



# A kinetic study on microwave-assisted conversion of cellulose and lignocellulosic waste into hydroxymethylfurfural/furfural



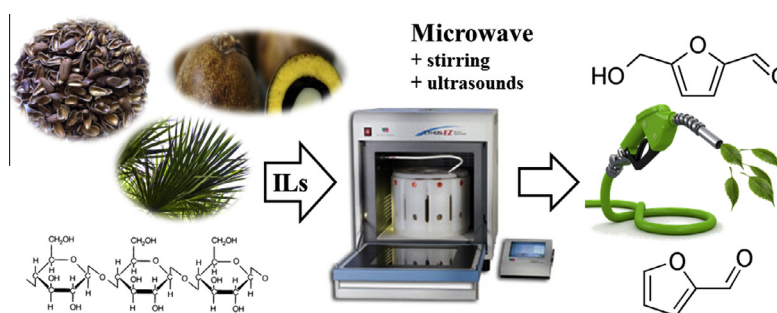
Viviane da Silva Lacerda, Juan Benito López-Sotelo, Adriana Correa-Guimarães, Salvador Hernández-Navarro, Mercedes Sánchez-Bascones, Luis M. Navas-Gracia, Pablo Martín-Ramos, Eduardo Pérez-Lebeña, Jesús Martín-Gil\*

Department of Agricultural and Forestry Engineering, Higher Technical School of Agricultural Engineering, University of Valladolid, Avenida de Madrid 44, 34004 Palencia, Spain

## HIGHLIGHTS

- Furan compounds have been produced from cellulose and four lignocellulosic wastes.
- MW-assisted hydrolysis is assayed for different ILs, catalysts and organic diluents.
- Water dosage, reaction times and temperatures have been optimized.
- Kinetic models confirm optimal time and temp for separate HMF and furfural production.
- Ultrasound pretreatment + stirring in the microwave oven drastically enhance yields.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Native cellulose, lignocellulosic materials from Brazil (carnauba palm leaves and macauba pulp and shell) and pine nut shell from Spain have been studied as substrates for the production of HMF and furfural in a conventional microwave oven. In order to promote the dissolution of native cellulose, several ionic liquids, catalysts, organic solvents and water doses have been assessed. The most suitable mixture (5 mL of choline chloride/oxalic acid, 2 mL of sulfolane, 2 mL of water, 0.02 g of TiO<sub>2</sub> and 0.1 g of substrate) has been chosen to conduct kinetic studies at different reaction times (5–60 min) and various temperatures (120–200 °C) and to evaluate the best conditions for HMF + furfural production according to Seaman's model. The best production yields of HMF + furfural have been attained for native cellulose, with a yield of 53.24% when an ultrasonic pretreatment was used prior to a microwave treatment with stirring.

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## 1. Introduction

At present, the regular supply of clean and renewable energy has become one of the greatest challenges that Humanity faces. Although improvements are being made as a result of the use of technologies that control the emission of conventional pollutants,

CO<sub>2</sub> emissions remain a difficult issue to resolve. Consequently, it is essential to find new fuels to replace existing ones, which can simultaneously meet the energy needs of the population and protect the environment.

Lignocellulosic biomass is the most abundant renewable source of organic carbon and it has a very low cost (Talebnia et al., 2010). Lignocellulosic materials can be considered as composed of cellulose fibrils which are held together by a matrix of lignin and hemicellulose. Cellulose is a polymer of D-glucose linked by

\* Corresponding author. Tel.: +34 979 108347.

E-mail address: [jesusmartingil@gmail.com](mailto:jesusmartingil@gmail.com) (J. Martín-Gil).

$\beta$ -1,4-*O*-glucoside bonds which is structured into long linear chains (*microfibrils*), linked by hydrogen bonds and intramolecular van der Waals forces, forming a crystalline structure resistant to hydrolysis and amorphous regions susceptible to enzymatic degradation. Due to these structures, which are difficult to attack, it is necessary to resort to different types of pre-treatments to make the different carbohydrates present in the lignocellulosic material more accessible. Thus, it is necessary to find cheaper and easily recoverable ionic liquids, catalysts and organic solvents, and to carry out the hydrolysis in the presence of an optimal amount of water so as to promote the formation of biofuels such as furfural and HMF.

HMF is considered a key building block in biorefinery, as it is the starting point for the production of 2,5-dimethylfuran, 2,5-diformylfuran, 2,5-furandicarbaldehyde and 2,5-furandicarboxylic acid (Rosatella et al., 2011). HMF and furfural can be obtained from biomass by dissolution (Swatloski et al., 2002), hydrolysis (Tao et al., 2011) or isomerization and dehydration of mono-, di- and polysaccharides, using acid catalysts (Guo et al., 2011) or base catalysts in mild conditions. Nonetheless, HMF production yields are very low and reaction conditions have not yet been fully optimized.

Ionic liquids have been the subject of intense research, and have been used as solvents for the treatment of lignocellulosic biomass and also in chemical synthesis, catalysis, biocatalysis, electrochemical devices and industrial applications. Ionic liquids are a novel class of solvents with low melting points (<100 °C), high liquid temperature, high polarity, high thermal and chemical stability, non-flammability properties, negligible vapor pressure and good solvating properties (Zavrel et al., 2009).

The aim of this study has been to optimize the conversion of native cellulose and lignocellulosic residues into HMF and furfural in the presence of an ionic liquid. Several eutectic mixtures have been assessed, namely choline chloride:urea, choline chloride:oxalic acid, choline chloride:betaine and tetraethylammonium chloride. In a first stage, different catalysts and organic solvents have been studied in order to find the most suitable eutectic mixture, working with a conventional microwave oven. Subsequently, the optimal dose of water for the production of furfural and HMF has been determined. The impact of different combinations of reaction times and temperatures on the combined HMF + furfural production has then been evaluated, and a kinetic study of the maximum yield has been repeated separately for HMF and furfural, fitting the data to Saeman's model (Saeman, 1945). Finally, the influence of ultrasonic pretreatment of the samples and of the incorporation of stirring to the microwave treatment to increase the furan compounds production has also been studied.

## 2. Methods

### 2.1. Materials

Commercial native cellulose (Merck KGaA, Darmstadt, Germany), carnauba palm (*Copernicia prunifera*) leaves from Ceará (Brazil), macauba palm (*Acrocomia aculeata*) pulp and endocarp from Minas Gerais (Brazil) and European stone pine (*Pinus pinea*) nut shell from Valladolid (Spain) have been selected as lignocellulosic raw materials to be used as substrates. Choline chloride (ChCl), betaine, urea, oxalic acid (ox), tetraethylammonium chloride (TEAC), potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium oxide (CaO), magnesium oxide (MnO), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>), boric acid (H<sub>3</sub>BO<sub>3</sub>), tungstic acid (H<sub>2</sub>WO<sub>4</sub>), triethylene glycol (TEG), glycerol carbonate (GC), magnesium carbonate (MgCO<sub>3</sub>) and sulfolane were purchased from PanReac AppliChem (Castellar del Vallès, Barcelona, Spain). Titanium dioxide (TiO<sub>2</sub>, anatase variety) was supplied by Sigma Aldrich Química

SL (Madrid, Spain). Halloysite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) was purchased from Intermark (Gliwice, Poland). Sulfonic acid incorporated to an ion-exchange resin was provided by Purolite Ltd. (Barcelona, Spain). 5-Hydroxymethyl-2-furaldehyde 98% (HMF), 2-furfural 98%, glucose, sucrose, xylose and lactose were purchased from Alfa Aesar GmbH & Co. KG (Karlsruhe, Germany). Hydrotalcite (Mg<sub>6</sub>Al<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4(H<sub>2</sub>O)) was prepared *in situ* at the laboratory.

The studied eutectic mixtures were: choline chloride:urea (1:1) (Morrison et al., 2009), choline chloride:oxalic acid (1.5:1) (Biswas et al., 2006), choline chloride:betaine (3:1) and TEAC (Cao et al., 2011). Liquefaction of the eutectic mixtures occurred at 80 °C under stirring in a hot-plate magnetic stirrer for 10 min, in agreement with Biswas et al. (2006).

The lignocellulosic materials were grounded using a Retsch ZM 100 ultra-centrifugal mill and sieved to a particle size <0.250 mm. The heating treatments were carried out in a Milestone Ethos-One microwave oven equipped with a magnetic stirrer system, and a JP Selecta ultrasonic cleaning bath with heating was used for the ultrasonic pretreatment. The UV spectroscopic analysis was conducted in a Hitachi U-2001 spectrophotometer and an Agilent 1200 series HPLC system was used for the chromatographic measurements.

### 2.2. Optimization of the hydrolysis process for HMF and furfural production

In order to optimize the hydrolysis process of native cellulose and aforementioned lignocellulosic materials, various ionic liquids, catalysts, organic solvents, water doses, reaction times and temperatures have been assessed, together with the effect of ultrasonic pretreatment and stirring in the microwave oven (vs. the use of a conventional microwave oven, MW).

The first stage involved the selection of the best ionic liquids, organic solvents and catalysts. Native cellulose was chosen as a substrate for these tests, working with a conventional MW system at 170 °C for 2 min. The amount of cellulose ranged between 0.18 and 0.20 g, the ionic liquid volume was in the 1.1–1.3 mL range, the amount of catalyst was increased from 0 to 22 mg, H<sub>2</sub>O content was studied in the 0–10 mL range and the organic solvent volume was varied from 0.8 to 0.9 mL.

The evaluation of the best water dose in order to optimize HMF and furfural production was conducted both for native cellulose and for the four lignocellulosic waste materials (carnauba leaves, macauba pulp, macauba shell and pine nut shell), using a conventional microwave oven and keeping the temperature constant at 140 °C for 30 min. So as to determine the most suitable water dose, different doses were assessed (1, 2, 3 and 5 mL) in combination with 5 mL of the eutectic mixture (ChCl/ox), 2 mL of sulfolane, 0.02 g of TiO<sub>2</sub> and 0.1 g of substrate.

For the selection of the optimal reaction time and temperature with a view to maximizing the HMF and furfural production, the most favorable reaction medium was kept fixed and different combination of times (5, 15, 30, 45 and 60 min) and temperatures (120, 140, 160, 180 and 200 °C) were studied.

Subsequently, a kinetic study of the hydrolysis reaction was separately conducted for HMF and furfural production as a function of time (5, 15, 30, 45 and 60 min) and temperature (120, 140, 160, 180 and 200 °C), fitting the data to the model proposed by Saeman (1945). This study was performed comparing cellulose and the four lignocellulosic materials, always using a conventional microwave oven and working with the most suitable reaction medium (5 mL of ChCl/ox eutectic mixture, 2 mL of sulfolane, 2 mL of water, 0.02 g of TiO<sub>2</sub> catalyst and 0.1 g of substrate).

Finally, the study was complemented with an evaluation of the impact of ultrasonic pretreatment and stirring on HMF and furfural production. A conventional microwave oven was used as a

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