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Hydrothermal fractionation of woody biomass: Lignin effect on sugars recovery

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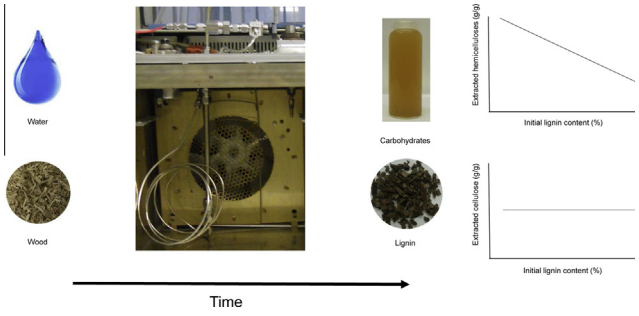
HIGHLIGHTS

- Hydrothermal fractionation of nine urban trees in a semicontinuous reactor.
- The pH behavior is similar for different feedstocks.
- Low content of lignin in raw material led to high hydrolysis of hemicelluloses.
- The lignin content do not affect the cellulose hydrolysis.
- Hemicelluloses and cellulose yield can be influenced by the structure of biomass.

GRAPHICAL ABSTRACT



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ABSTRACT

Subcritical water was employed to fractionate woody biomass into carbohydrates and lignin. Nine urban trees species (hardwood and softwood) from Spain were studied. The experiments were carried out in a semi-continuous reactor at 250 °C for 64 min. The hemicellulose and cellulose recovery yields were between 30% wt. and 80% wt. while the lignin content in the solid product ranged between 32% wt. and 92% wt. It was observed that an increment of solubilized lignin disfavored the hydrolysis of hemicelluloses. It was determined that the maximum extraction of hemicellulose was achieved at 20 min of solid reaction time while the extraction of celluloses not exhibited a maximum value. The hydrolysis of hemicellulose and cellulose would be governed by the hydrolysis kinetic and the polymers accessibility. In addition, the extraction of hemicellulose was negatively affected by the lignin content in the raw material while cellulose hydrolysis was not affected by this parameter.

1. Introduction

Lignocellulosic biomass has emerged as a potential renewable resource for the production of fuels (Thangavelu et al., 2014), energy and added value chemical products (Wijaya et al., 2014). To achieve this, different treatments should be applied to the raw material in a concept industry called: Biorefinery (Bozell, 2008). Lignocellulosic biomass is a complex material composed mainly of three biopolymers: hemicellulose, cellulose and lignin. The nature of these polymers is quite different; hemicellulose is composed of C-5 molecules like xylose, arabinose, mannose and galactose while cellulose is only composed of glucose. On the other hand lignin is the most complex polymer of biomass composed of phenolic units linked in a three dimensional network (Cantero et al., 2015b). These polymers interact between them by covalent, hydrogen and Van deer Walls bonds. So, prior the production of chemicals and fuels in a selective way, it is needed to break the interactions between the three main polymers of biomass, which will allow the separation of them.

Sub and supercritical water (SCW) have gained attention as a promising solvent for performing the reactions of fractionation

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and hydrolysis of biomass. One of the main advantages of SCW is that the used solvent is only water. Water is environmentally friendly and represents an alternative to corrosive and toxic solvents being an attractive reaction media for a large number of applications. The variations in the properties of water near to its critical point (374 °C and 22.1 MPa) only by changing pressure and temperature make it a promising reaction medium to set different reaction conditions depending on the desired product. The main properties of water that can be modified by pressure and temperature and will define the identity of the medium are: dielectric constant, ionic product, density, miscibility and transport properties (Pavlovič et al., 2013; Toor et al., 2011). Water can adopt different roles in the reaction medium: as solvent, reactant or catalyst (Knez et al., 2015). The ionic reactions are favored at high densities and high ionic products while the radical reactions are favored at supercritical water conditions (Peterson et al., 2008). The challenge is to find the experimental conditions, which can be adaptable to all kind of biomass contributing to the decentralization and versatility of the process to industrial scale (Arai et al., 2009).

The most abundant organic source of carbon on the earth is woody biomass. The annual production of wood is approximately $5.64 \cdot 10^{10}$ Mg-C (Liu et al., 2012). The forest activity produces a massive amount of resources and residues daily. This carbon source can be used to produce chemicals or energy through biorefinery operations. In addition, a good management of the forest will improve the health status of forests. This activity is greatly available in Spain. An increasing trend since 1990 has been observed. According to Eurostat data, Spain has increased its forest area to annual rate of 2.19%, being the second country (Sweden leads the first place) with major total forest area in Europe. According to the data from Ministry of Agriculture, Food and Environment (2011), Spain has 8.6 (46.4% of forest area) and 6.4 (34.5% of forest area) millions of hectares of hardwoods and softwoods species and the forestland occupy is 54% of the national area. Since 1975, the wood production volume was increased from 456.7 to 927.8 million of m^3 (Forestales, 2013). The use of woody biomass is imperative to the world economy and Spain has the resources to reach a sustainable society.

Several studies consider woody biomass as potential feedstock for the production of chemicals and fuels. Numerous pretreatments have been studied to determine the optimum conditions to obtain high yield of carbohydrates from plant biomass (Wijaya et al., 2014). The pretreatment is necessary to alter the structure of biomass and to increase the hydrolysis of hemicelluloses and celluloses to the enzymes for monosaccharide production (Gong et al., 1999) and increase the porosity of the materials. The fractionation of vegetal biomass using liquid hot water has been investigated obtaining high recovery of the biomass components in relative low treatment times. The hydrolysis enables the depolymerization of hemicelluloses (Grenman et al., 2011), the hydrolysis of lignin (Hu et al., 2014) and the hydrolysis of celluloses. These hydrolysis reactions are usually followed by the formation of byproducts such as furfural, 5-HMF, acetic acid and lactic acid (Du et al., 2010; Li et al., 2014). The hydrothermal fractionation of biomass is usually carried out between 150 °C and 250 °C, at pressures lower than 10 MPa (Mok and Antal, 1992a; Sun et al., 2014b; Wei et al., 2011). The recovery yields of hemicellulose usually range between 60% wt. and 100% wt. while cellulose recovery is lower than 60% wt. However, the fractionation yields of plant biomass showed to be highly affected by the nature of the biomass: structural and chemical properties. So, the selection of the experimental conditions plays an important role in the obtaining of high yields of the hydrolyzed biopolymer. For instance, hardwood hemicelluloses can be removed/hydrolyzed at lower temperatures than the softwood hemicelluloses (Wei et al., 2011). The main compound in hemicellulose is xylose for hardwood and mannose for softwood. The content of lignin for hardwood is generally lower than softwood (Lim and Lee, 2013). The hardwood has higher content of acetyl groups than softwood, which increases the concentration of acetic acid during the hydrolysis of hemicelluloses being this specie a catalyst in the hydrolysis of carbohydrates (Garrote et al., 1999).

In this work the influence of the composition and nature of the biomass on the hydrothermal treatment of hardwood and softwood material was studied. The experimentation was focused in the obtaining of high hemicelluloses and cellulose yield with low byproduct generation and a solid rich in lignin. The main objective of this work was the study of the biomass composition influence over the biomass fractionation yields using subcritical water as reaction medium. To do so, various woody biomasses were fractionated in a semi-continuous reactor using subcritical water as reaction medium. Also, it was studied the relationship between the fractionation yields and the initial lignin content in biomass. This manuscript contributes to the design of industrial scale processes, which should be capable of processing various biomass materials in the same facility.

2. Methods

2.1. Materials

The raw materials used in this work to conduct the extraction/hydrolysis process were 9 species of urban trees from Valladolid region, in Spain. These species were: Linden (*Large-leaved linden*), Plane (*Platanus × acerifolia*), Eucalyptus (*Eucalyptus globulus*), Catalpa (*Catalpa bignonioides*), Holm oak (*Quercus ilex*), Maple (*Acer saccharum*), Almond (*Prunus dulcis*), Pine (*Pinus pinea*) and Cedar (*Juniperus oxycedrus*).

The standards used in High Performance Liquid Chromatography (HPLC) analysis were: cellobiose (>98%), glucose (>99%), fructose (>99%), glyceraldehyde (95%), pyruvaldehyde (40%), arabinose (>99%), 5-hydroxymethylfurfural (99%), lactic acid (85%), formic acid (98%), acrylic acid (99%), mannose (>99%), xylose (>99%) and galactose (>99%) purchased from Sigma and used without further modification.

For the determination of extractives, n-hexane (96%) supplied by Sigma was used. For the determination of carbohydrates, lignin and ash, sulfuric acid (96%) and calcium carbonate ($\geqslant$99.0%) were purchased from Panreac and used as reagents without further modification. Distilled water was used as reaction medium in the experiment and Milli-Q water was used as mobile phase in the HPLC analysis.

2.2. Methods

Two products were obtained after the hydrothermal treatment (explained in Section 2.3) of the raw material: solid and liquid. The solid sample was the remaining amount of biomass in the fixed bed reactor after the treatment. On the other hand, the liquid sample was produced due to the extraction/hydrolysis of the hemicellulose and cellulose fractions of the raw material during the treatment. The raw materials and samples (liquid and solid) taken during hydrothermal fractionation were analyzed to determine the carbohydrates and lignin content. The content of hemicelluloses, celluloses, lignin and ash were determined according to the National Renewable Energy Laboratory (NREL) – Determination of Structural Carbohydrates and Lignin in Biomass (Laboratory, 2011; Sluiter et al., 2010; Sun et al., 2014a). The content of extractives was determined according to the Determination of Extractives in Biomass (Sluiter et al., 2008, 2010). The solid