (Sannigrahi and Ragauskas, 2013). It is known that the cleavage of these aryl ether bonds is responsible for the break-down of lignin. The α-O-aryl ether are separated more easily, while the β-O-aryl ether linkages need more severe conditions (McDonough, 1993). As mentioned before, through this solubilization lignin and lignin-carbohydrate compounds (in lower extent) can be precipitated from the liquid phase whereas cellulose and some hemicellulose remain in the solid residue.

The high content of cellulose remaining in the solid residue allows its utilization for several applications such as the production of bioethanol. Romaní et al. (2016) studied the use of the solid residue of Eucalyptus wood after organosolv pretreatment for this application. They concluded that process integration of a suitable pretreatment, with intensified SSF stages resulted in a good strategy for the co-production of high ethanol titers, oligosaccharides and lignin in an integrated biorefinery.

In the organosolv pretreatment, several operational parameters are said to influence the results of the process namely temperature, reaction time, ethanol and catalyst concentration (in case it is needed). Regarding the temperature, it is reported that higher temperatures usually lead to higher percentage of lignin extracted (Kim and Pan, 2010). On the other hand, lignin's solubility in ethanol is maximized at 70% as shown by Ni and Hu 1995 (Ni and Hu, 1995). Concerning the other two parameters, longer times and higher catalyst concentrations provide a bigger extent of delignification (Sannigrahi and Ragauskas, 2013).

In this work, the valorization of almond shells was intended by means of a green extraction process. The extraction of lignin from almond shells was carried out through a novel multi-step organosolv system composed of three sequential extraction stages. Through this system, the maximization of the lignin extraction yields was aimed. Furthermore, the comprehensive characterization of the raw materials and products from each stage and the complete mass balance of the whole extraction process were carried out. Thereby, it was possible to elucidate the selectivity of the process towards the different lignocellulosic compounds, to determine their availability along the whole system and to assess the potential applications of the different products obtained.

2. Materials and methods

2.1. Raw material and equipment

The almond shells, which were provided by local farmers, were coming from almond trees (*Prunus amygdalus*) of the variety *Marcona*. These almond shells were crushed and sieved by means of a Retsch Hammer mill to chips with a size lower than 1 cm prior to the extraction process. Thus, impurities such as little stones, soil or dust could be removed. The chemical reagents employed for the extraction process and chemical assays were kindly supplied by Sigma-Aldrich.

2.2. Experimental process set up

A multi-step extraction process was developed to maximize the delignification of the almond shells. Thereby three sequential organosolv pulping cycles were carried out resulting in highly pure lignins and rich-cellulose content solid pulps from each cycle. The description of the process set up was provided in Section 1 of supplementary information.

2.2.1. Organosolv process and lignin precipitation

The organosolv delignification process was carried out employing a mixture of ethanol/water (70:30 v/v) at 200 °C during 90 min with a ratio solid to liquid 1:6. During this process, the heat up time was 1.25 h before reaching the set temperature (200 °C). Once the delignification was over, the reactor was cool down during 1 h until the temperature descended to 40–50 °C and the pressure inside the reactor and outside were leveled. These parameters were dependent on the reactor operation.