



# Acidic processing of hemicellulosic saccharides from pine wood: Product distribution and kinetic modeling



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## HIGHLIGHTS

- Autohydrolysis liquors from *Pinus pinaster* were subjected to acidic processing.
- Treatments were carried out with 1 wt% sulfuric acid at temperatures up to 250 °C.
- Concentration profiles were employed to develop a generalized kinetic model.
- Levulinic acid can be obtained at high yields at the lower temperatures.
- High temperatures favor furfural production (78.2% molar yield at 250 °C).

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## ABSTRACT

Water soluble compounds were removed from *Pinus pinaster* wood by a mild aqueous extraction, and the treated wood was subjected to hydrothermal processing to convert most hemicelluloses into soluble saccharides (including low molecular weight polymers, oligomers and monosaccharides). The liquid phase containing hemicellulose-derived saccharides was acidified with sulfuric acid and heated up to 130–250 °C to obtain furans and levulinic acid as major products. The concentration profiles of the major compounds participating in the reactions were interpreted by a kinetic model. A maximum conversion of pentoses into furfural near 80% was predicted at high temperature and short time, conditions leading to 24% conversion of hexoses into HMF. Production of levulinic acid was favored at low temperatures. Maximum molar conversion of hexoses into levulinic acid (66.7% at 130 °C) needed a long reaction time (235 h). A value of 53.0% can be achieved at 170 °C after 5 h.

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## 1. Introduction

The interest in manufacturing chemicals and fuels from renewable feedstocks is increased by sustainability issues involving the utilization of fossil resources. Just a limited part of chemicals are produced from renewable resources, like citric acid, enzymes, or ethanol (Lucia et al., 2006). Nowadays, it is worth noting the pro-

duction of lactic acid as an intermediate for the further production of polylactic acid (140,000 metric tons/year) by NatureWorks LLC in Blair, Nebraska. Among the renewable resources, lignocellulosic biomass is largely available, widespread, and could allow a reliable supply. On the other hand, specific economic advantages could be obtained when cheap raw materials, such as agricultural wastes or forest residues, are employed as substrates (Xu et al., 2008). In this context, the development of cost-effective applications for lignocellulosic biomass is a crucial aspect. FitzPatrick et al. (2010) reviewed the treatments applicable to lignocellulosic materials for manufacturing a number of value-added products, and discussed the existing biorefinery schemes.

Forests are important sources of lignocellulosic biomass, and softwoods are the dominant type of trees in the Northern hemisphere (Galbe and Zacchi, 2002). Multistep processing of wood may result in the separation of the structural components (cellulose, hemicellulose and lignin), enabling their separate

*Abbreviations:* POS, poly- and oligo-saccharides; FA, formic acid; GM, glucomannan; NVC, non-volatile compounds; G, glucose; Ar, arabinose; AcH, acetic acid; XOS, xylosyl units in POS; ArOS, arabinosyl units in POS; AcOS, acetyl groups in POS; LevA, levulinic acid; HMF, hydroxymethylfurfural; GGM, galactoglucomannan; Ga, galactose; Mn, mannose; X, xylose; GOS, glucosyl units in POS; GaOS, galactosyl units in POS; MnOS, mannosyl units in POS; UA, uronic acids.

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utilization. Some schemes proposed for softwood fractionation involve the separation of hemicelluloses in the first process stage (Carvalho et al., 2008; Willför et al., 2008).

Softwood hemicelluloses are made up of a number of structural units, including hexoses and pentoses. *Pinus pinaster* wood hemicelluloses include several polysaccharides, among which glucomannan substituted with acetyl and galactosyl moieties is the major one, whereas the presence of arabinoglucuronoxylans was also reported (Ebringerova et al., 2005). In general, pine mannans (including glucomannans, denoted GM and/or galactoglucomannans, denoted GGM) possess backbones made up of randomly distributed D-glucose and D-mannose structural units linked by  $\beta$  (1  $\rightarrow$  4) glycosidic bonds, which can be substituted with irregularly distributed acetyl groups (Kenne et al., 1975).

González-Muñoz et al. (2012) considered the solubilization of *P. pinaster* wood hemicelluloses by hot, compressed water (autohydrolysis or hydrothermal processing). Under selected conditions, hemicellulose-derived saccharides were obtained at high yield, together with acetic acid (coming from acetyl groups linked to hemicelluloses) and small quantities of furans (furfural and hydroxymethylfurfural, denoted HMF, from pentoses and hexoses, respectively).

Levulinic acid (LevA) is a versatile platform chemical that has been considered as a basic chemical raw material for decades, since its reactivity makes it suitable as a starting compound for the manufacture of high-volume organic chemicals employed as solvents, food flavoring agents, monomers for polymer synthesis, plasticizers, herbicides, or antifreeze and pharmaceutical agents (Carpenter et al., 2011; Hayes et al., 2008; Rackemann and Doherty, 2011).

The current LevA market is limited owing to a number of factors, including: (a) the cost of the raw materials, (b) the equipment costs (including reactor and recovery facilities), (c) the high temperatures required, (d) other issues related to waste disposal and catalyst recovery, and (e) low yields (Rackemann and Doherty, 2011). Even though high purity LevA is commercially produced from maleic anhydride, the comparatively lower cost of lignocellulosic materials (typically, less than 5% of the one of maleic anhydride) makes the production of LevA from biomass interesting (Rackemann and Doherty, 2011; Girisuta et al., 2013). The US Department of Energy identified LevA as one of the “12 top value-added chemicals from biomass” (Manzer, 2006).

LevA can be obtained by acidic processing of biomass (Dautzenberg et al., 2011; Runge and Zhang, 2012; Girisuta et al., 2013; Weingarten et al., 2012b; Cha and Hanna, 2002; Fang and Hanna, 2002; Yan et al., 2008; Yang et al., 2013). Recent studies in this field deal with improvements in yields and selectivity. Rackemann and Doherty (2011) reviewed the technologies for LevA manufacture from lignocellulosic materials, including the utilization of homogeneous acid catalysts, ionic liquids, biphasic media or heterogeneous catalysts. However, little information has been reported on the manufacture of LevA from wood hemicelluloses. LevA was produced from pine wood at 66% of the stoichiometric yield operating in aqueous media at temperatures in the range 120–135 °C (Rivas et al., 2013).

Sugar processing in acidic media leads to the formation of LevA through a complex mechanism involving hexose dehydration into HMF, rehydration of HMF leading to the formation of LevA and formic acid (FA), and degradation reactions leading to the formation of humins (Rackemann and Doherty, 2011; Weingarten et al., 2012a; Girisuta et al., 2013). In this field, Girisuta et al. (2006) reported a deep study on the acid-catalyzed decomposition of HMF in a batch reactor, determining the preferential formation of LevA leading to yields higher than 90% when the initial HMF concentration was 0.1 M. The stability of the formed LevA and FA in the used acidic media was determined by Girisuta et al. (2007) and Rivas

et al. (2013). Patil and Lund (2011) reported that humins were derived from HMF and not from LevA or FA. Recently Van Putten et al. (2013) reviewed the role of HMF as a versatile and renewable platform chemical, as well as the process technology and underlying chemistry and applications.

In a related way, pentoses can be dehydrated to furfural in acidic media, and furfural can be converted into FA and other compounds generated from side reactions. Pentoses can be obtained from C5 hemicellulosic polymers in biomass by catalyzed hydrolysis reactions, providing a potential substrate for furfural production. For example, delignified palm fiber (containing xylan) was hydrolyzed in acidic media to yield xylose, which was converted into furfural in a subsequent step (Riansa-ngawong and Prasertsan, 2011). ÓNeill et al. (2009) studied the kinetics of xylose dehydration into furfural in aqueous media catalyzed by zeolites, and proposed a reaction scheme based on dehydration of xylose into furfural, fragmentation of furfural into organic acids, oligomerization of furfural yielding bi- and tridimensional furylic species, and complete dehydration of organic acids to chars. Yemis and Mazza (2011) provided information suitable for understanding the effect of operational parameters on furfural production from biomass using microwave heating.

This work provides an experimental assessment on the acidic processing of hemicellulose-derived saccharides under harsh conditions (temperatures up to 250 °C), as well as a kinetic interpretation of data. The reactions considered include hydrolysis of poly- and oligosaccharides into sugars (including hexoses and pentoses), conversion of sugars into furans (HMF and furfural, respectively), conversion of HMF into LevA and FA, and reactions leading to decomposition products. This work has been carried out in the framework of a research project focused on the development of a pine wood biorefinery intending the integral valorization of the feedstock, including water-soluble phenolic extractives (containing phenols, pinosylvins and flavonoids), hemicelluloses (by treating extractive-free wood in aqueous media under intermediate severity conditions), and separation of cellulose from lignin by organosolv pulping of hemicellulose-free solids.

## 2. Methods

### 2.1. Materials

*P. pinaster* wood chips were kindly provided by Orember-Finsa, Ourense (Spain). Samples were air-dried, milled to a particle size below 8 mm, homogenized in a single lot to avoid compositional differences among samples and stored until use.

### 2.2. Aqueous processing

*P. pinaster* wood samples were subjected to two sequential water treatments. In the first one, performed to remove extractives, samples were mixed with distilled water at a liquid to solid mass ratio of 8:1 g/g (oven dry basis) in a 3.75 L stainless steel reactor (Parr Instrument Company, Moline, Illinois). The reactor was heated up to 130 °C, and then the medium was cooled immediately and filtered. Solids from this treatment were washed, air dried and subjected to a second aqueous treatment (in the same reactor, using the same liquid to solid ratio) at 175 °C for 26 min, and cooled. These experimental conditions are known to be optimal for converting hemicelluloses into soluble poly- and oligo-saccharides (POS) (González-Muñoz et al., 2011, 2012). The obtained POS-containing liquors were employed as reaction substrates in further experiments.

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