



Towards the development of a novel “bamboo-refinery” concept: Selective bamboo fractionation by means of a microwave-assisted, acid-catalysed, organosolv process



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ABSTRACT

This work addresses a novel microwave-assisted, acid-catalysed, organosolv (EtOH/H₂O) system for the selective fractionation of bamboo, examining the effects of the temperature (110–190 °C), solvent system (EtOH/H₂O) and catalyst amount (0–5 vol.% formic acid) on the process. The statistical analysis of the results revealed that the operating variables have a significant influence on bamboo fractionation, allowing the selective production of (i) a cellulose-rich solid fraction, (ii) a hemicellulose rich water-soluble fraction and (iii) a lignin rich solid fraction. The yields of each of these fractions varied between 51 and 94%, 2 and 23% and 2 and 32%, respectively. Increasing temperature exerted a positive effect on bamboo decomposition, increasing the overall bamboo conversion and influencing the effect that the solvent system (EtOH/H₂O) has on the process. At low temperature (110 °C) the solvent system does not have much influence, while a synergetic interaction between EtOH and H₂O took place at higher temperatures, which allowed better results to be obtained with EtOH/H₂O mixtures than with the pure solvents alone. The effect of the catalyst was relatively weak, being greatest when using a high temperature (190 °C) and high proportions of water (> 85 vol.%) in the solvent system. With respect to the properties of each fraction, the cellulose rich solid fraction was made up of un-reacted cellulose (44–83 wt. %), hemicellulose (0–21 wt.%) and lignin (12–34 wt.%); the water-soluble hemicellulose rich fraction consisted of a mixture of oligomers, sugars, carboxylic acids, ketones and furans; and the solid rich lignin fraction comprised high purity (> 95 wt.%) organosolv lignin. The optimisation of the process revealed that by using a temperature of 190 °C, a solvent system consisting of 45 vol.% EtOH and 55 vol.% H₂O with a concentration of formic acid of 5 vol.% it is possible to fractionate bamboo into a high purity (84 wt.%) cellulose solid fraction, very pure (> 95%) organosolv lignin and a rich water-soluble hemicellulose fraction consisting of a mixture of oligomers (27 wt.%), sugars (56 wt.%) and carboxylic acids (14 wt.%); thus converting this process into a very promising method for the selective fractionation of bamboo.

1. Introduction

Throughout the world new policies to mitigate global climate change have led researchers to seek new processes, alternative renewable materials and more sustainable strategies to replace the current petroleum-based energy industry with a greener and more environmentally-friendly energy market. As part of this, the bio-refinery concept is gaining increasing attention, as biomass is the only renewable source of carbon that can be converted into gas, liquid and solid products [1]. Unfortunately, the development of a lignocellulosic biorefinery has received some criticism, since energy and chemical production in this way could affect the food supply and total forestry

area. To overcome this issue, researchers are looking for fast growing and low “food-conflict” biomasses.

Among all the potential biomass feedstocks, bamboo is regarded as an excellent candidate. Bamboo is a big wooden plant large, which is widely distributed in subtropical temperature zones around the world (latitudes from 46°N to 47°S) [2]. As one of the fastest growing woody plants, bamboo can grow at a rate of 30–60 cm/day to 15–40 m with a culm diameter of 30 cm [2,3]. Due to its fast-growing property, bamboo generally could produce a higher yield of biomass than other common crops [4]. Typically, bamboo contains 37–47 wt.% cellulose, 15–30 wt.% of hemicellulose and 18–31 wt.% lignin, depending on the species [4]. In the past, bamboo was widely cultivated in Asian countries and

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used as a raw material for food, handicrafts, paper and construction. In recent years, bamboo has shown a huge potential to be used for the production of biofuel and other value-added chemicals via bioconversion [4–7].

Bioconversion is believed to be one of the most attractive methods for lignocellulosic biomass utilisation [8,9]; enzymes and bio-catalytically active cells (fermentation) being the two pathways commonly employed [10]. This biotechnology is mainly used for bioethanol, biodiesel, biobutanol, methane and fine chemicals production [11]. In the past few years, bioconversion technology has undergone dramatic growth, which has increased the attention of researchers and industry. Nevertheless, the intrinsic complexity of biomass hampers the development of this technology, and more research is needed. In particular, within the lignocellulosic biomass structure, cellulose and hemicellulose are intimately associated with lignin in the cell wall, and part of the cellulose is in crystalline status. This hinders enzymes and microbes from achieving biomass digestion and, therefore, the pre-treatment of biomass for its selective fractionation into its main constituents (cellulose, hemicellulose and lignin) is still a challenge.

In the midst of the different strategies for biomass fractionation, the use of water/organic solvent (organosolv) processes is gaining increasing attention. Several works have been conducted with rice straw [12], cotton stalk [13], wheat straw [14–16], hemp hurds [17,18], corncob [19,20], maple wood [21], reed [22], corn stover [23] and bamboo [24,25]. This route is well known for its higher efficiency in removing lignin under acidic condition than other processing methods. Organosolv systems can be classified into two categories: pure organic (simple) and aqueous-organic solvent (multiple) systems. In general, aqueous-organic systems perform better than single solvent systems [26,27]. The multiple systems consist of a nucleophile agent (H_2O , in the vast majority of the cases, to react with the activated linkages in biomass) and an organic solvent to help dissolve the liberated fragments [20]. This water/organic mixture has a significant influence on biomass depolymerization kinetics and thermodynamics, which affects not only the solubility of biomass but also the dissolution of biomass-derived products. This is of particular interest for the solubilisation of lignin which has both nonpolar and polar functional groups [28]. In addition, a homogeneous acid catalyst is used in some cases to increase the kinetics of biomass depolymerization in organosolv systems and, therefore, help increase the overall efficiency of the process.

Regarding the organic compounds used in H_2O /co-solvent systems, alcohols are the most commonly used as they have a low boiling point and can efficiently fractionate biomass into relatively high purity lignin and cellulose for further applications [29]. In particular, Hu et al. [30] regarded the H_2O /ethanol organosolv system catalysed by oxalic acid as one of the greenest co-solvent systems for biomass fractionation. They reported that by using this organosolv system and employing a temperature of 140 °C and a pressure of 2 MPa for 1 h, it was possible to recover 88 wt.% of the hemicellulose and 89 wt.% of the lignin present in corn stover, the cellulose remaining in the solid residue. Quignard et al. [16] worked on the extraction of lignin from wheat straw by using a H_2O -ethanol organosolv system at 160 °C for 2 h, examining the effect of different homogeneous Lewis acidic catalysts, such as $FeCl_2$, $CuCl_2$, $FeCl_3$, $Ga(OTf)_3$, and $ZrOCl_2$. It was found that lignin extraction was related to the acidity of the catalyst, with a maximum of 80% lignin conversion. Methanol has also been used in water-organic systems. In particular, Shimizu and Usami [31] used a catalysed (0.2 wt.% of HCl) methanol/ H_2O mixture at 170 °C for 45 min to fractionate pine wood, achieving very high hemicellulose (100%) and lignin (90%) recoveries. In addition, high boiling point alcohols, such as ethylene glycol and glycerol, have also been tested in the presence of H_2O for organosolv processes. This allows a low-pressure treatment to be conducted, but hinders solvent removal; thus decreasing the energy efficiency of the overall treatment [29].

Besides alcohols, other organic solvents have also been tested with positive results for biomass fractionation. For example, the H_2O / γ -

valerolactone (GVL) co-solvent system was positively used for the simultaneous separation of lignin from corn stover at 150 °C for 30 min, employing H_2SO_4 as a catalyst, achieving high yields for both lignin (75%) and hemicellulose (72%) [23]. H_2O /tetrahydrofuran (THF) assisted by Na_2CO_3 also showed 94.6% conversion of lignin from corncob residue, at 2 MPa of pressure at 140 °C for 1 h, preventing the dissolution of cellulose [20]. Wyman et al. [21] compared the difference between two H_2SO_4 catalysed systems: H_2O /tetrahydrofuran (THF) and pure H_2O for maple wood degradation. The experiments were conducted at temperatures ranging 170–200 °C with several reaction times (40–120 min). This comparison revealed that THF could significantly boost the efficiency of organosolv processes due to the good solubility of biomass decomposition products in THF, with more than 90% lignin recovery [21]. Furthermore, several organic acids were also tested in organosolv processes. Sun et al. [25] used an acetic acid-water system catalysed with HCl to extract lignin from bamboo. 95% of lignin and 48% of cellulose were recovered. The optimal delignification degree was achieved with 4 wt.% HCl in a 90 wt.% acetic acid-water solution using a batch reactor at 114 °C for 2 h.

All these works published to date provide valuable information on the use of different organosolv systems for biomass fractionation. However, the work on analysing bamboo fractionation is very scarce [24,25,32–34] and, consequently, more research is needed for the valorisation of this biomass. In addition, these studies showed that the reaction conditions (especially the temperature, solvent system and catalyst) exert a significant influence on biomass fractionation, however parametric studies to thoroughly analyse the specific effect of the variables have never been conducted. Therefore, the large number of factors significantly influencing the process increases its intrinsic complexity. Moreover, some interactions between some of these factors could occur so that the effects of some variables may depend on others, resulting in different consequences for the process. These interactions have never been considered in the works addressing organosolv processes for biomass fractionation. In addition, optimum conditions for bamboo fractionation and synergetic effects between solvents have never been analysed in depth. Given this background, this work addresses the microwave-assisted fractionation of bamboo by means of an ethanol/water organosolv process catalysed by formic acid. In particular, the effects of the ethanol/water concentration (0–100 vol.%), catalyst (formic acid) amount (0–5 vol.%) and temperature (110–190 °C) together with all the possible interactions between these variables on bamboo fractionation have been analysed in depth. Microwave heating represents a potentially faster, more efficient and selective process for the thermal treatment of biomass [35,36]. As water and ethanol are highly effective in microwave energy absorption, the combination of an organosolv system together with microwave assisted heating offers an interesting new technology for the valorisation not only of bamboo but also of many other types of biomass. The fact that the combined effects of the operating variables and their interactions on an organosolv system has never been reported before demonstrate, together with the results provided by the in-depth study and the optimisation and energetic assessment conducted, that this work represents a novel investigation in this field, which can help to develop a novel biorefinery concept based on bamboo fractionation, “the bamboo-refinery”.

2. Experimental

2.1. Material

Dried bamboo (*Phyllostachys heterocycle cv. pubescens*) was purchased from Anji County, Zhejiang Province, China. The raw bamboo was ground to 300 meshes. After grounding, the bamboo powder was washed by 50 °C distilled water and then dried overnight at 105 °C. This bamboo powder was characterised by means of proximate, ultimate and fibre (cellulose, hemicellulose and lignin) analyses, calorific value and ash content. Proximate analyses were performed according to standard

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