



Sustainable conversion of *Pinus pinaster* wood into biofuel precursors: A biorefinery approach



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HIGHLIGHTS

- Pine wood was subjected to aqueous fractionation to solubilize hemicelluloses.
- Hemicellulosic saccharides were efficiently saccharified by posthydrolysis.
- Solids from fractionation were processed in acidic media under microwave heating.
- The conversion of cellulose into formic acid and levulinic acid was optimized.
- Lignin was recovered as the insoluble residue from acidic processing.

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ABSTRACT

Pinus pinaster wood was fractionated by aqueous treatments to yield a solution containing hemicellulose-derived saccharides (mainly of polymeric or oligomeric nature) and a solid phase enriched in cellulose and lignin. The solution containing polymeric or oligomeric hemicellulosic saccharides was acidified with sulfuric acid (up to 4 wt%) and heated (up to 130 °C) to assess the conversion of substrates into sugars. The interpretation of the experimental data was done on the basis of a mechanism involving 10 first-order, kinetic parameters. Almost total saccharification was achieved under a range of operational conditions, and the hydrolyzates presented compositions favorable for their further utilization as fermentation media. The solid phase coming from aqueous processing was mixed with HCl solutions and reacted under microwave irradiation to yield the target products levulinic acid (precursor of valeric biofuels) and formic acid (suitable for fuel cell devices). The effects of the most influential parameters (temperature, reaction time and acid concentration) were assessed by empirical modeling. The highest cellulose conversion into levulinic acid (61.9% of the stoichiometric value as an average) was achieved at 190 °C operating for 15 min in a medium containing 1 wt% HCl.

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1. Introduction

The sustainable growth of the chemical and energy industries has become an indispensable component of our society [1]. The current development pattern of the industrial sector, defined by a strong dependence on fossil resources, is far from being sustainable [2], and must be replaced by an alternative one, based on renewable resources. Lignocellulosic materials are a widespread,

renewable resource with an enormous potential as feedstocks for the industry. Their extensive utilization for this purpose is expected to enable the development of a biobased economy [3], in which biorefineries could play a key role. Cellulose and hemicelluloses are polysaccharide constituents of biomass, which can be depolymerised to free sugar monomers that can be further transformed into different platform chemicals [4].

Pinus pinaster is widely distributed in the South-West of Europe and North Africa, and represents a major resource in Galicia (North-West of Spain). In previous studies, the fractionation of *P. pinaster* wood by two-stage aqueous processing (extraction to remove water-soluble extractives followed by autohydrolysis to cause the partial breakdown of hemicelluloses into polymeric

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and oligomeric saccharides, here denoted POHS) has been assessed [5,6]. The extraction stage leads to a complex mixture of compounds (among which phenolic compounds concentrate the added value) [7], whereas the soluble hemicellulose-derived products solubilized upon autohydrolysis can be converted into monosaccharides by acidic postprocessing, yielding a solution of hemicellulosic sugars suitable as a fermentation media (for example, for ethanol or butanol production). On the other hand, the solid leaving the autohydrolysis stage (here denoted extracted, autohydrolyzed solid EAS) is enriched in cellulose and lignin, and can be processed in acidic media to convert its cellulosic fraction into organic acids (levulinic acid, denoted LA, and formic acid, denoted FA). The production of these organic acids from cellulose pulps has been reported in a previous study [8].

The insoluble fraction remaining after aqueous extraction and acidic processing is essentially made up of lignin, and could be employed for a number of purposes, including power generation, chemical modification (for example, by liquefaction or gasification), or as an intermediate for manufacturing polymers or chemicals (including antioxidants for foods or cosmetics, gels or emulsifiers). The processing scheme considered in this work is shown in Fig. 1.

This study focuses on the production of hemicellulosic sugars from POHS and on the generation of lactic and formic acids from EAS under microwave heating. Both routes are compatible and lead to fuel precursors, since: (i) hemicellulosic sugars can be fermented into fuels (for example ethanol, butanol or biogas) [9–12]. Even if the fermentability of conventional hemicellulose-derived hydrolyzates can be limited by the presence of inhibitors such as weak acids, furan derivatives and/or phenolic compounds [13], it can be noted that the approach followed in this work limits this drawback in a multiple way: POHS are obtained from an extractive free substrate; the acidic post-processing of POHS is carried in absence of solids that could release unwanted compounds; and monosaccharides are obtained under mild conditions (limited temperature and low acid concentration), keeping the concentration of furans far below the threshold resulting in inhibitory effects; (ii) LA is an intermediate for the production of liquid fuels, including γ -valerolactone (GVL) and related compounds [14–16], in a way that LA has been identified as one of the “12 top value-added chemicals from biomass” [17]; and (iii) FA is the power source for “Direct Formic Acid Fuel Cells” suitable for portable devices [18].

2. Materials and methods

2.1. Materials

P. pinaster wood chips were kindly provided by a local particle-board industry (Oremer-Finsa, Ourense, Spain). Samples were air-dried, milled to pass an 8 mm screen, homogenized in a single lot to avoid compositional differences among samples and stored until use.

2.2. Aqueous extraction and autohydrolysis

P. pinaster wood samples were first subjected to an aqueous extraction under non isothermal-conditions up to reach 130 °C in a stirred, pressurized reactor; and then immediately cooled by circulating tap water through an internal coil. This method enables the removal of water-soluble extractives, as discussed in an earlier work [7]. The resulting solids were autohydrolyzed at 175 °C for 26 min, conditions reported as optimal for POHS production [5,6]. Both treatments were performed in a 3.75 L stainless steel reactor (Parr Instrument Co., Moline, IL, USA), operating with 8 kg water/kg oven-dry solid. The solid obtained after extraction and autohydrolysis (EAS) was employed as a substrate for producing LA and FA under microwave irradiation (see below).

2.3. Wood and solid analysis

Wood was assayed for ethanol extractives (TAPPI 264 method). Wood and EAS were assayed for moisture (oven-drying at 105 °C until constant weight) and subjected to two-step quantitative acid hydrolysis (with 72% and 4% sulfuric acid, respectively) following the TAPPI 249 method. The solid residue from the quantitative acid hydrolysis was considered as Klason lignin, and the liquid phase was assayed by HPLC for sugars, sugar oligomers, acetic acid and uronic acids (see below).

2.4. Production of furans and levulinic acid in microwave-heated, stirred vessels from hemicellulose free solid

EAS samples were mixed with aqueous HCl solutions, and processed in a Microwave Accelerated Reaction System (MARS 6, CEM Corporation, Matthews, NC, USA). Reactions were carried out in

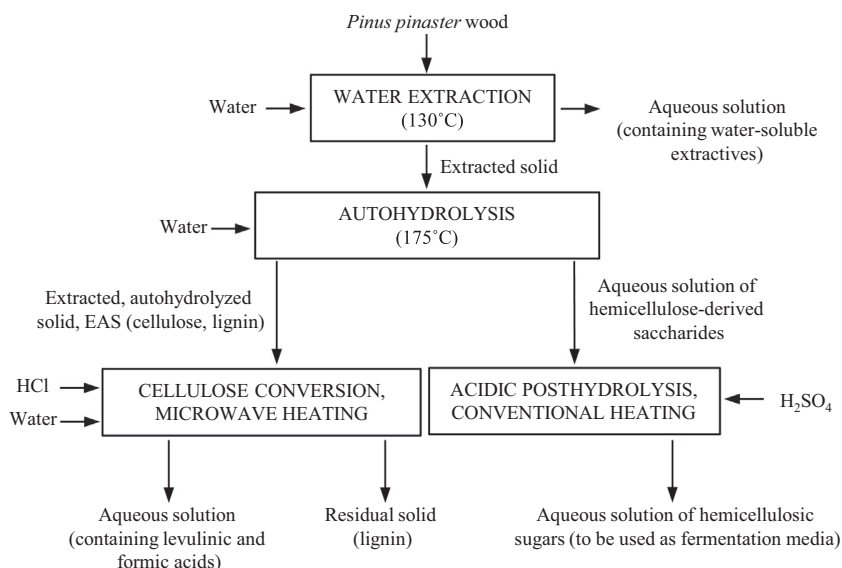


Fig. 1. Processing scheme proposed for *Pinus pinaster* wood utilization.

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