



Optimization of furfural production by acid hydrolysis of *Eucalyptus globulus* in two stages



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HIGHLIGHTS

- Production of furfural from eucalyptus in two stages was optimized.
- Conversions to furfural were quite substantial, greater than 10 g/L.
- The process provides furfural that are scarcely contaminated with cellulose derivatives.

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ABSTRACT

The aim of this study was to optimize the production of furfural by hydrolysis with dilute acid of *Eucalyptus globulus* wood in two stages, using a factorial experimental design and multiple regression models to maximize furfural yields. The two-stage process could provide a solid phase with less degraded cellulose and older applications that the solid phase of a conventional acid hydrolysis. The selectivity for furfural of the process was increased by effect of the glucan and lignin fractions being efficiently removed after the first acid hydrolysis stage.

The operational ranges are especially suitable for the extraction of xylose, which was virtually quantitative at 170 °C and virtually independent of the operation time. It is therefore advisable to use non-isothermal conditions or short times. This is quite important if one considers the low acid concentration used. The liquid phase obtained after autohydrolysis of the raw material under the optimum conditions contained 2.3% glucose, 9.8% xylose, 2.5% xylo-oligomers, 0.6% arabinose, 1.1% furfural and 0.1% 5-OH methyl furfural.

After the residual solid from the first hydrolysis stage is removed, the acid concentration is the most influential variable on the conversion of xylo-oligomers or xylose into furfural. Conversions to furfural were quite substantial (greater than 10 g/L). Hemicelluloses in the raw material were extracted by 32–57.7% and xylan by 40.5–84%. The highest conversions to furfural were obtained by using a medium operation time (15 min) and low temperature (170 °C) and pH = 2.

The process additionally provides hemicellulose derivatives that are scarcely contaminated with cellulose derivatives. The concentrations of gluco-oligomers were very low and those of glucose in the region of 3% of the raw material.

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1. Introduction

To date fossil sources have been the main resources to obtain energy or chemicals but these resources produce negative effects due to environmental pollutions [1]. To remedy this situation, among the potential industrial biorefineries, the lignocellulose biorefinery will most probably be pushed through with the

greatest success, because the raw material situation is optimal and conversion products have a good position in the traditional petrochemical as well as in the future bio-based product market [2–4]. In these biorefinery schemes, the hemicelluloses fraction, are not being isolated for industrial use yet, but they have a high potential and they could be used in many applications, not only for liquid biofuels production, notably bioethanol [5,6], and butanol [7,8]. An important derivative from hemicelluloses fraction is furfural [9]. Furfural, an important derived from hemicelluloses, is used for the production of a wide range of important

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non-petroleum derived chemicals such as furan, tetrahydrofuran, and furfuryl alcohol [10]. It is also used as an extractive, fungicide, nematocide [11], in oil refineries, as well as in the plastics, food, pharmaceutical and agricultural industries [12,13]. Resins with excellent thermosetting properties and extreme physical strength can also be produced by condensation of furfural with formaldehyde, phenol, acetone, or urea [11]. There is no synthetic route available for furfural production in chemical industry. Furfural is exclusively produced from hemicelluloses of lignocellulosic biomass [14]. About 250,000 tons of furfural, probably the only unsaturated, large volume, organic chemical, are prepared from carbohydrate sources annually [15].

A lot of literature is written about different pretreatment methods to enhance the extraction of carbohydrates in the process from lignocellulosic materials. Hot water or weak acid hydrolysis at an elevated temperature is the first step that is typically used to hydrolyze carbohydrates from lignocellulosic materials [16–18]. Steam explosion and dilute acid pretreatment are the two most commonly used methods because of their effectiveness and inexpensiveness [19]. In research, acid prehydrolysis has already found a broad area of applications, however, most of them are not commercially applied yet. For example, acid prehydrolysis is applied to remove hemicelluloses for (dissolving) pulp production [20]. Furfural production is carried out by hydrolysis of hemicelluloses pentosans to monomeric pentoses, and their subsequent acid-catalyzed dehydration into furfural [21]. This reaction would occur with or without mineral acids addition due to the liberation of acetic acid from the acetyl groups of the hemicelluloses. Industrial production of furfural requires a minimum content of 15–20% of pentosans and only a third of this amount can be converted into furfural [22]. Currently, furfural is obtained mainly from agricultural wastes as a source of hemicellulose or pentosan and by using acid catalyzed hydrolysis [22,23] or steam pressure [24]. The application of various catalysts in the furfural conversion has been well documented in the literature, including mineral acids, organic acids and solid acids [25]. In one-stage technology, depolymerization of xylans in xylose and dehydration into furfural occur simultaneously. The solid residue can be used as a source of fuel [26]. In two-stage technology, a dissolution and partial depolymerization of hemicelluloses occur, followed by dehydration in furfural. In this manner, the residual lignocelluloses is almost unaltered and can be used for conversion to ethanol, glucose [14] or pulp and paper [3,4,27,28] and the process has a higher furfural yield [26].

Actually, in the field of exploitation of the forest resources (pulp and paper industry), it accepts the idea of prior extraction of hemicelluloses, makes that the mechanical properties of handsheets prepared with previous autohydrolysis/hot water extraction or exploded chips were slightly lower [29,30]. However, recently much interest has developed on the concept of the forest product biorefinery, where wood is hydrolyzed prior to conventional pulping and papermaking processes and the hydrolyzate consisting of hemicellulose sugars are to be used as a feedstock for biofuels, bioplastics or other uses [31].

The aim of this study was to optimize the production of furfural by hydrolysis with dilute acid of *Eucalyptus globulus* wood in two stages, using a factorial experimental design and multiple regression models to maximize furfural yields. The two-stage process could provide a solid phase with less degraded cellulose and older applications that the solid phase of a conventional acid hydrolysis. Therefore, the process was optimized for a twofold purpose, namely: to maximize furfural yield while minimizing cellulose degradation. Also, a two-step process including separation of the solid phase after the first hydrolysis step would facilitate the obtainment of fractions containing less degradation products (e.g., polyphenols or furfural derivatives acting as microbial inhibitors and hindering potential uses in fermentation processes). The

selectivity for furfural of the process was increased by effect of the glucan and lignin fractions being efficiently removed after the first acid hydrolysis stage. The material balances and compositions of the solid and liquid phases were assessed, especially as regards the concentration of furfural and the composition of the liquid phase. Fig. 1 depicts the operational scheme used to optimize the two stages of the process.

2. Materials and methods

2.1. Characterization and storage of raw material

E. globulus samples from local plantations (Huelva, Spain) were milled to pass an 8 mm screen, since in preliminary studies no diffusional limitations were observed for this particle, air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored.

Aliquots of raw material were milled to particle size <0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88 and Tappi 204 cm-07), 1% NaOH soluble (Tappi 212 om-98) and to quantitative acid hydrolysis with 72% H₂SO₄ following standard methods (TAPPI T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. The compounds (glucose, xylose and arabinose, furfural and 5-hydroxymethylfurfural –HMF–) and acetic acid contained in the hydrolysates were determined by HPLC, so the HPLC features are below mentioned. Then, glucan, xylan, arabinan and acetyl groups in raw material can be calculated. Ashes were determined by calcination (TAPPI 211 om-07).

The chemical characterization of *E. globulus* used in this study and the characterization by various authors are shown in Table 1. The major fraction is cellulose (analyzed as glucan), to 42.8% or 41.0% (at TAPPI T 203-om-93), followed by the Klason lignin to 21.2% (after quantitative acid hydrolysis) and hemicelluloses fraction (calculated as the sum of xylan, araban, acetyl groups and others) to 28.5%. This composition is similar to that found by other authors [32,35]. In this sense, *E. globulus* could be used as suitable raw material according with criteria of a industrial production of furfural that requires a minimum content of 15–20% of pentosans [22].

2.2. Acid hydrolysis processing of wood samples. First stage

Raw material and water were mixed in the desired proportions and treated in a 2 dm³ stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture content of material was considered as water). The liquid/solid ratio had been recognized as an important factor in furfural yield at low acid concentration and its optimal value (8–10) has been found in previous studies [21]. In our study, liquid-solid rate was 8:1 in all experiments. The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle and cooled by cool water circulating through an internal loop. The reaction media stirred at 150 rpm and heated to reach the desired temperature. Time zero was considered to be the beginning of the isothermal stage. The operating conditions were 130 °C, 150 °C and 170 °C temperature; 30, 45 and 60 min operating time and 0.5%, 1.25% and 2% H₂SO₄ content and a liquid/solid ratio of 8 kg water by kg raw material, on a dry basis. When the pretreatment was finished, the reactor was immediately cooled down by cooling water and then removed from heating jacket.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, weighted for yield determination. Aliquots of the solid phase were analyzed for moisture and

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