Research article

Optimization of hydrothermal conversion of bamboo (*Phyllostachys aureosulcata*) to levulinic acid via response surface methodology

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A B S T R A C T

In this study, the dilute acid hydrolysis of lignocellulosic bamboo (*Phyllostachys aureosulcata*) particles to levulinic acid in a hydrothermal synthesis reactor is reported. The aim of the study was to optimize the reaction conditions for maximum levulinic acid production in terms of reaction time (t), reaction temperature (T) and HCl concentration (c_{HCl}) via Response Surface Methodology (RSM). A maximum levulinic acid yield of 9.46 w% was predicted at the following reaction conditions: t of 3 h, T of 160 °C and c_{HCl} of 0.37 M. A maximal experimental yield of levulinic acid of 10.13 w% was observed, which in respect to the cellulose fraction of the bamboo particles corresponds to 34.60 w% or 48.05 mol%. Furfural, which is formed by the hemicellulose fraction of bamboo, has not been observed within the boundaries of the RSM model, since it is already degraded under the given reaction conditions. The conversion of levulinic acid and furfural occurred more or less simultaneously, however, furfural was more vulnerable to degradation reactions at the given process conditions. Therefore, if both fractions (cellulose + hemicellulose) are required to be valorized, further optimization is required. However, the global results of this study provide insight in the potential of lignocellulosic bamboo as an alternative platform to fossil sources.

1. Introduction

The depletion of non-renewable fossil resources and the environmental pollution associated with the exploitation of these resources have resulted in a growing awareness for a transition towards a bio-based economy. Sugars and starch extracted from agricultural crops are much desired feedstocks for the production of bio-based chemicals and materials. However, competition with the existing food and feed production questions the sustainability of using these feedstocks (Mohr and Raman, 2013; Naik et al., 2010). Lignocellulosic biomass, being the most abundant and renewable resource on earth, can be used as a raw feedstock for the production of a large variety of chemical building blocks and polymers (Kumar et al., 2008). Lignocellulosic biomass sources which include corn stover, bagasse, forestry residues, sawdust, municipal waste, etc. are currently considered as low-value waste (Yan et al., 2015). When applying lignocellulosic biomass on a large scale, a vast demand of feedstock is required and thus, energy crops dedicated to bio-fuel and bio-based chemicals need to be grown (Yan et al.,

2015; Li et al., 2014). This demand can be met by growing energy crops on polluted, infertile and non-arable land, where there is no competition with food and feed production. In this study, bamboo (Phyllostachys aureosulcata) was used as a lignocellulosic biomass feedstock. Bamboo is ranked within the C4 crops, which can be grown in high biomass yield, even in polluted and infertile land (Li et al., 2014; Sweygers et al., 2017a). Plant biomass resources (e.g. bamboo) consists primarily of three polymer constituents: lignin, hemicellulose and cellulose along with smaller amounts of lipids, proteins, extractives and inorganic ash. The composition of these constituents vary from one biomass species to another and even within a single plant species, the composition can vary dependent on the age, geographic location, *etc.* Lignin is a complex, high molecular weight structure containing heterogeneously linked monomeric phenolic compounds.

Levulinic acid has been reported as being a building block (Bozell et al., 2000; Morone et al., 2015; Pileidis and Titirici, 2016; Yan et al., 2015) that can be produced from lignocellulosic biomass. It can be used for the production of wide variety of fine chemicals such as diphenolic acid, valeric acid, methyltretrahydrofuran, etc (Mukherjee et al., 2015). The development and optimization of chemical processes involved in levulinic acid

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production can help reducing the cost to a sufficiently low level so that the production becomes more economically viable. This can help opening the market for a broader range of applications. The thermocatalytic conversion of carbohydrates from lignocellulosic biomass to platform chemicals in the presence of an acid catalyst has been reported extensively in literature (Li et al., 2014; Sweygers et al., 2017a; Yang et al., 2013; Chang et al., 2007; Wyman, 2013; Girisuta et al., 2013). A schematic overview of the different reactions taking place during acid hydrolysis of lignocellulosic carbohydrates is presented in Fig. 1.

When applying dilute acid hydrolysis to lignocellulosic biomass, cellulose and hemicellulose are converted into their respective platform chemicals but lignin remains unaffected, due to its high recalcitrant structure. Processes applying extreme conditions (high temperature), such as pyrolysis, are required to convert lignin to hydrocarbon fuels (Ge et al., 2017; Liu et al., 2015). The hemicellulose fraction primarily consists of C5 sugars such as xylose and arabinose that can be converted to furfural under acidic conditions. The cellulose fraction of lignocellulosic biomass consists solely of C6 carbohydrates that can be hydrolyzed to glucose monomers in the presence of an aqueous medium at high temperature ($>100\,°C$). Furthermore, this glucose monomers can be converted into fructose through isomerization in an acidic medium. Upon fructose formation, fructose is dehydrated to 5-hydroxymethylfurfural (HMF). When a monophasic system is applied, i.e., solely containing an aqueous medium, HMF is immediately rehydrated to levulinic acid and formic acid. This ring opening reaction, leading to the formation of levulinic acid, does not occur with furfural due to the absence of the hydroxylmethyl group. When applying a biphasic system, an organic solvent (e.g. MIBK, THF, etc), the formation of HMF from cellulose can be promoted by suppressing the rehydration reaction of HMF to levulinic acid (Sweygers et al., 2017b; Shi et al., 2013). However, in this study, a monophasic reaction system consisting of acidified (HCl) water is used, which allows the conversion of cellulose and hemicellulose to levulinic and furfural, respectively. From literature, it is known that furfural is formed under milder reaction conditions (lower T and/or lower c_{HCl}) than

levulinic acid (Sweygers et al., 2017c). Under the more harsh conditions of levulinic acid production, furfural is prone to degradation reactions, which makes a simultaneous production of furfural and levulinic acid difficult (Sweygers et al., 2017a; Yang et al., 2013; Dussan et al., 2013). For this reason and the fact that levulinic acid is ranked amongst the top 10 bio-based platforms chemicals for the future (Bozell and Petersen, 2010), the focus of this study is the optimization of levulinic acid production. Furthermore, during the course of the reaction, intermediary products can undergo unwanted polymerization reactions to produce humins (insoluble carbonaceous species), resulting in a lower yield of the desired reaction products. Up to date, the molecular structure as well as the stoichiometry involved in humin formation have not been identified (Van Zandvoort et al., 2013).

Generally, two types of acidic catalyst can be applied in this conversion process with both their (dis)advantages. A first group are the liquid homogenous catalysts (i.e. HCl, H_2SO_4, etc.) which are used extensively for the conversion of C6 carbohydrates to levulinic acid. This type of catalysts are relatively low-cost and highly effective (Morone et al., 2015; Pileidis and Titirici, 2016; Wang et al., 2014). However, the drawback of homogeneous catalysts is that they are difficult to recover. This leads to excessive amounts of wastewater, which is not convenient from a sustainable and environmental point of view (Wang et al., 2014). A second type of catalysts are the solid heterogeneous acid catalysts (i.e. zeolites, ion exchange resins, etc.). The greatest advantage of this type of catalysts is the ease of separation, and thereby overcoming the recovery difficulties (Morone et al., 2015; Mondal et al., 2015; Lin and Huber, 2009). However, heterogeneous catalysts often suffer from limited activity and selectivity, resulting in lower reaction yields, slower reaction rates and a higher catalyst/substrate ratio compared to homogeneous catalysts (Morone et al., 2015; Mondal et al., 2015). Heterogeneous catalysts are difficult to separate from the solid lignin residue formed in the present study and therefore, the liquid homogeneous HCl was chosen as the acidic catalyst for this study.

The aim of this study is the optimization of T, c_{HCl} and t for maximizing the yield of levulinic acid from bamboo particles. The
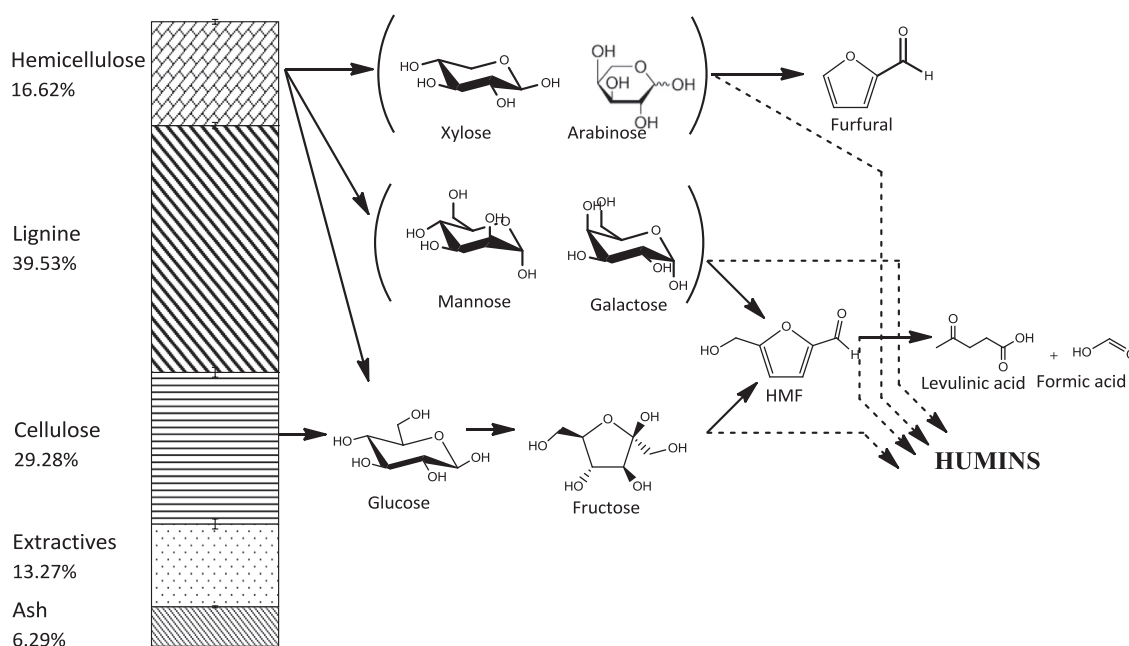

Fig. 1. Composition of lignocellulosic bamboo (*Phyllostachys aureosulcata*) particles and the conversion pathway to furfural and levulinic acid.