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Manufacture of Furfural from Xylan-containing Biomass by Acidic Processing of Hemicellulose-Derived Saccharides in Biphasic Media Using Microwave Heating

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ABSTRACT

Furfural was produced in biphasic media using a microwave-heated reactor. Diverse substrates were considered: xylose (considered as a reference compound) or hemicellulosic saccharides from *Eucalyptus globulus* wood or corncobs. Operation was carried out at 170° C for the desired reaction time in the presence of an acidic catalyst (sulfuric acid or HCl). The best furfural yields (67.8% and 72.5% from *Eucalyptus globulus* wood and corncobs, respectively) were obtained operating for 10 min or 20 min with 1% or 0.5% HCl, respectively. These results were slightly lower than the ones obtained using xylose (a model substrate) under comparable reaction conditions, a fact ascribed to differences in the complexity of substrates and to the presence of contaminants.

Keywords: Furfural; Hemicellulose; MIBK; Microwave heating; Wood; Xylan

1 INTRODUCTION

The massive utilization of fossil resources to satisfy the demand for energy, chemicals and materials cannot continue indefinitely, and important issues related to the availability of raw materials, environmental issues and sustainability have to be solved in a near future. The development of a new bio-economy, based on the utilization of renewable raw materials by efficient technologies based on the principles of the green chemistry, provides a suitable framework for this purpose, in a way compatible with the sustainable development principles.

Biomass is expected to play a key role in the coming bio-economy, as it is the most important source of organic carbon in earth. In quantitative terms, most biomass corresponds to lignocellulosic materials, from which a scope of commercial products (including fuels, chemicals and materials) can be produced. Following the biorefinery concept, lignocellulosic feedstocks can be processed to yield separate “fractions”, which can be further employed to obtain the target products. This operational principle enables a high degree of utilization of the feedstocks, limiting the generation of waste.

A number of fractionation methods (usually based on consecutive stages of reaction and/or separation) have been proposed in literature. For example, the raw materials can be first subjected to a mild hydrolysis stage for hemicellulose solubilization, leaving a solid enriched in cellulose and lignin that can be used for further fractionation and processing.⁽¹⁾ When the mild hydrolysis stage is performed with hot, compressed water (autohydrolysis or hydrothermal processing), most hemicelluloses are converted into soluble saccharides (including monosaccharides and higher saccharides of oligomeric or polymeric nature). If the lignocellulosic material used as a substrate contains significant amounts of xylan (a hemicellulosic polymer made up of anhydroxylose units), the liquid phase from autohydrolysis is rich in xylose, xylooligosaccharides and soluble polymers containing anhydroxylose units, which can be further converted into furfural.⁽²⁻⁶⁾

Furfural, a platform chemical with a well established market, is a potential target product for biorefineries. Besides its multiple current applications,^(5,7-10) furfural can be transformed into new families of bio-based compounds, which are expected to play a key role in the development of the coming bio-economy.^(3,11-13)

Furfural can be produced from pentoses (typically, xylose) in acid-catalyzed media, through a complex mechanism that involves a number of series and parallel reactions (including isomerization, dehydration, and undesired reactions leading to the consumption of furfural and productive species), as reported in literature.^(5,14) Alternatively, other compounds or materials (for example, soluble saccharides made up of anhydropentoses, xylan, arabinan, or native lignocellulosic materials containing pentosans) can be used as substrates for furfural production. In the presence of water and an acidic catalyst, the anhydropentoses are hydrolyzed

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3 into pentoses, which undergo the complex set of reactions cited previously to yield furfural and
4 byproducts. This operational method has been employed to produce furfural from
5 hemicellulosic saccharides obtained by autohydrolysis of xylan-containing lignocellulosic
6 biomass.^(10,15-18)
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9 When furfural is produced from biomass hydrolyzates, saccharides derived from native
10 polymers containing anhydrohexose units (for example, cellulose, starch, or glucomannan) can
11 be also present in the reaction media. In these cases, the hexoses may undergo reactions similar
12 to the ones described for pentoses, leading to the formation of 5-hydroxymethylfurfural (HMF)
13 and byproducts. In this case, both furfural (produced from pentoses and anhydropentoses) and
14 HMF (produced from hexoses and anhydrohexoses) are present in the reaction media.^(5,10,19)
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17 One-pot furfural manufacture in aqueous media by acidic processing of a polymeric
18 substrate usually results in limited yields, owing to the participation of undesired side-reactions
19 (particularly, the ones leading to condensation products known as humins).^(5,20-23) Several
20 strategies have been proposed to improve the furfural yields, including the utilization of fast
21 heating profiles (which can be achieved using microwave heating)^(23,24) and the extraction of
22 furfural from the aqueous reaction media into an organic phase (in order to limit the effects of
23 the undesired furfural-consuming reactions taking place in the aqueous phase).
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29 Over the last years, the interest in microwave-assisted reactions has been increasing to
30 become a very popular and useful technology.^(18,20) Microwave heating offers many comparative
31 advantages over conventional heating methods, including shorter reaction times, and in many
32 cases, improved yields and selectivities, with decreased generation of by-products.^(25,26) Several
33 studies have shown that microwave heating may increase the yield of dehydration products from
34 carbohydrates.^(18,20,27,28)
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38 In this work, two native lignocellulosic materials rich in xylan (*Eucalyptus globulus*
39 wood and corncobs) were subjected to autohydrolysis to produce hemicellulosic saccharides,
40 which were used as substrates for furfural manufacture. The reactions were performed in a
41 microwave-heated reactor (to ensure a fast-heating profile) in the presence of a strong acid (HCl
42 or H₂SO₄) and an organic solvent (methyl isobutyl ketone, MIBK). In order to establish a basis
43 for comparison, parallel experiments were carried out using commercial xylose as a substrate.
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49 2 EXPERIMENTAL

50 2.1 Materials and Characterization

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55 *E. globulus* wood samples and corncobs were collected locally, air-dried, milled to pass
56 an 8 mm screen, homogenized in a single lot to avoid compositional differences among samples
57 and stored until use. The raw materials were assayed for composition by quantitative acid
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3 hydrolysis (TAPPI 249 method) before gravimetric determination of lignin and HPLC analysis
4 of the sugars, sugar oligomers and acetic acid present in the hydrolyzates. HPLC analysis were
5 performed using an Agilent 1260 instrument fitted with a refractive index detector using a 300 x
6 7.8 mm Aminex HPX-87H column (BioRad, Life Science Group Hercules, CA) and a guard
7 column, operating under the conditions recommended by the supplier. The content of non-
8 volatile compounds (NVC) in liquors was measured by oven-drying at 105 °C until constant
9 weight. All determinations were made by triplicate.
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14 15 16 **2.2 Autohydrolysis and Characterization of the Liquid Phase**

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18 Milled samples of the native raw materials (*E. globulus* wood or corncobs) were mixed
19 with water (liquid to solid ratio, 8 kg water/kg oven-dry raw material), heated in a 3.75 L
20 stainless steel reactor (Parr Instrument Co., Moline, IL, USA) up to reach the target temperature,
21 and then cooled immediately. The target temperatures (196 °C and 202 °C in experiments with
22 wood and corncobs, respectively) were selected according to reported studies.^(29,30) The liquid
23 phases from the autohydrolysis media were recovered by filtration, and assayed by HPLC for
24 monosaccharides, higher saccharides, and bound acetyl groups before and after a quantitative
25 post-hydrolysis (NREL/TP-510-42623 method). HPLC analyses were performed using the same
26 method mentioned above.
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32 **2.3 Furfural Production**

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34 The starting solutions (containing 20 g xylose/L or hemicellulose-derived saccharides in
35 concentrations equivalent to 20 g potential pentoses/L) were supplemented with the desired
36 amounts of catalyst (HCl or H₂SO₄) and MIBK, and kept at the target temperature (measured by
37 a fiber optic sensor) for the desired reaction time (in the range 5-60 min) under magnetic stirring
38 in a monomodal microwave reactor CEM Discover S-class System. The amount of MIBK (0.5
39 g/g aqueous solution) and the temperature at which the experiments were performed (170 °C)
40 were selected according reported studies.^(20,31) Zero time was fixed when the target temperature
41 was reached (it can be noted that partial substrate conversion may occur during the heating
42 period). After the desired reaction time, the vessel was quickly cooled at room temperature by
43 forced air flow, and samples from the aqueous and organic phases were withdrawn, diluted
44 immediately at the desired proportions, homogenized, filtered through 0.45 µm nylon
45 membranes and assayed for composition by HPLC using the method described above.
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3 RESULTS AND DISCUSSION

3.1 Composition of the Lignocellulosic Feedstocks and Soluble Autohydrolysis Products

The compositional data determined for the lignocellulosic raw materials are shown in Table 1. Both feedstocks presented contents of lignin, cellulose and hemicelluloses within the ranges reported in related studies.^(29,32-36) Autohydrolysis processing of these substrates resulted in extensive hemicellulose solubilization (with hemicellulose recovery yields accounting for 71.6 and 87.4% of the initial ones for *E. globulus* and corncob, respectively), yielding soluble saccharides made up of anhydroxylose units (of oligomeric or polymeric nature) as major reaction products. Since glucose and higher saccharides made up of glucose were also present in the reaction media, the processing of the liquid phases from autohydrolysis under harsh acidic conditions is expected to result in the simultaneous formation of furfural and HMF.

3.2 Furfural Manufacture in Media Containing Commercial Xylose Solutions

The production of furfural from commercial xylose solutions in reaction media containing HCl as a catalyst and MIBK as an organic solvent was studied by Weingarten *et al.*⁽²⁰⁾ Operating with 0.1 M HCl (referred to the aqueous phase), aqueous solutions containing 10 wt% xylose were reacted at 130-170 °C in the presence of 1 g MIBK/g aqueous phase. The maximum furfural yield (over 80%) was achieved after 70 min in an experiment performed at the highest temperature assayed. Furfural was predominantly distributed in the organic phase (at a relative proportion of 7.1 g furfural in MIBK phase/g furfural in aqueous phase).

Starting from this information, the following experimental conditions were assessed in this work: xylose concentration, 20 g/L (close to the concentration of potential pentoses in autohydrolysis solutions); temperature, 170 °C (considered as the maximum temperature allowing a safe operation with the available equipment); relative amount of the organic phase, 0.5 g/g aqueous phase; type and concentration of catalysts HCl (0.5 or 1 wt% referred to the aqueous phase) or H₂SO₄ (1 or 1.6 wt% referred to the aqueous phase). The utilization of two catalysts at diverse concentrations was included in experiments in order to obtain preliminary experimental information suitable for further application to biomass-derived media.

In the experiments performed with 1% H₂SO₄ (see Table 2.a), xylose was consumed with a fast kinetics, achieving more than 50% conversion after 10 min and nearly depletion after 60 min. In agreement with the expected kinetics (based on the mechanisms proposed in literature), furfural behaved as a reaction intermediate, reaching its maximum yield (72.3% of the stoichiometric value) after 25 min. In comparison, the selectivity varied in a limited range (71 - 86%) when the xylose conversion was below 93%, and reached 81.9% at the optimal reaction time. Increasing the catalyst concentration to 1.6% (see Table 2.b) resulted in faster

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3 kinetics (near 60% xylose consumption was observed after 5 min of isothermal processing), but
4 in lower conversion into furfural at the optimal reaction time (66.8% after 20 min) and
5 decreased selectivity under these conditions (73.9%).
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8 The experiments performed with 0.5% HCl (see results in Table 2.c) presented
9 experimental trends closely related to the ones observed for experiments in media catalyzed
10 with sulfuric acid. In comparison, xylose was consumed faster (achieving near 60% conversion
11 after 5 min of isothermal processing), and the substrate was depleted 30 min. The maximum
12 conversion into furfural (71.6 after 20 min) and the selectivity under these conditions (73.6%)
13 were near the ones achieved in media containing 1% H₂SO₄. Increasing the HCl concentration
14 to 1% (see data in Table 2.d) improved the reaction kinetics: the maximum furfural
15 concentration was achieved at a shorter reaction time, whereas the maximum furfural yield
16 (76.4%) and selectivity (82.3%) were reached only after 7.5 minutes. This result compares well
17 with the results reported for experiments with MW-irradiation (Weingarten *et al.* 2010).
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21 The furfural distribution between phases (measured at the ratio between the furfural
22 concentration in organic and aqueous phases, respectively) was similar for both catalysts at
23 corresponding reaction times (reaching average values of 9.9 and 10.3 for H₂SO₄ and HCl,
24 respectively).
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31 **3.3 Furfural Production from Hemicellulosic Saccharides from *E. globulus* Wood** 32 **in Biphasic Media** 33

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35 The production of furfural from wood autohydrolysis solutions in the presence of
36 H₂SO₄ (see data listed in Tables 3.a and 3.b) presented a kinetic pattern similar to the one
37 observed for commercial xylose solutions, even if the maximum molar conversions of substrates
38 into furfural (59.0% in the experiment with 1 wt% H₂SO₄, and 53.3% in the experiment with 1.6
39 wt% H₂SO₄) were lower than the ones obtained with synthetic media (72.3 and 66.8%,
40 respectively). The major difference corresponded to the co-generation of HMF from hexose-
41 containing saccharides and its further decomposition. However, it must be considered that the
42 potential HMF concentrations were comparatively low (1.76 g/L or 1.73 g/kg solution, in
43 comparison with the potential furfural concentrations of 10.82 /L or 10.6 g/kg), owing to the
44 limited amount of suitable precursors in the reaction media. The lower yields achieved from
45 hemicellulosic saccharides from *E. globulus* wood are ascribed to the more complex nature of
46 the potential substrates (which have to be hydrolyzed into pentoses before being dehydrated into
47 furfural), and to the presence of contaminants in the reaction media (for example, derived from
48 hexoses, hexose precursors or non-polysaccharide wood fractions) that can participate in
49 reactions consuming the productive species (xylose, reaction intermediates and/or furfural).⁽¹⁹⁾
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3 On other hand, the eventual presence of inorganic components with neutralizing ability could
4 result in lower concentration of hydronium ions acting as catalysts.
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6 The results obtained in experiments using HCl as a catalyst (see Tables 3.c and 3.d)
7 showed a faster kinetics (the maximum furfural yields were obtained at shorter reaction times
8 than in experiments using sulfuric acid), and resulted in improved furfural yields (64.1% in the
9 experiment with 0.5 wt% HCl after 20 min, and 67.8% in the experiment with 1% HCl after 10
10 min) and almost comparable with those obtained with solutions of commercial xylose under
11 analogous operational conditions (71.6 and 75.0%, respectively). In particular, the results
12 reached with 1% HCl after 10 min is noticeable, considering the short reaction time. On the
13 other hand, the aqueous phase also contained sugars (mainly, xylose) and organic acids (as
14 formic, acetic and levulinic acids) derived from the various reaction substrates (see Table 3).
15 The xylose concentrations decreased markedly along the isothermal reaction stages, reaching a
16 minimum value (0.3 g/kg solution) under the harshest conditions assayed. Acetic acid was
17 produced by acetyl group hydrolysis, and reached a fairly constant concentration (close to 3
18 g/kg solution) in the various experiments. The concentrations of levulinic and formic acids
19 (resulting from HMF rehydration) increased with the reaction time up to achieve maximum
20 values of 2 and 1 g/kg, respectively.
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30 **3.3 Furfural Production in Media Containing Hemicellulosic Saccharides from** 31 **Corncoobs** 32

33 The processing of the liquid phases from corncob autohydrolysis solutions was
34 performed in the presence of H₂SO₄ or HCl (see data in Table 4) operating at the same catalyst
35 charges employed previously. As observed in experiments with samples from *Eucalyptus* wood,
36 HMF was obtained as a reaction co-product and behaved as a reaction intermediate, reaching
37 limited maximum concentrations (due to its limited potential concentration, 2.10 g/L or 2.06
38 g/kg).
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40 The maximum conversions of potential substrates into furfural obtained in media
41 containing 1 or 1.6% H₂SO₄ (69.8 or 69.4%, see Tables 4.a and 4.b) were improved (up to 72.5
42 or 70.7%) when using HCl as a catalyst at 0.5 or 1% concentration, respectively (see Tables 4.c
43 and 4.d). In this last case, the best yield was reached just after 10 min. The general kinetic
44 pattern observed in these experiments was similar to the one observed for media containing
45 commercial xylose or wood-derived saccharides, and the differences observed in furfural
46 production were ascribed to both the specific properties of the potential substrates (degree of
47 polymerization) and to the different nature of the contaminants present in the reaction media.
48 Under these operational conditions, furfural was predominantly distributed in the organic phase
49 (at a relative average proportion of 10.1 g furfural in MIBK phase/g furfural in aqueous phase).
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3 As described for *E. globulus* processing, heating resulted in the generation and partial
4 decomposition of xylan, and further processing under isothermal conditions led to extensive
5 consumption. The sugars in solution were consumed according to their respective
6 susceptibilities to dehydration.⁽³⁷⁾ The concentration profiles measured for the various organic
7 acids (formic, acetic and levulinic acids) were similar to the ones previously described for *E.*
8 *globulus*: acetic acid was the most abundant organic acid (average concentration, 3 g/kg
9 solution), whereas the maximum concentrations of levulinic and formic acids (2.08 and 0.75
10 g/kg, respectively) were obtained in experiments with 1% H₂SO₄ after 60 min, and with 1% HCl
11 after 45 min, respectively.
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17 18 3.4 Comparative Evaluation of Results

19 The results reported in this study compare well with literature, beyond the differences in
20 the types of substrates and operational conditions. Weingarten *et al.*⁽²⁰⁾ reported a kinetic model
21 for xylose dehydration into furfural in a water/MIBK system with HCl as a catalyst at 170 °C,
22 and estimated furfural yields about 80%, in contrast with 30% yield for single phase operation.
23 Yemis and Mazza⁽²⁷⁾ studied the acid-catalyzed conversion of xylose and xylan into furfural
24 under microwave irradiation at selected conditions of temperature, time, substrate concentration
25 and pH; and identified optimal conditions under which the furfural yields from wheat straw,
26 triticale straw, and flax shives were 48.4%, 45.7%, and 72.1%, respectively. Rivas *et al.*⁽³⁸⁾
27 employed MIBK as an extraction agent and H₂SO₄ as a catalyst for the dehydration of
28 hemicellulosic saccharides from aqueous solutions derived from autohydrolysis of *Pinus*
29 *pinaster* wood, achieving 71.4% furfural yield in the presence of HMF and LA operating at 165
30 °C for 68.5 min. Sánchez *et al.*⁽¹⁵⁾ obtained furfural from corncob autohydrolysis liquors in
31 single-phase experiments under MW irradiation, and reported 37.1% furfural yield operating at
32 180 °C for 5 min in the presence of 2% (v/v) HCl. Rivas *et al.*⁽³¹⁾ considered the production of
33 furfural from *Betula*-derived saccharides, and reported 44.8% furfural yield in single-phase
34 experiments (performed at 170 °C for 60 min in the presence of 1% H₂SO₄) or 75% yield in the
35 presence of MIBK. In this context, the furfural yields obtained in this study (up to 76.4%,
36 72.5% and 67.8% in experiments with xylose, hemicellulosic saccharides from corncob and
37 hemicellulosic saccharides from *E. globulus*, respectively) confirm the interest of the approach
38 considered in this study for furfural manufacture, which is compatible with the production of
39 additional added-value chemicals derived from cellulose and lignin, according to the biorefinery
40 philosophy.
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55 4. Conclusion

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Furfural was produced in a microwave-heated reactor from soluble hemicellulose saccharides obtained by hydrothermal processing of two xylan-rich materials (*E. globulus* wood and corncobs) in biphasic media. Operation was carried out at 170 °C in the presence a strong acid (sulfuric acid or HCl), considering the reaction time as an operational variable. The best furfural yields (67.8% and 72.5% from *E. globulus* wood and corncobs, respectively) were obtained at 170 °C operating with 1% or 0.5% HCl for 10 or 20 min, respectively. These results were slightly lower than the ones obtained using xylose (a model substrate) under comparable reaction conditions, a fact ascribed to the diverse complexity of substrates and to the presence of contaminants. The best results obtained in this work compare well with literature.

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Table 1. Compositional data determined for the raw materials and for the liquid phases from autohydrolysis treatmentsa) Composition of *E. globulus* wood and corncobs

Component	Mass (g/100 g oven-dry material)	
	<i>Eucalyptus</i> wood	Corncoobs
Cellulose	46.7	28.5
Xylan	16.4	23.2
Anhydroarabinosyl units	0.22	3.24
Acetyl groups	3.20	10.6
Klason lignin	27.2	20.2
Ash	0.23	1.90
Extractives	1.95	3.34
Other (by difference)	4.10	9.02

b) Composition of liquid phases from autohydrolysis treatments

Component	Concentration (g/100 g oven-dry material)	
	<i>E. globulus</i> wood	Corncoobs
Glucose	0.68	0.92
Xylose	1.63	4.57
Arabinose	0.28	1.63
Acetic acid	1.06	2.02
Potential glucose in higher saccharides (as equivalent glucose)	1.84	2.09
Potential xylose in higher saccharides (as equivalent xylose)	14.92	23.9
Potential arabinose in higher saccharides (as equivalent arabinose)	0.07	1.43
Acetyl groups in higher saccharides (as equivalent acetic acid)	4.12	2.77
Additional data. Contents of non-volatile components (kg/kg solution): <i>E. globulus</i> wood, 0.028; corncoobs, 0.044		

Table 2. Results achieved at 170 °C in biphasic media using xylose as a substratea) Results obtained using 1% H₂SO₄

	Reaction time (min)								
	5	10	15	20	25	30	35	45	60
Xylose conversion (%)	45.3	60.3	76.5	80.07	88.3	91.2	92.8	97.3	98.3
Furfural yield (%)	34.5	43.03	64.6	69.0	72.3	70.2	67.0	66.5	65.5
Furfural selectivity (%)	76.1	71.3	84.4	86.17	81.9	77.0	72.1	68.3	66.7
Concentration of the aqueous phase (g/kg solution)									
Xylose	11.4	8.23	4.87	4.13	2.43	1.83	1.49	1.38	0.56
Furfural	0.76	1.07	1.22	1.32	1.32	1.38	1.29	1.49	1.36
Organic phase									
Furfural	7.71	9.38	14.9	15.9	16.7	16.0	15.4	16.0	15.1

b) Results obtained using 1.6% H₂SO₄

	Reaction time (min)								
	5	10	15	20	25	30	45	60	
Xylose conversion (%)	58.2	65.6	87.2	90.4	95.0	97.0	98.7	99.0	
Furfural yield (%)	58.2	64.8	66.2	66.8	65.1	57.8	56.6	45.5	
Furfural selectivity (%)	100	98.7	75.9	73.9	68.5	59.6	57.3	46.0	
Concentration of the aqueous phase (g/kg solution)									
Xylose	7.91	6.03	2.24	1.68	0.87	0.53	0.23	0.18	
Furfural	1.01	1.18	1.38	1.48	1.46	1.42	1.39	1.37	
Organic phase									
Furfural	12.3	12.4	12.3	12.0	11.9	10.3	10.1	7.61	

c) Results obtained using 0.5% HCl

	Reaction time (min)								
	0	5	10	15	17.5	20	25	30	
Xylose conversion (%)	12.5	59.9	77.9	82.7	90.3	97.2	98.4	99.2	
Furfural yield (%)	6.56	44.4	56.9	62.6	67.7	71.6	70.7	72.0	
Furfural selectivity (%)	52.4	74.1	73.0	75.7	75.0	73.6	71.9	72.6	
Concentration of the aqueous phase (g/kg solution)									
Xylose	17.8	8.15	4.49	3.52	1.97	0.56	0.32	0.17	
Furfural	0.15	1.01	1.36	1.44	1.59	1.67	1.65	1.67	
Organic phase									
Furfural	1.56	10.6	13.4	14.8	16.0	16.9	16.7	17.0	

d) Results obtained using 1% HCl

	Reaction time (min)								
	0	2.5	5	7.5	10	12.5	15	20	
Xylose conversion (%)	24.4	70.0	82.7	92.8	95.1	97.9	98.5	99.2	
Furfural yield (%)	16.9	56.1	68.9	76.4	75.0	71.4	72.9	-	
Furfural selectivity (%)	69.4	80.2	83.3	82.3	78.8	72.9	74.0	78.8	
Concentration of the aqueous phase (g/kg solution)									
Xylose	15.4	6.11	3.51	1.46	0.99	0.43	0.30	0.15	
Furfural	0.37	1.20	1.42	1.61	1.61	1.63	1.61	1.61	
Organic phase									
Furfural	4.05	12.3	15.2	16.8	16.5	15.5	15.9	17.3	

Table 3. Results achieved at 170 °C in media containing hemicellulosic saccharides from *E. globulus* wooda) Results obtained with 1% H₂SO₄

	Reaction time (min)				
	0	15	30	45	60
HMF yield (%)	46.6	6.74	4.49	3.38	2.26
Furfural yield (%)	8.89	54.3	59.0	55.9	52.9
Concentration of the aqueous phase (g/kg solution)					
Glucose	1.97	1.27	0.92	0.57	0.74
Xylose	14.1	3.24	1.37	0.69	0.81
Arabinose	0.35	0.12	0.06	0.05	0.00
Formic acid	0.00	0.31	0.60	0.70	0.63
Acetic acid	3.12	3.25	3.26	3.24	3.04
Levulinic acid	0.00	0.52	0.80	1.01	0.95
HMF	0.12	0.19	0.13	0.08	0.07
Furfural	0.12	1.11	1.19	1.03	0.92
Concentration of the organic phase (g/kg solution)					
HMF	1.45	0.24	0.16	0.09	0.08
Furfural	1.73	9.67	10.5	10.4	9.74

b) Results obtained with 1.6% H₂SO₄

	Reaction time (min)									
	0	5	10	15	20	25	30	35	45	60
HMF yield (%)	6.07	16.3	16.2	12.8	9.39	12.3	9.39	10.4	5.35	3.51
Furfural yield (%)	6.39	28.5	41.2	46.1	51.1	53.3	50.8	53.3	47.6	41.3
Concentration of the aqueous phase (g/kg solution)										
Glucose	2.07	1.69	1.48	1.34	1.21	1.11	1.06	0.78	0.78	0.57
Xylose	14.3	8.20	5.19	3.76	2.49	2.07	1.48	1.50	0.86	0.63
Arabinose	0.36	0.26	0.20	0.13	0.12	0.10	0.15	0.00	0.00	0.00
Formic acid	0.00	0.19	0.19	0.46	0.52	0.50	0.85	0.56	0.99	0.78
Acetic acid	3.22	3.51	3.46	3.53	3.54	3.45	3.69	3.16	3.74	3.60
Levulinic acid	0.00	0.18	0.36	0.47	0.62	0.69	0.88	0.85	1.07	1.13
HMF	0.11	0.17	0.17	0.16	0.14	0.12	0.10	0.10	0.06	0.04
Furfural	0.10	0.60	0.84	0.91	1.03	0.98	1.04	0.92	0.96	0.93
Concentration of the organic phase (g/kg solution)										
HMF	0.00	0.23	0.23	0.21	0.06	0.20	0.14	0.17	0.07	0.05
Furfural	1.20	5.06	7.33	7.80	9.12	9.72	9.04	9.83	8.49	7.17

c) Results obtained with 0.5% HCl

	Reaction time (min)									
	0	5	10	15	17.5	20	25	30	45	
HMF yield (%)	12.0	7.70	7.08	6.37	5.66	3.94	3.18	6.03	1.16	
Furfural yield (%)	7.99	38.4	55.3	59.1	62.8	64.1	62.2	59.9	57.9	
Concentration of the aqueous phase (g/kg solution)										
Glucose	2.00	1.70	1.33	1.19	1.01	0.73	0.88	0.59	0.44	
Xylose	13.8	7.75	3.61	2.66	1.71	0.87	1.20	0.61	0.50	
Arabinose	0.38	0.30	0.16	0.10	0.06	0.04	0.08	0.00	nd	
Formic acid	0.00	0.00	0.36	0.50	0.57	0.66	0.62	0.75	nd	
Acetic acid	3.20	3.28	3.27	3.28	3.29	3.27	3.26	3.25	3.18	
Levulinic acid	0.00	0.21	0.49	0.60	0.74	0.97	0.88	1.10	0.00	
HMF	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	
Furfural	0.19	0.78	1.15	1.17	1.24	1.20	1.21	1.17	1.03	
Concentration of the organic phase (g/kg solution)										
HMF	0.17	0.28	0.25	0.23	0.20	0.14	0.11	0.09	0.04	
Furfural	1.38	6.84	9.82	10.9	11.3	11.6	11.2	10.8	10.6	

d) Results obtained with 1% HCl

	Reaction time (min)									
	0	5	10	15	20	25	30	35	45	60
HMF yield (%)	16.3	21.3	13.8	8.86	6.12	4.34	2.18	1.25	1.77	0.48
Furfural yield (%)	23.4	61.7	67.8	67.2	65.1	63.9	60.3	55.5	54.3	53.1
Concentration of the aqueous phase (g/kg solution)										
Glucose	1.85	1.31	0.85	0.65	0.54	0.48	0.37	0.33	0.36	0.16
Xylose	11.2	3.45	1.20	0.78	0.60	0.55	0.44	0.37	0.36	0.30
Arabinose	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	nd
Formic acid	0.00	0.28	0.66	0.74	0.81	0.84	0.92	0.97	0.96	nd
Acetic acid	3.30	3.41	3.38	3.35	3.33	3.35	3.36	3.37	3.38	nd
Levulinic acid	0.08	0.51	0.91	1.07	1.19	1.25	1.36	1.40	1.39	2.06
HMF	0.17	0.22	0.14	0.09	0.06	0.04	0.02	0.01	0.02	0.00
Furfural	0.40	1.00	1.07	1.16	1.07	1.02	0.98	0.85	0.89	0.83
Concentration of the organic phase (g/kg solution)										
HMF	0.25	0.32	0.21	0.13	0.09	0.07	0.04	0.02	0.03	0.02
Furfural	4.30	11.5	12.7	12.3	12.1	11.9	11.2	10.4	11.6	9.93

Table 4. Results achieved at 170 °C in media containing hemicellulosic saccharides from corncobsa) Results obtained with 1% H₂SO₄

	Reaction time (min)				
	0	15	30	45	60
HMF yield (%)	9.35	8.28	6.75	4.46	3.87
Furfural yield (%)	8.44	57.9	63.4	69.7	69.8
Concentration of the aqueous phase (g/kg solution)					
Aqueous phase					
Glucose	2.35	1.83	1.37	0.97	0.77
Xylose	25.7	8.47	3.06	1.13	0.86
Arabinose	1.92	1.25	0.69	0.27	0.17
Formic acid	0.00	0.32	0.53	0.67	0.75
Acetic acid	2.78	2.89	2.94	2.91	2.91
Levulinic acid	0.00	0.32	0.57	0.74	0.83
HMF	0.12	0.15	0.12	0.08	0.08
Furfural	0.36	2.05	2.66	2.45	2.26
Concentration of the organic phase (g/kg solution)					
HMF	0.16	0.06	0.04	0.03	0.00
Furfural	2.72	19.5	20.6	23.5	24.0

b) Results obtained with 1.6% H₂SO₄

	Reaction time (min)							
	0	5	10	15	20	25	30	45
HMF yield (%)	30.7	16.7	18.1	15.3	14.0	13.1	15.2	11.05
Furfural yield (%)	34.9	47.4	62.1	68.4	69.4	67.1	64.5	67.5
Concentration of the aqueous phase (g/kg solution)								
Glucose	2.36	2.12	1.80	1.71	1.34	1.23	1.32	0.95
Xylose	25.6	13.5	8.01	3.86	2.89	1.98	2.52	0.19
Arabinose	1.96	1.62	1.19	0.72	0.56	0.41	0.52	0.29
Formic acid	0.00	0.23	0.33	0.60	0.62	0.77	0.67	0.41
Acetic acid	2.92	3.18	3.18	3.32	3.16	3.32	3.28	1.43
Levulinic acid	0.04	0.21	0.34	0.66	0.58	0.72	0.64	0.14
HMF	0.13	0.15	0.15	0.12	0.11	0.10	0.11	0.07
Furfural	0.42	1.22	1.83	1.95	2.68	2.10	2.02	2.49
Concentration of the organic phase (g/kg solution)								
HMF	1.06	0.41	0.47	0.40	0.37	0.36	0.43	0.33
Furfural	13.4	16.9	21.7	24.0	22.9	23.2	22.3	22.6

c) Results obtained with 0.5% HCl

	Reaction time (min)									
	0	5	10	15	17.5	20	25	30	45	
HMF yield (%)	11.4	13.4	14.0	11.0	11.4	9.74	8.80	8.68	5.04	
Furfural yield (%)	14.0	41.4	49.0	65.2	66.6	72.5	72.1	71.2	65.6	
Concentration of the aqueous phase (g/kg solution)										
Glucose	2.47	2.04	1.74	1.20	1.42	1.13	1.08	0.98	0.74	
Xylose	25.4	13.9	7.12	2.62	3.54	1.64	1.37	1.16	0.69	
Arabinose	2.10	1.67	1.16	0.58	0.72	0.43	0.36	0.27	0.13	
Formic acid	0.00	0.09	0.14	0.21	0.19	0.23	0.26	0.24	0.49	
Acetic acid	2.71	3.59	3.59	3.55	3.55	3.61	3.59	3.60	3.88	
Levulinic acid	0.00	0.31	0.58	0.92	0.88	1.12	1.17	1.22	1.62	
HMF	0.14	0.17	0.17	0.14	0.14	0.12	0.11	0.11	0.07	
Furfural	0.49	1.63	2.14	2.30	2.60	2.53	2.71	2.39	2.19	
Concentration of the organic phase (g/kg solution)										
HMF	0.20	0.22	0.25	0.19	0.19	0.17	0.16	0.15	0.07	
Furfural	4.71	13.6	15.6	21.9	21.9	24.4	23.9	24.2	22.3	

d) Results obtained with 1% HCl

	Reaction time (min)							
	0	5	10	15	20	25	30	45
HMF yield (%)	17.4	14.0	9.08	7.21	4.10	4.07	2.27	0.00
Furfural yield (%)	25.9	54.2	70.7	64.9	63.3	61.7	58.5	47.0
Concentration of the aqueous phase (g/kg solution)								
Glucose	2.34	1.60	0.91	0.85	0.62	0.63	0.46	0.33
Xylose	19.9	6.30	1.28	1.12	0.76	0.68	0.61	0.63
Arabinose	1.96	1.25	0.35	0.30	0.16	0.21	0.09	0.04
Formic acid	0.00	0.43	0.25	0.27	0.33	0.33	0.34	0.43
Acetic acid	2.84	2.95	3.44	3.46	3.57	3.64	3.48	3.58
Levulinic acid	0.14	0.44	1.27	1.40	1.69	1.75	1.80	2.08
HMF	0.17	0.18	0.11	0.09	0.05	0.06	0.03	0.00
Furfural	0.95	1.57	2.15	2.06	1.75	1.96	1.86	1.31
Concentration of the organic phase (g/kg solution)								
HMF	0.40	0.24	0.16	0.12	0.07	0.06	0.04	0.00
Furfural	8.65	18.9	24.4	22.3	19.4	21.2	20.1	16.5