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Lignin extraction from Mediterranean agro-wastes: Impact of pretreatment conditions on lignin chemical structure and thermal degradation behavior

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ABSTRACT

Three different types of Mediterranean, agro-industrial wastes (olive kernels, grape pomace/seeds, peach kernels), were subjected to two pretreatment processes, a chemical/organosolv and a physicochemical one. The organosolv process included lignocellulosic biomass treatment with formic acid/acetic acid/water (30/50/20, v/v%), for 3 h at 107 °C, while the physicochemical method was conducted by immersing the biomass in a water/ethanol (8/92, v/v%), H_2SO_4 0.32 M, solvent and further exposing the slurry to microwave irradiation (maximum 250 W) for 1/2 h at 150 °C. Both processes were evaluated regarding the achieved delignification and the purity of the extracted lignins. The effect of the pretreatment processes onto the structure and thermal decomposition behavior of the extracted lignins was investigated via FT-IR and TGA analysis, respectively. The objective of the research work was to investigate potential valorization routes for these biomass agro-residues in the context of a biorefinery, focusing on lignin extraction. The pretreatment results showed that the obtained lignins, derived from both procedures, were of high purity (>82 wt%). Under the organosolv procedure, peach kernel delignification showed the maximum value (~16 wt%), while under microwave pretreatment, olive kernel delignification showed the maximum value (~35 wt%). Grape pomace/seeds appeared to be the most resistant in both treatments.

1. Introduction

Lignocellulosic biomass species are composed of cellulose, hemicellulose, lignin, extractives, and several inorganic materials in a highly complex architecture; the structural and compositional features of lignocellulosic biomass form strong barriers to its degradation taking place within biotechnical/chemical biorefinery pretreatment processes [1]. The separation of the three basic biopolymers of lignocellulosic biomass is limited by many factors, such as lignin content, cellulose crystallinity, water content and available surface area, which affect the further exploitation and conversion of the pretreated materials [2]. Lignin accounts for 15–30 wt% in the lignocellulosic biomass [3] and it is a key compound in the present and future biorefinery, rendering its valorization of great importance [4]. The large number of environmentally friendly pretreatment/lignin extraction technologies that have been developed result in lignin materials with different physicochemical characteristics [5–7].

Pretreatment of biomass aims to remove and/or modify the surrounding matrix of lignin and hemicellulose and convert lignocellulosic biomass into a form which renders cellulose hydrolysis much more effective and facilitates lignin conversion [8]. In general, pretreatment methods could be classified into three categories, including physical, chemical, biological pretreatment, and their combinations. Several studies have been performed reporting that among other issues an effective pretreatment should meet the following major requirement [1,9,10]; overcome lignocellulosic biomass recalcitrance, deconstructing the three-dimensional structure of lignocelluloses and breaking down the semi-crystalline cellulose and hemicelluloses while recovering lignin to be converted into valuable co-products.

Cellulosic pulp could be potentially used in paper production industries, while by cellulose saccharification, glucose can be obtained and readily fermented to produce fuel ethanol [11], organic acids [12], and other chemicals [13]. Through cellulose hydrolysis, cellooligosaccharides can be produced. These are expected as ingredients for functional foods [14,15]. Among the cellooligosaccharides, disaccharide cellobiose offers a number of applications; as a raw material for preparing cosmetic products and dendrimers [16,17].

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Additionally, potential lignin applications include [18–22]: (a) lignin valorization for bio-fuels and energy production, (b) lignin exploitation toward high molecular mass applications like polymers (e.g. polyurethane foams), wood adhesives and carbon fibers and (c) lignin utilization for the production of polymer building blocks, aromatic monomers including benzene, toluene, and xylene, phenol, and vanillin. Among all options, the lignin to energy and bio-fuels valorization route is considered to be the field with the most plausible, time to market, commercial application. Lignin characterization via FT-IR and TGA facilitates its further exploitation. FT-IR provides data concerning lignins chemical structure and functional groups, while TGA provides the appropriate information about thermal stability and decomposition behavior of lignins in order to further, at a next step, develop thermal degradation kinetics, which are a key element in the efficient design of lignocellulosic biomass thermochemical conversion processes into energy and materials.

In the present study three Mediterranean agro-industrial wastes, such as olive kernels, grape pomace/seeds and peach kernels, were subjected to two pretreatment/fractionation processes. These agro-residues are abundant in Greece and Mediterranean countries due to the intensive production of olive oil, wine and fruits and are intended to be the feeding biomass of decentralized bioenergy units [23,24]. These agro-wastes could also provide the raw material for a Mediterranean thermochemical biorefinery since they have great potential for the production of fuels and chemicals due to its large availability and low or zero cost and environmental impact comparing to energy crops. The objective of the research work was to valorize these biomass residues in the context of a biorefinery, focusing on lignin extraction and indicating its potential applications via thermochemical conversion processes, while adding value to the original lignocellulosic resources and enhancing, as well, the production cost-competiveness of the plant. Toward that direction, the purpose of the study was threefold: (a) to investigate two pretreatment processes, (b) characterize the lignocellulosic materials before and after pre-treatment protocol and (c) to discuss the influence of the extraction conditions on lignin's chemical structure and thermal degradation behavior.

2. Materials and methods

2.1. Raw material

Olive kernels, grape pomace/seeds and peach kernels, provided by Greek agro-industries, were used for the purposes of this study. The samples were naturally dried in the atmosphere (25 °C) for five days resulting in the moisture content that is presented in Section 3.1. The particle size of biomass used for the analyses and also the hydrolysis and thermal degradation experiments was the specified for the standard procedures that were followed in the study and was <1 mm.

2.2. Lignocellulosic material characterization

According to the needs of the present study, the following portfolio of analytical methods was applied to the lignocellulosic materials before and after the pretreatment protocol.

2.2.1. Total solids and extractives quantification

Total solids (or moisture content) in biomass, were quantified based on the NREL method [25]. The determination of extractives in biomass was carried out according to the published NREL method [26], using traditional soxhlet extraction apparatus. The extractives included water soluble compounds and ethanol soluble ones. Ash is determined gravimetrically, as the residue remaining after combustion of the biomass material at 575 °C [27].

2.2.2. Lignin and carbohydrates measurements

Monosaccharides were determined as alditol acetates using gas chromatography according to the procedure described in Blakeney et al. [28]. The analyses were carried out with a Hewlett Packard (HP6890) gas chromatograph, equipped with a flame ionization detector. The components were identified using a high performance capillary column, HP1-methylsiloxane (30 m × 0.32 mm i.d, 0.25 μm film thickness, Scientific Glass Engineering, S.G.E. Pty. Ltd., Melbourne, Australia). Data were analyzed using ChemHP software. Glucose, xylose, arabinose, mannose and galactose, 2-deoxyglucose (internal standard), were obtained from Sigma-Aldrich (St.-Louis, USA), while solutions of known concentrations were used as standards. Analyses were performed in duplicate. The anhydro corrections were used to obtain the concentration of the polymeric sugars from the concentration of the corresponding monomeric sugars (conversion factor for monosaccharide to polysaccharide (0.88 for pentoses and 0.90 for hexoses)).

Acid insoluble, Klason, lignin and acid soluble lignin, was determined according to the procedure described in Sluiter et al. [29].

2.2.3. Protein

In order to estimate the crude protein content in biomass, the nitrogen content of the material was measured by Kjeldahl methods (1015 TECAROR) and multiplied by a commonly used conversion factor, equal to 6.25, which is used for animal feeds and other materials [30]. The method was also applied to determine the protein content in the isolated lignins.

2.2.4. Elemental analysis

Ultimate analysis is performed in Thermofinnigan CHNS EA 1112 instrument of CE Instruments. The C, H N, Cl and S contents of the samples were determined by an elemental analyzer.

2.3. Pretreatment

A chemical (organosolv) and a physicochemical (microwave) pretreatment process were applied in the present study for the three selected Mediterranean agro-wastes. Both pretreatment products (pulp and lignin) were characterized for their lignin content according to the procedure described in Section 2.2.2.

2.3.1. Chemical pretreatment (organosolv-formic/acetic acid)

Olive kernels, grape pomace/seeds, peach kernels were pretreated by the protocol described in Lam et al. [31] with some modifications [5]. Pre-treatments were performed in 500 mL double-necked boiling flasks and heated by heating plates. The material was pre-soaked at 50 °C for 30 min in a formic acid/acetic acid/water mixture (30/50/20 volume ratio) at a liquid/dry matter ratio of 25/1. After soaking completion, the mixture was further treated at 107 °C, for 3 h. During thermal processing, stirring was continuously performed with a stir bar at 450 rpm. After heating completion, by removing the flasks from the heating plates, reactions were terminated, and the mixture was allowed to cool down at room temperature. The pulps were filtered with a vacuum filter funnel (500 mL, 95 mm diameter) assembled with a fritted disk (40–100 μm pore size; Robu Glasfilter-Geräte GmbH). Vacuum was continued till no more liquor was being collected. Following filtration, pulps were washed twice with the same aqueous solvent. The liquor and washes were combined and 9 volumes of water were added, while stirring, in order to precipitate the lignins (around pH 2). Lignins were recovered after centrifugation and washing with