Citation	Nick Sweygers, Delphine E.C. Depuydt, Aart Willem Van Vuure, Jan Degrevé, Geert Potters, Raf Dewil, Lise Appels (2020), Simultaneous production of 5-hydroxymethylfurfural and furfural from bamboo (<i>Phyllostachys Nigra</i> “Boryana”) in a biphasic reaction system Chemical Engineering Journal, 386, 123957.
Archived version	Author manuscript: the content is identical to the content of the published paper, but without the final typesetting by the publisher
Published version	https://doi.org/10.1016/j.cej.2019.123957
Journal homepage	https://www.journals.elsevier.com/chemical-engineering-journal
Author contact	your email raf.dewil@kuleuven.be your phone number + 32 (0)496 074990

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**Simultaneous production of 5-hydroxymethylfurfural and furfural from bamboo
(*Phyllostachys nigra* "Boryana") in a biphasic reaction system**

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Abstract

In this study, the microwave-assisted hydrolysis of bamboo (*Phyllostachys nigra* "Boryana") to 5-hydroxymethylfurfural (HMF) and furfural in a dilute acid (H_2O) / methyl isobutyl ketone (MIBK) biphasic system is investigated. Building on previous studies using model components cellulose and xylan, main emphasis in this study is given to the effect of particle size on the reaction rates that are involved in the conversion of bamboo particles by incorporating solid-liquid interactions into the reaction kinetics. Conversion yields of 37% HMF and 35% furfural from bamboo culm and 35% HMF and 34% furfural from bamboo leaves (based on cellulose and xylan content) were achieved, applying 0.13 M HCl and 177 °C under microwave (MW) heating. The results showed that the required reaction time to reach a maximum HMF and furfural yield increased significantly with increasing particle size. For particles having a diameter < 2.5 mm, the reaction rates follow first-order homogeneous kinetics, whereas for particle ≥ 2.5 mm, the reaction kinetics follow the shrinking core model. The chemical reaction (i.e., hydrolysis) at the surface of the unreacted particle core was shown to be the rate limiting step. The reaction rate constants for the hydrolysis of cellulose and xylose decreased with increasing particle size. Moreover, for bamboo culm particles with a particle size of 5 mm, the hydrolysis reaction rate constant decreased by a factor 10 compared to 1 – 1.5 mm particles.

Keywords

shrinking core model, bamboo, 5-hydroxymethylfurfural, furfural, kinetic analysis, particle size.

1. Introduction

In recent years, the production of bio-based chemicals (produced from renewable biomass resources) has gained worldwide attention due to the environmental pollution associated with the exploitation of fossil resources. In bio-based economy concepts, renewable biomass is considered as the primary feedstock. In contrast to fossil resources, biomass is over-functionalized with hydroxyl groups and hence has a high oxygen content. Understanding how to convert these oxygenated molecules into high-quality and high-value chemicals is of great importance as they can outperform their fossil-based equivalents. These bio-based chemicals and materials are produced from carbohydrate and starch-based feedstocks. However, the use of arable land for fuel and chemical production, which potentially compromises the food supply on a global scale, is strongly criticized [1,2]. Lignocellulose biomass holds the key for a sustainable and continuous supply of renewable feedstock for chemicals production since it is the most abundant biomass resource on Earth [3]. Low cost lignocellulosic biomass that is available as residue or waste material from different sectors, such as corn stover, bagasse, verge cuttings, food waste and sawdust, is targeted primarily [4–6]. However, when the bio-based economy gains traction on a global scale, the vast demand of feedstock will require the cultivation of dedicated crops for bio-fuel and bio-based chemicals production [3], which should be able to grow on polluted, infertile and non-arable land to limit (or even avoid) the competition with food and feed crops. In this study, bamboo (*Phyllostachys nigra* "Boryana") is used as lignocellulosic feedstock, characterized by a high biomass yield per acre and meeting the requirements of an energy crop [7]. More specifically, the *Phyllostachys* genera is a promising energy crop in the European climate since it has the highest biomass potential compared to the *Sasa* and *Fargesia* genera [8]. Field tests in Ireland with several *Phyllostachys* species by Potters et al. reported an annual biomass yield (dry weight) between 5 and 18 ton ha⁻¹ [9]. Bamboo showed a higher return on investment after 30 years and has a higher or comparable calorific value than other wood species originating from other common energy crops such as willow, poplar and *Miscanthus* [10]. *Phyllostachys nigra* "Boryana" originates from Japan and has been reported to grow on average to a height of 15 m and a diameter of 7.5 cm [11]. However, in Western Europe, an average height of 8 m, a diameter of 4 cm and a culm wall thickness of 7 mm is more common [10]. Culm diameter and thickness are important parameters as they influence the energy required for the comminution of bamboo, a necessary pretreatment step prior to any chemical conversion process.

A promising technique for the conversion of lignocellulosic carbohydrates to platform chemicals that has been reported extensively in the literature is the dilute acid hydrolysis [12–18]. However, most papers focus on the production of one chemical component from a specific lignocellulosic feedstock since each polysaccharide requires different process conditions for the conversion to a certain chemical compound [19–23]. One of the key challenges to enable a sustainable and industrially viable process for the production of bio-based chemicals from lignocellulosic materials is the simultaneous conversion of both C5 and C6 sugars into high-value chemicals [24]. Previous research by the authors - conducted with the model compounds xylan (for C5 sugars) and cellulose (for C6 sugars) - established the simultaneous conversion of these sugars to furfural and 5-hydroxymethylfurfural (HMF) in a biphasic reaction system consisting of an aqueous phase and methyl isobutyl ketone (MIBK) as the organic phase with HCl as the homogeneous catalyst [24]. The reaction mechanism of cellulose and xylan to HMF and furfural, respectively, is well described in the literature [24–27]. An overview of the reactions taking place in the presence of an acid catalyst (HCl) is depicted in Figure 1. In brief, cellulose and xylan are hydrolyzed in the acidified water phase to glucose and xylose monomers, respectively, followed by an isomerization of glucose to fructose. After dehydration of fructose and xylose to HMF and furfural, both products are immediately extracted into the organic MIBK phase. This approach avoids the rehydration of HMF to levulinic acid. For cellulose, two parallel reactions form unwanted polymerization products (i.e., humins) from glucose and fructose [28]. In the case of xylan, the xylose monomer is involved in

the formation of humins [22]. The key advantages of this biphasic system are: (i) suppression of unwanted side reactions due to the in-situ extraction of HMF and furfural into the MIBK phase, (ii) no formation of unwanted solid particles and (iii) an easy recovery of HMF and furfural from the reaction system. In most studies, the aforementioned reaction kinetics are evaluated through the construction of a homogeneous first-order irreversible kinetic (FO) model [28,29]. As bio-based furanics, HMF and furfural are key platform chemicals for the production of a wide spectrum of fine chemicals (such as FDCA and furfuryl alcohol). HMF has a large potential in the bio-plastics market since it is the precursor of 2,5-furandicarboxylic acid (FDCA) and thereby a potential substitute for the fossil-based terephthalic acid [30,31]. Furfural is the most commonly produced chemical from lignocellulosic biomass, offering a rich source of derivatives for the bio-fuel, paint and resin industry [32,33]. In Table 1, a literature overview of a variety of biomass feedstocks mixtures is presented for the production of HMF and furfural applying the biphasic system H₂O/MIBK.

Figure 1: Reaction mechanism for the conversion of cellulose and xylan to HMF and furfural, respectively.

Table 1: Literature overview of furanic production from lignocellulosic biomass feedstocks in the biphasic H₂O/MIBK system

Entry	Feedstock	Product	Catalyst	Biphasic system	Temperature (°C)	Reaction time	Yield (mol%)	Reference
1	Corn stover	HMF	ChH ₂ PW ₁₂ O ₄₀	0.5 mL H ₂ O - 5 mL MIBK	140	8 h	27.6	[34]
2	Pinewood	HMF	ChH ₂ PW ₁₂ O ₄₀	0.5 mL H ₂ O - 5 mL MIBK	140	8 h	11.6	[34]
3	Switchgrass	Furfural	H ₂ SO ₄	5 g ChCl (70 wt %) - 5 mL MIBK	170	1 h	84.0	[35]
4	Corn stover	Furfural	H ₂ SO ₄	1.5 mL H ₂ O - 3 mL MIBK	170	20 min	80.0	[36]
5	Maple wood	Furfural	H ₂ SO ₄	380 g H ₂ O - 400 g MIBK	170	50 min	85.3	[37]
6	Microalgae	HMF	H-ZSM-5	18 mL H ₂ O - 12 mL MIBK	200	2 h	43.9	[38]
7	Straw	HMF and Furfural	Sulphanilic acid	1 mL H ₂ O - 2 mL MIBK	150	1 h	41.0 and 50.0	[39]
8	Barley husk	HMF and Furfural	Sulphanilic acid	1 mL H ₂ O - 2 mL MIBK	150	1 h	41.0 and 41.0	[39]
9	Corn cobs	Furfural	HCl	0.5 g MIBK/ g H ₂ O	170	20 min	72.5	[40]
10	Bagasse	Furfural	H-USY	1 mL MIBK/mL H ₂ O	170	6 h	55.0	[41]
11	Jerusalem Artichoke	HMF	HCl	1.2 mL H ₂ O - 4 mL MIBK	180	30 min	57.0	[42]
12	Bamboo	HMF and Furfural	HCl	0.25 mL H ₂ O - 4.75 mL MIBK	177	60 min	43.0 and 46.0	[24]

Direct conversion of xylan and cellulose enclosed within the complex lignocellulosic structure is more challenging for the catalysts than the direct conversion of model compounds. In lignocellulosic biomass, cellulose and hemicellulose are strongly intermeshed and bound via covalent and non-covalent bonds, forming a complex and recalcitrant lignocellulosic matrix [43]. The recalcitrance is biomass-specific since it is affected by particle-related factors (pore and particle size, specific area, ...), chemical composition and cellulose-related factors (crystallinity, polymerization degree) [44]. Since the recalcitrant structure has an impact on the reaction kinetics, its effect should be assessed for any developed conversion process that is validated by model compounds. Because lignocellulosic polysaccharides (i.e. cellulose and xylan) are insoluble in water and MIBK, solid-liquid interactions take place between feedstock and reaction system. These interactions are limited for smaller particles, which is the case with thoroughly ground lignocellulosic biomass or commercial model compounds such as cellulose or xylan [45]. However, with increasing particle size of the feedstock particles, the solid-liquid interactions become more pronounced and should be incorporated into the reaction kinetics. The occurrence of these solid-liquid interactions and their effect on the reaction kinetics is only investigated in a limited number of studies [45–47]. For example, Wang et al. [45] found that with increasing particle size, the homogeneous first-order irreversible kinetics for lignocellulose hydrolysis under high temperature and dilute acid are no longer valid and, therefore, the reaction kinetics should be expressed via an alternative, two phase kinetic model. With this information, one could argue to solely work with small particles in a way that the influence on the reaction rate is limited, but it is already known that the energy consumption for creating small particles significantly increases as the particle size decreases [48–50]. The three most important models that have been developed to describe solid-liquid reactions are the shrinking core, the shrinking particle and the grain model [51,52]. The shrinking core (SC) model is applicable for initially non-porous particles and is characterized by the formation of a reacted shell around the unreacted core. The shrinking particle model is similar to the SC model except that no reacted shell is formed around the unreacted core. The grain model can be applied when agglomerated particles or so-called grains form a dense pellet. In this study, the SC model has been applied to explain the liquid-solid phase phenomena for the conversion of bamboo to HMF and furfural. During dilute acid hydrolysis, the lignin is not converted and remains present as a porous shell through which acidified water can migrate to hydrolyze cellulose and hemicellulose at the surface of the unreacted core [17,45].

The goal of this study is to (i) apply a biphasic reaction system previously developed for model compounds on bamboo as the lignocellulosic biomass, and (ii) evaluate the effect of the particle size on the reaction rates that are involved in the dilute acid hydrolysis of bamboo to furfural and HMF.

2. Materials and methods

2.1 Feedstock & Chemicals

All experiments were conducted using bamboo (*Phyllostachys nigra* (Lodd. ex Lindl.) Munro "Boryana") samples that were obtained from the Arboretum at Bokrijk, Belgium. Bamboo samples were taken from crops having an age of approximately 9 months: age determination was done by visual features indicating the age range of the bamboo species. Directly after sampling, the culm was separated from the leaves and oven dried at 105 °C for 48 h. The composition of bamboo leaves and culm was determined in a previous study and is added in Table 2 [53]. The oven-dried samples were subjected to a rough grinding step with a disk mill (Fritsch Pulverisette 13) resulting in particle sizes 1 mm - 150 mm. Subsequently, the obtained particles were ground in a centrifugal mill (Retsch ZM 100) and sieved to retain particles < 250 µm (< 60 mesh). Then, the particles were fractionated with a Retsch vibratory sieve shaker into particle size intervals. The particle size intervals used in this study are 200 - 250 µm, 600 - 700 µm, 1 - 1.5 mm, 2.5 - 3 mm for the culm and 200 - 250 µm, 600 - 700 µm, 1 - 1.5 mm for the

bamboo leaves. The 5 mm culm particles were manually crafted with a scalpel. The hydrolysis experiments were performed in an aqueous medium (demineralized water) acidified with HCl (Fisher Scientific, 5M) as the homogeneous acid catalyst and an organic phase consisting of MIBK (Acros Organics, 99.5%).

Table 2: Lignocellulosic composition of bamboo culm and bamboo leaves [53].

	BAMBOO CULM		BAMBOO LEAVES	
	w%	std	w%	std
Cellulose	40.87	1.00	27.28	0.44
Hemicellulose	14.81	0.52	16.62	0.40
Extractives	15.77	0.86	11.27	0.82
Lignin	26.73	0.79	38.53	0.79
Ash	1.81	0.10	6.30	0.14

2.2. Experimental set-up

The experiments were performed in a dedicated microwave reactor system (Monowave 300, Anton Paar, 2.45 GHz). The temperature was monitored by means of a ruby temperature sensor (optical fiber) placed inside the borosilicate glass reaction vessel and was set at 177 °C. The volume of the reaction vessel was 30 mL. The reaction vessel is closed with a Teflon-coated seal cap. A constant pressure of 11 bar was obtained when the reaction temperature was reached (temperature and pressure profiles are depicted in Figure A in the Supplementary Material). For each experiment, the reaction vessel was filled with 50 mg of the raw material (bamboo culm particles or bamboo leaf particles), 500 μ L acidified water (0.13 M HCl) and 9.5 mL MIBK. The stirring rate was set at 800 rpm for all experiments. The maximum power output of the microwave device was set at 800 W. It was shown in a previous paper that a simultaneous conversion of cellulose and xylan to HMF and furfural is achieved under these conditions [24]. As soon as the reaction time was complete, the reaction vessel was cooled rapidly by placing it in an ice bath to stop the reaction. After cooling, the reaction mixture was filtered before analysis. Since it is not possible to take samples during the (batch) microwave-assisted reaction, each reaction was terminated at the given reaction time and subsequently sampled. HMF, levulinic acid and furfural concentrations were measured in the organic phase of the filtrate. Glucose, fructose and xylose concentrations were measured in the aqueous phase of the filtrate. All experiments were conducted in triplicate.

2.3. Analytical techniques

Samples (extract of 1 μ L) of the organic phase were analyzed using a gas chromatograph (Agilent 7890A-series) equipped with a flame ionization detector (FID) to determine HMF, levulinic acid and furfural concentrations. The GC was equipped with a HP-FFAP column (Agilent, J&W HP-FFAP length 30 m, internal diameter 0.25 mm, film thickness 0.25 μ m). The aqueous phase was analyzed using an Agilent HPLC (Agilent 1100 series) equipped with a HILIC column (Xbridge, HILIC Amide, diameter 2.1 mm, length 150 mm, particle size 3.5 μ m) and an ELSD detector (70 °C, 2 L N₂ min⁻¹) (Alltech 3300 series). A gradient HPLC method was used for the analysis of glucose, fructose and xylose concentration at 70 °C. The mobile phase consisted of solvent A (10 mM ammonium formate, Acros Organics) and solvent B (acetonitrile, Acros Organics) with a flowrate of 0.200 ml min⁻¹. The mobile phase composition was initially 5% A and was linearly changed to 40% A in 15 min, then kept constant for 5 min, followed by a linear return to the initial conditions in 15 min and kept constant again for 5 min.

The injection volume was 2 μL . The mass residual particulate matter was determined by filtering the reaction medium through a glass fiber filter (Macherey Nagel, 0.6 μm retention capacity), washing it with 20 mL of demineralized water and drying it for 24 h at 105 $^{\circ}\text{C}$. After drying, a modified Van Soest method was applied to determine cellulose and xylan content, following the procedure that is described in Sweygers et al. [53]. In short, a first fraction, the so-called “soluble” fraction or extractives, is determined by an extraction step with a neutral detergent at 100 $^{\circ}\text{C}$ using microwave irradiation. The residual particulate matter is subsequently treated with sodium chlorite and acetic acid at 75 $^{\circ}\text{C}$. The loss in particulate matter is attributed to the lignin fraction. The remaining solid matter is holocellulose (hemicellulose + cellulose). In a final extraction step with a mildly acidified detergent at 100 $^{\circ}\text{C}$ using microwave irradiation, hemicellulose is extracted, hence only leaving cellulose as the sole particulate matter. The ash content is determined by heating the bamboo particles for 2 h at 550 $^{\circ}\text{C}$ in a muffle furnace. The residual inorganic matter is the ash content.

2.4. Shrinking core model development

2.4.1. Controlling regime

In the SC model, the solid reactant, in this case the biomass particle, is considered to be non-porous and is initially surrounded by an acid liquid film through which mass transfer occurs between the solid reactant and the bulk liquid as depicted in Figure 2. Throughout the course of the reaction, an inert intermediate layer forms around the unreacted core, which is lignin in the case of a biomass particle. The expression of the overall rate equation is determined by the conversion equation of the rate limiting step(s), governed by one or a combination of the following three regimes: (i) diffusion of reactant through the liquid film surrounding the solid particle, (ii) chemical reaction at the surface of the unreacted core and (iii) diffusion through the inert intermediary solid layer. The derived equations for these regimes are summarized in Table 3.

Table 3: Different possible controlling regimes in the SC model [54].

Controlling regime	Conversion equation	Rate constant
Chemical reaction	$k_{CR}t = 1 - (1 - X)^{1/3}$ (1)	$k_{CR} = \frac{k_L C_{W,L} M_H}{\rho_{WH} R \alpha}$
Diffusion through ash layer	$k_{D,L}t = 1 - 3(1 - X)^{2/3} + 2(1 - X)$ (2)	$k_{D,L} = \frac{6D_e C_{W,L} M_H}{\rho_{WH} R^2 \alpha}$
Diffusion through liquid film	$k_{D,S}t = X$ (3)	$k_{D,S} = \frac{3k_g C_{W,L} M_H}{\rho_{WH} R \alpha}$

To determine the controlling regime in the SC model, the equations listed in Table 3 are applied on the 4 datasets where the SC model contributes to the rate equation, i.e., the hydrolysis of cellulose and xylan [54]. The conversion of cellulose can be calculated by the following equation:

$$X = 1 - \frac{C}{C_0} \quad (4)$$

The rate constant of each regime can be iteratively determined by fitting the experimental conversion to the equation of the different controlling regimes (using the Excel solver function, Generalized Reduced Gradient nonlinear method).

The 95% confidence intervals (CI) are calculated based upon Student-t distribution, by following equation:

$$x = y \pm t_{\alpha/2} S_{y,x} \sqrt{\frac{1}{n} + \frac{(x - x_n)^2}{SS_{xx}}} \quad (5)$$

The 95% prediction intervals (PI) are also calculated based on a Student-t distribution:

$$x = y \pm t_{\alpha/2} S_{y,x} \sqrt{1 + \frac{1}{n} + \frac{(x - x_n)^2}{SS_{xx}}} \quad (6)$$

with $S_{y,x} = \sqrt{\frac{SS}{DF}}$, $SS = \sum_{i=1}^n (y_{e,i} - y_{p,i})^2$ and $SS_{xx} = \sum_{i=1}^n (x_i - x_n)^2$

2.4.2. Shrinking core model for bamboo particles

A schematic overview of the SC model applied on a lignocellulosic bamboo particle is depicted in Figure 2. At the surface of the bamboo particle, the hydrolysis of cellulose and xylan occurs. After the hydrolysis, the products (glucose and xylose) diffuse to the bulk solution and the reaction pathway presented in Figure 1 is followed, leading to the formation of HMF and furfural in the bulk solution. The model includes the following assumptions: (i) the particles are spherical, (ii) during the reaction, the unreacted core of the particles shrinks uniformly, thus maintaining its spherical shape, (iii) the bulk concentration is well distributed in the high speed microwave reactor and (iv) the chemical reaction (i.e., hydrolysis) on the unreacted particle surface is considered the rate limiting step in the SC model. This last assumption is moreover validated in the section in 3.2.1.

Figure 2: Shrinking core model for the hydrolysis of a lignocellulosic biomass particle.

During dilute acid hydrolysis, lignin remains unaffected and the glycosidic bonds of cellulose and hemicellulose are hydrolyzed by α units of water to generate α sugar monomers (glucose and xylose).

Due to the abundance of water, α is presumed to be large and, therefore, it is assumed that one water molecule is responsible for the cleavage of one glycosidic bond, yielding one sugar monomer. Therefore, the rate of polysaccharide hydrolysis (r_H) is equal to sugar monomer formation (r_P) and water molecule diffusion (r_W) and can be expressed as Equation 7.

$$-\frac{r_H}{1} = \frac{r_P}{\alpha} = -\frac{r_W}{\alpha} \quad (7)$$

The hydrolysis of lignocellulosic polysaccharides (cellulose, hemicellulose) can be written as:

$$\frac{dN_H}{dt} = \frac{\rho w_H}{M_H} 4\pi r_c^2 \frac{dr_c}{dt} \quad (8)$$

The consumption of water molecules can be written as:

$$\frac{dN_w}{dt} = -4\pi r_c^2 k'' C_{W,L}^* \quad (9)$$

From Equation 7, the sugar monomer formation can be written as:

$$\frac{dN_P}{dt} = -\frac{dN_W}{dt} = -\alpha \frac{dN_H}{dt} \quad (10)$$

$$\alpha \frac{dN_H}{dt} = \alpha \frac{\rho w_H}{M_H} 4\pi r_c^2 \frac{dr_c}{dt} = \frac{dN_w}{dt} = -4\pi r_c^2 k'' C_{W,L}^* \quad (11)$$

The concentration of water on the surface of the unreacted core is considered equal to the concentration of water molecules in the bulk solution ($C_{W,L}^* = C_{W,L}$). Equation 11 can be written as:

$$dt = -\frac{\alpha \rho w_H}{M_H k'' C_{W,L}} dr_c \quad (12)$$

$$\int_{t=0}^t dt = -\frac{\alpha \rho w_H}{M_H k'' C_{W,L}} \int_{r_c=R}^{r_c=r_c} dr \quad (13)$$

At $t = 0$, $r = R$, where R is the initial radius the bamboo particle.

$$t = -\frac{\alpha \rho w_H}{M_H k'' C_{W,L}} (r_c - R) = \frac{\alpha \rho w_H}{M_H k'' C_{W,L}} (R - r_c) = \frac{\alpha \rho w_H}{M_H k'' C_{W,L} R} \left(1 - \frac{r_c}{R}\right) \quad (14)$$

The conversion X of a single biomass particle can be written as:

$$1 - X = \frac{V_i - V_r}{V_i} = \left(\frac{r}{R}\right)^3 \quad (15)$$

Combining Equation 14 and 15, these can be expressed as follows:

$$\frac{M_H k'' C_{W,L} t}{\alpha \rho w_H R} = 1 - (1 - X)^{1/3} \quad (16)$$

Assuming:

$$k_{CR} = \frac{M_H k'' C_{W,L}}{\alpha \rho w_H R}$$

Equation 16 can be rewritten as,

$$k_{CR} t = 1 - (1 - X)^{1/3} \text{ or } X = 1 - (1 - k_{CR} t)^3 \quad (17)$$

Therefore, the hydrolysis of lignocellulosic polysaccharides can be written as:

$$-\frac{dN_H}{dt} = N_{H0} \frac{dX}{dt} = 3N_{H0}k_{CR}(1 - k_{CR}t)^2 \quad (18)$$

or in function of conversion as:

$$-\frac{dN_H}{dt} = N_{H0} \frac{dX}{dt} = 3N_{H0}k_{CR}(1 - X)^{2/3} \quad (19)$$

By incorporating Equation 18 for the hydrolysis of lignocellulosic particles in the complete reaction pathway presented in Figure 1, a set of rate equations are developed for the cellulose and hemicellulose conversion in lignocellulosic bamboo particles. All rate equations are listed in Table 4 and Table 5. The SC model is compared to the traditional FO kinetic model. Regarding the FO model, the following assumptions are made: (i) the reactions are considered irreversible, pseudo-homogeneous and of first order, (ii) during the reaction, the proton concentration is considered constant so it can be incorporated into the rate constants, (iii) glucose, fructose and xylose are involved in humin formation and humins are soluble in MIBK. The difference between the SC model and the first-order kinetic model is in the hydrolysis step where the rate equation is given by Equation 18. All other reactions in the reaction pathway are considered irreversible homogeneous first order.

Table 4: Overview of rate equations involved in the conversion of the cellulose part in lignocellulosic bamboo particles (with C, G, F, H and L representing cellulose, glucose, fructose, HMF and levulinic acid concentration, respectively, and $k_1, k_2, k_3, k_4, k_5, k_6$ (h^{-1}) are the first order reaction rate constants).

Homogeneous first-order model	Shrinking core model
$\frac{dC}{dt} = -k_1C$ (20)	$\frac{dC}{dt} = -3k_{CR}C_0(1 - k_{CR}t)^2$ (25)
$\frac{dG}{dt} = k_1C - (k_2 + k_3)G$ (21)	$\frac{dG}{dt} = 3k_{CR}C_0(1 - k_{CR}t)^2 - (k_2 + k_3)G$ (26)
$\frac{dF}{dt} = k_2G - (k_4 + k_5)F$ (22)	$\frac{dF}{dt} = k_2G - (k_4 + k_5)F$ (27)
$\frac{dH}{dt} = k_4F - k_6H$ (23)	$\frac{dH}{dt} = k_4F - k_6H$ (28)
$\frac{dL}{dt} = k_6F$ (24)	$\frac{dL}{dt} = k_6F$ (29)

Table 5: Overview of rate equations involved in the conversion of the hemicellulose (xylan) part in lignocellulosic bamboo particles (with A, O, U representing xylan, xylose, fructose and furfural respectively, and k_1, k_2, k_3 (h^{-1}) are the first order reaction rate constants).

Homogeneous first-order model	Shrinking core model
$\frac{dA}{dt} = -k_1A$ (30)	$\frac{dA}{dt} = -3k_{CR}A_0(1 - k_{CR}t)^2$ (33)
$\frac{dO}{dt} = k_1A - (k_2 + k_3)O$ (31)	$\frac{dO}{dt} = 3k_{CR}XA_0(1 - k_{CR}t)^2 - (k_2 + k_3)O$ (34)
$\frac{dU}{dt} = k_3O$ (32)	$\frac{dU}{dt} = k_3O$ (35)

2.4.3. Validation and assessment of the shrinking core model

The derived reaction rate equations depicted in Table 4 and Table 5 are solved by using the fourth-order Runge-Kutta method, using the ode23s function in Matlab (version R2015a).

There are two possibilities to determine whether the SC model or the FO kinetics are applicable for the hydrolysis of cellulose and xylan: (i) determining the root-mean-square-error (RMSE) for both models for each particle size by Equation 36, the RMSE describes the error between the value predicted by the model and the observed experimental value; a smaller RMSE, therefore, represents a better fit of the model and (ii) rate constants are constant for a given temperature, catalyst concentration and reactant concentration. If rate constants differ between particle sizes under given constant conditions, this effect is attributed to the difference in particle size.

$$RMSE = \sqrt{\frac{\sum_{j=i}^n (P_j - E_i)^2}{n}} \quad (36)$$

3. Results and discussion

3.1. Controlling regime in the shrinking core model

The controlling regime is determined after fitting the experimental data on conversion with the equations of the different possible regimes, i.e., Equations 1, 2 and 3. Figure 3 shows the three possible controlling regimes in terms of conversion versus reaction time with the best fit rate constants for the different regimes. From this figure it is clear that the chemical reaction controlling regime is the rate limiting step since it lies within the 95% confidence interval (CI) and 95% prediction interval (PI) of data points. For each dataset where the SC model has an influence on the rate equation a likewise approach is undertaken to determine the controlling regime. In total, 4 datasets are subjected to investigation. These graphs can be found in the supplementary material (Figure B3.1, B3.2 and B3.3). It is concluded that the chemical reaction at the surface of the unreacted particle core is the rate limiting step (or controlling regime) for all evaluated datasets.

Figure 3: Controlling regime in the shrinking core model (dataset: hydrolysis of cellulose of bamboo culm with a particle size of 5 mm).

3.2. Validation and assessment of the shrinking core model

Figure 4 depicts the conversion of bamboo culm particles in the biphasic $\text{H}_2\text{O}/\text{MIBK}$ system to HMF (4A and 4C) and furfural (4B and 4D). Figure 5 shows the conversion of bamboo leaf particles to HMF (5A) and furfural (5B). The maximum HMF yield is found to be 37 mol% ($0.045 \text{ mol}_{\text{HMF}}/0.123 \text{ mol}_{\text{CEL}}$) for bamboo culm particles and 35 mol% ($0.026 \text{ mol}_{\text{HMF}}/0.074 \text{ mol}_{\text{CEL}}$) for leaf particles. For furfural, a maximum yield of 35 mol% ($0.017 \text{ mol}_{\text{FUR}}/0.048 \text{ mol}_{\text{XYL}}$) is achieved for culm particles and 34 mol% ($0.017 \text{ mol}_{\text{FUR}}/0.05 \text{ mol}_{\text{XYL}}$) for leaf particles. The resulting yields are in good agreement with the literature, where model compounds xylan and cellulose are used [24]. It is shown that the developed biphasic $\text{H}_2\text{O}/\text{MIBK}$ system is applicable to real lignocellulosic biomass since (i) cellulose and xylan are completely converted to HMF and furfural respectively, (ii) there are no unwanted solid polymerization products formed and (iii) the formation of levulinic acid is suppressed due to the immediate extraction of HMF and furfural in the organic phase.

Figure 4: Production of (A,C) HMF and (B,D) furfural from bamboo culm particles. For particle sizes $\geq 2.5 \text{ mm}$ the shrinking core model is applied, for particle sizes $< 2.5 \text{ mm}$ first-order homogeneous kinetics are applied.

Figure 5: Production of (A) HMF and (B) furfural from bamboo leaves particles. For particle sized ≥ 2.5 mm the shrinking core model is applied, for particle sizes < 2.5 mm first-order homogeneous kinetics are applied.

To determine which model provides the best fit, the RMSE is calculated for both models for the hydrolysis step, considering each particle size interval by Equation 35. The RMSE values for the hydrolysis step in the SC and FO model are shown in Table 6. The quality of the RMSE values is assessed by coupling the values to the confidence interval, since there is no absolute criterion for a “good” RMSE value as it depends on the units in which a variable is measured. It is expected that 95% of the y-values (i.e., molar yield) to be within plus or minus 2 RMSE units of its predicted value. For the small particle sizes (i.e., 200 - 250 μm , 600 - 700 μm and 1 - 1.5 mm), the lowest RMSE values are obtained when the FO model is applied. The order of magnitude for these RMSE values is approximately 0.003, which corresponds to a CI of ± 0.006 mol. The SC model yields RMSE values ranging from 0.00925 to 0.0141 for small particle sizes, corresponding to a CI of ± 0.0185 to 0.0282 mol. This indicates that a better fit is obtained when applying the FO model for small particles. This is the case for both cellulose and xylan hydrolysis in bamboo culm and bamboo leaf particles. However, this trend shifts when larger particle sizes are subjected to the acid hydrolysis. For 2.5 mm bamboo culm particles the RMSE value of the SC model is 0.00267 and 0.00383 for the first-order kinetic model. This corresponding to a CI of ± 0.00534 mol and ± 0.00766 mol, respectively, showing that the SC model results in a better fit for particles larger than 2.5 mm. With further increasing particle size, the RMSE decreases for the SC model and increases for the FO kinetic model. For this reason, the rate equation set for the SC model is applied for particle sizes ≥ 2.5 mm, while for particle sizes < 2.5 mm the rate equation set for the FO kinetic model are applied. The kinetic parameters in the rate equations were calculated by fitting the experimental data of each component for both the SC model and the traditional FO kinetic model and are presented in Table 7, where the dotted cells represent the reaction rate constants involved in humin formation.

Table 6: RMSE values for the conversion of bamboo culm and bamboo leaves for SC (≥ 2.5 mm) and FO model (< 2.5 mm). k_1 is used for particle sizes < 2.5 mm and k_{CR} is used for particle sizes ≥ 2.5 mm.

Root-Mean-Square-Error			
Shrinking core model			Homogeneous first-order kinetic model
BAMBOO CULM	Cellulose hydrolysis		
	<i>Particle size</i>		
	200-250 μm	0.01414	0.00354
	600-700 μm	0.01371	0.00316
	1-1.5 mm	0.01348	0.00411
	2.5-3 mm	0.00389	0.00493
	5 mm	0.00295	0.00585
	Xylan hydrolysis		
	<i>Particle size</i>		
	200-250 μm	0.00372	0.00183
	600-700 μm	0.00363	0.00145
	1-1.5 mm	0.00372	0.00235
	2.5-3 mm	0.00267	0.00383
	5 mm	0.00260	0.00425
BAMBOO LEAVES	Cellulose hydrolysis		
	<i>Particle size</i>		
	200-250 μm	0.00925	0.00315
	600-700 μm	0.00949	0.00432
	1-1.5 mm	0.00974	0.00275
	Xylan hydrolysis		
	<i>Particle size</i>		
	200-250 μm	0.00356	0.00170
	600-700 μm	0.00383	0.00119
	1-1.5 mm	0.00393	0.00226

Table 7: Reaction rate constants (h^{-1}) calculated by the 4th order Runge-Kutta method. The dotted cells represent the rate constants involved in humin formation.

Feedstock	Lignocellulosic compound	Reaction rate constants (h^{-1})					
		k_1 or k_{CR}	k_2	k_3	k_4	k_5	k_6
BAMBOO CULM	Cellulose						
	<i>Particle size</i>						
	200-250 μm	3.9834	9.7484	2.5952	92.2268	80.7872	0.1175
	600-700 μm	3.8905	10.2448	1.0664	68.1986	80.6553	0.0990
	1-1.5 mm	3.7166	9.0734	2.0527	88.8937	1.6051	0.1299
	2.5-3 mm	0.5304	3.4506	2.7869	68.4553	25.5021	0.0952
	5 mm	0.3517	3.7896	0.0000	32.0789	41.3003	0.1033
	Xylan						
	<i>Particle size</i>						
	200-250 μm	3.5866	2.9561	4.8867			
	600-700 μm	3.2390	3.6178	4.9267			
	1-1.5 mm	2.9064	3.1222	1.1863			
	2.5-3 mm	0.5462	2.0706	3.8789			
	5 mm	0.3647	1.2959	2.0527			
BAMBOO LEAVES	Cellulose						
	<i>Particle size</i>						
	200-250 μm	4.1918	14.7473	3.9489	50.7888	50.7674	0.1429
	600-700 μm	4.0851	11.8478	7.8897	107.0367	58.9592	0.1467
	1-1.5 mm	4.4377	12.8041	2.1874	48.2475	55.1663	0.1354
	Xylan						
	<i>Particle size</i>						
	200-250 μm	3.0740	3.6442	3.4167			
	600-700 μm	3.3517	3.0879	4.4478			
	1-1.5 mm	2.9637	3.4585	5.2581			

For the conversion of cellulose to HMF, two parallel reactions are involved in humin formation from glucose and fructose. For the conversion of xylan to furfural, xylose can be converted to humins in an acidic environment. Some researchers state that humins can also be formed from HMF and furfural [29,55–57]. However, for this specific MIBK/water system, recent studies show that humin formation occurs through condensation polymerization of monosaccharides (i.e., glucose, fructose and xylose) in the aqueous phase [28]. Since glucose, fructose and xylose are only soluble in the acidified aqueous phase, and HMF and furfural are in-situ extracted in the MIBK phase, it is unlikely that the furanics are involved in humin formation [28]. Previous research already demonstrated that no particulate matter was formed in the MIBK/water system during the hydrolysis of the model compounds cellulose and xylan [24]. However, a color shift of the reaction medium indicated that humins were formed and solubilized in MIBK. This color shift was also found by Cheng et al. [58] in a variety of organic solvents. Since there are no quantitative analytical methods available in the literature to quantify dissolved humins, the concentration of humins was not measured. However, the Runge-Kutta method allows to calculate rate constants of non-measured components. In case of a single reaction with a non-measured component, a correct reaction rate can be obtained based on the mass balance of the reaction. However, in this case the calculated value can differ from the true value of the reaction rate constant, since it is impossible to

know the source component (glucose, fructose or xylose) of humin formation. For these reasons, there will be no further elaboration on the rate constants involved in humin formation.

As illustrated in Figures 4 and 5, the experimental results are well predicted by the fitted curves derived from the rate equations. For particle sizes < 2.5 mm, the rate equations are based on FO kinetics, as for particle sizes ≥ 2.5 mm the rate equation is described by the SC model for the hydrolysis step in the reaction pathway (Equations 25 and 33). For bamboo culm and leaf particles it is clear that for smaller particles (200 - 250 μm , 600 - 700 μm and 1 - 1.5 mm) the rate constant (described by FO reaction kinetics) for the hydrolysis of cellulose and xylan are in the same order of magnitude, i.e., approx. 4 h^{-1} for the hydrolysis of cellulose to glucose and approx. 3 h^{-1} for the hydrolysis of xylan to xylose. This is also clear from Figure 4A, 4B and Figure 5A and 5B, where the fitted curves are almost an exact overlay. For bamboo culm, larger particle sizes (2.5 mm - 3 mm and 5 mm) can be used and the SC model is applied to describe the liquid-solid reaction. It is clear that the particle size has an effect on the hydrolysis step of both cellulose and xylan. The cellulose hydrolysis rate constants decrease almost tenfold with increasing particle size: from 3.98 h^{-1} for 200-250 μm to 0.3517 h^{-1} for 5 mm. For xylan hydrolysis, a similar trend is observed: the rate constants drop from 3.58 h^{-1} for 200-250 μm to 0.3647 h^{-1} for 5 mm sized particles. Since the rate constant is fixed at a given temperature, catalyst and reactant concentration, the particle size is concluded to be the sole contributor to these differences in rate constants. The effect of the particle size is also observed in Figure 4C for the hydrolysis of cellulose and in Figure 4D for the hydrolysis of xylan. For 200 - 250 μm , the hydrolysis of cellulose is complete after 1 h, whilst for 5 mm, the hydrolysis takes up to 3 h. Xylan hydrolysis follows the same trend. The rate constants involved in the isomerization of glucose to fructose also decrease with increasing particle size (from 9.74 h^{-1} for 200 - 250 μm to 3.78 h^{-1} for 5 mm). A similar trend is observed for the dehydration of xylose to furfural. The dehydration of fructose to HMF is characterized by high rate constants. For extremely fast reactions, such as the dehydration of fructose to HMF, caution is advised. Fructose is consumed so rapidly that its concentration cannot be monitored over such a short period of time, resulting in a finished reaction before an initial reaction rate can be observed. For this reason, rate constants k_4 are not further discussed, since no fructose was observed during the reaction, which indicates that the dehydration reaction is complete before the reaction rate can be quantified. The limited production of levulinic acid is represented by the small rate constants for the rehydration of HMF to levulinic acid. For both bamboo culm and leaf particles, these are in the same order of magnitude (i.e., $0.10\text{-}0.15 \text{ h}^{-1}$). For small particle sizes (< 2.5 mm), the maximum product yields are reached between 40 min and 1 h. For bamboo culm particles, a maximum 37% HMF and 35% furfural yield was obtained. For bamboo leaf particles, a maximum of 35% HMF and 34% furfural yield was observed. These small particles have a higher surface area, characterized by high reaction rates. The surface area of the particle is inversely proportional to the particle size and therefore directly proportional to the time for the reaction to be completed. Therefore, with increasing particle size, especially for 5 mm particles, a longer reaction time for maximum furanics production is observed. Although the maximum HMF and furfural yield is in the same order of magnitude as the small particles, it is only reached after 1.67 h for 2.5 mm particles and 2.67 h for 5 mm particles.

The dilute acid hydrolysis reaction is carried out under microwave radiation. Previous research by the authors already showed that microwave radiation has a positive effect on the depolymerization of cellulose: (i) the hydrolysis of cellulose accelerated by 2.3 fold and (ii) the isomerization of glucose increased by 2.5 fold [28]. Since microwave-irradiation is directly applied to the molecules of the reaction mixture, it has the advantage that heat is generated within the material rather than from an external source, resulting in rapid heating and high heating efficiency [59]. Therefore, it is likely that with conventional means of heating, the above stated particle size related phenomena are even more pronounced, because unlike microwave heating, the driving force of conventional heating is conductive

and convective heat transfer [28,60]. With increasing particle size, the conductive and convective heat transfer inside the bamboo particle will become more significant and will therefore have an additional effect on the reaction rate constants.

4. Conclusion

The biphasic reaction system water/MIBK was successfully applied for the production of HMF and furfural from bamboo (*Phyllostachys nigra* "Boryana") under microwave heating with HCl as the acid catalyst. Bamboo culm produced a maximum 37% HMF and 35% furfural yield and bamboo leaves yielded a maximum 35% HMF and 34% furfural yield. The biphasic system allows to (i) completely convert cellulose and xylan to HMF and furfural, respectively, (ii) inhibit the formation of unwanted solid particles by unwanted polymerization reactions and (iii) suppress the formation of levulinic acid by immediately extracting HMF and furfural into the organic MIBK phase. The significant effect of the biomass particle size on the dilute acid hydrolysis was determined by means of a kinetic analysis. This effect was further explained and quantified by incorporating the SC model for the hydrolysis reaction in the overall reaction pathway. It is concluded that the chemical reaction at the surface of the unreacted biomass core is the rate limiting step in the SC model. From the kinetic analysis, it was clear that for particles ≥ 2.5 mm, the SC model becomes more accurate and should be used to describe the solid-liquid hydrolysis reaction. The cellulose hydrolysis rate constants are decreasing with increasing particle size from 3.98 h^{-1} for 200-250 μm to 0.3517 h^{-1} for 5 mm. For the hydrolysis of xylan, a similar effect has been observed where the rate constants drop from 3.58 h^{-1} for 200-250 μm to 0.3647 h^{-1} for 5 mm sized particles. For particles < 2.5 mm, the hydrolysis rate constants are in the same order of magnitude.

Nomenclatures

HMF	5-hydroxymethylfurfural
MIBK	methyl isobutyl ketone
FDCA	2,5-furandicarboxylic acid
SC	shrinking core
FO	homogeneous first-order
r_H	rate polysaccharide hydrolysis, mmol h^{-1}
r_P	rate of sugar monomer formation, (glucose, xylose), mmol h^{-1}
r_W	rate of water molecule consumption, mmol h^{-1}
t	reaction time (h)
N_H	amount polysaccharides (cellulose, xylan), mmol
N_{H0}	initial amount polysaccharides (cellulose, xylan), mmol
r	particle radius, m
r_c	radius of unreacted core, m
ρ	density of the particle, kg m^{-3}
w_H	cellulose and xylan fraction, kg kg^{-1}
M_H	average molecular weight of cellulose and xylan, kg mol^{-1}

N_w	molar amount water molecules, mmol
k''	reaction rate constant, $m\ s^{-1}$
$C_{W,L}$	concentration of water in the bulk solution, $mmol\ m^{-3}$
$C_{W,L}^*$	concentration of water on particle surface, $mmol\ m^{-3}$
N_P	molar amount sugar monomers (glucose, xylose), mmol
R	initial radius of the bamboo particle, m
X	conversion
V_i	initial volume of biomass particle, m^3
V_r	reacted volume of biomass particle, m^3
C	Cellulose amount, mmol
C_0	initial cellulose amount, mmol
G	glucose amount, mmol
F	fructose amount, mmol
H	HMF amount, mmol
L	levulinic acid amount, mmol
A	xylan amount, mmol
A_0	initial xylan amount, mmol
O	xylose amount, mmol
U	furfural amount, mmol
k_{1-6}	homogeneous first-order rate constant, h^{-1}
k_{CR}	rate constant for chemical reaction controlled regime, h^{-1}
$k_{D,L}$	rate constant for diffusion through solid lignin regime, h^{-1}
$k_{D,S}$	rate constant for diffusion through liquid film regime, h^{-1}
D_e	effective diffusion coefficient of liquid through inert lignin layer, $m^2\ s^{-1}$
k_g	mass transfer coefficient of liquid through inert lignin layer, $m\ s^{-1}$
k_l	chemical reaction rate constant, $m\ s^{-1}$
CI	confidence interval
PI	prediction interval
x	reaction time, h
y	fitted conversion

$t_{\alpha/2}$	t distribution multiplier for a two sided interval with (n-p) degrees of freedom
α	0.05 for a 95% distribution
$\bar{x}_n$	mean value of all reaction times, h
SS	sum of squares
$S_{y,x}$	root mean square
DF	degrees of freedom
SS_{xx}	error sum of squares
RMSE	root mean square error
P_j	predicted value of an experiment
E_i	experimental value of an experiment
n	number of experiments

Acknowledgments

This research was financed in part by projects IMP/14/034 (KU Leuven Impulse Fund) and HB/14/005 (KU Leuven Industrial Research Fund). The authors would like to thank Dr. ing. Jonas De Coster for proofreading the manuscript.

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