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Furfural production from birch hemicelluloses by two-step processing: a potential technology for biorefineries

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Abstract: Birch samples were subjected to non-isothermal autohydrolysis to obtain a solution of hemicellulosic saccharides and a solid phase mainly made up of cellulose and lignin. Based on kinetic modeling, operational conditions were identified which give rise to soluble saccharides and furfural derived from xylan in a yield of 80.5%. The soluble mixture was supplemented with 1% sulfuric acid and heated (directly or in the presence of methyl isobutyl ketone, MIBK) for furfural production. MIBK is used as an extraction agent to limit furfural consumption by side reactions. Operating in single phase at 170°C, up to 44.8% of the potential substrates were converted into furfural. In experiments performed in biphasic media, the effects of MIBK were assessed by empirical modeling and about 75% of the potential substrates were converted under selected conditions.

Keywords: autohydrolysis, biorefinery, biphasic media, birch, furfural, hemicelluloses, hydroxymethylfurfural, MIBK, optimization of furfural production, RSM experimental design, sugar analysis

Introduction

Lignocellulosic materials (LCM) are important renewable sources of organic carbon with potential as a partial

substitute for partly fossil resources. For the conversion of LCM to fuels, chemicals, and polymeric materials, the term “lignocellulose biorefinery” was coined, which also includes the effective separation of the polymeric components of LCM and the application of the principles of green chemistry in the course of the transformation processes towards commercial products.

The utilization of LCM is usually accomplished by multistep processes. The “Agenda 2020 Technology Alliance” advocates the selective extraction of hemicelluloses prior to pulping of wood in modern biorefineries. This goal can be achieved by a hot water extraction (also called autohydrolysis, hydrothermal treatment, or water prehydrolysis) (Yáñez et al. 2009; Helmerius et al. 2010; Gullón et al. 2011; Vila et al. 2012), which is considered to be an environmentally friendly technology and enables a selective separation of soluble hemicellulose-derived saccharides, while the solid phase residue is enriched in cellulose and lignin. The latter can be further fractionated via autohydrolysis, for example, to produce pulp (Helmerius et al. 2010), dissolve pulp (Borrega et al. 2013; Testova et al. 2014), microcrystalline cellulose (Vila et al. 2014), or sugar solutions suitable as fermentation media for the biotechnological manufacture of chemicals or fuels (Garrote et al. 2008).

Hardwoods (HW) are important raw materials for pulp production in Europe (Patt et al. 2006). Birch (*Betula alba*) covers about 49 000 ha in northwestern Spain, with an annual harvest volume of 17 000 m³ (Gorgoso-Varela et al. 2008). Birch is also employed as a soil improver and for reforestation of degraded soils. HW hemicelluloses are mainly composed of acetyl-4-*O*-methylglucuronoxylan, with glucomannans and other compounds in lower amounts (Ebringerová et al. 2005). Native birch xylan consists of a backbone of β (1-4)-D-xylopyranosyl units, with *O*-acetyl substituent at positions C2 (23.7%), C3 (22.5%), or C2,3 (9.5%). Additionally, 4-*O*-methyl-D-glucuronic acid side groups are α -(1-2) linked to the xylopyranosyl residues in an average molar ratio of 1 acid group per 15 xylose units, preferentially those with an acetyl (OAc) substituent at position C3 (Teleman et al. 2001; Testova et al. 2011).

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When HW autohydrolysis is performed under suitable operational conditions, the resulting liquid phase contains hemicellulose-derived poly and oligosaccharides made up of pentoses and other reaction products. The relative proportions of the various saccharides depend on the severity of the operational conditions. Pentoses and higher saccharides made up of pentoses can be converted to furfural (F) by hydrolysis/dehydration reactions (Sánchez et al. 2013; Nakagame et al. 2014; Baktash et al. 2015; García-Domínguez et al. 2015; Koch and Kindler 2015; Liu et al. 2015). F, a commercial product with a favourable market forecast (Dalín Yebo 2015), was considered as one of the top 12 platform chemicals derived from biomass in a report from the U.S. Department of Energy (Werpy et al. 2004), which was updated 6 years later (Bozell and Petersen, 2010; De Jong et al. 2012). F is an intermediate for manufacturing other chemicals (such as methylfuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, methyltetrahydrofuran, or furoic acid), and has a potential for further conversion into fuel or fuel additives (Lange et al. 2012; Yan et al. 2014; Choi et al. 2015). The current technology for F production, based on the acid hydrolysis of native xylan-containing raw materials, can be significantly improved in terms of yield and energy efficiency (Lange et al. 2012; Cai et al. 2014).

In the course of F production via acid hydrolysis, xylose is first set free, and then loses 3 mol water to give rise to F. The obtained yields are essentially lower than the theory as a complex set of parallel reactions lead to undesired co-products, including xylose fragmentation products, intermediates, humins, and organic acids (Cai et al. 2014). F losses have been mainly ascribed to self-polymerization or cross polymerization with reactive species present in the medium (Cai et al. 2014; Yan et al. 2014). Operating in aqueous media without addition of catalysts, García-Domínguez et al. (2013) reported the production of 4.4 g F per 100 g of *Eucalyptus globulus* under optimised conditions (8 g water g⁻¹ wood, 60 min, 220°C), which were determined by neural modeling. Based on the composition of the raw material (17.1% xylan, 0.4% arabinosyl groups), the corresponding F yield is 34.6%. The same authors found 28% and 34% F yields, respectively, in case of wheat straw and *E. globulus* treatment under non-isothermal conditions. F production can be improved by a combination of autohydrolysis and acidic hydrolysis/dehydration under mild operational conditions. Following this approach, Sánchez et al. (2013) employed HCl as a catalyst in a system with microwave heating to obtain F from corn cob autohydrolysis liquors at 37% yield.

The side reactions can be limited by F removal from the reaction medium, for example, by stripping or

extraction (Weingarten et al. 2010; Agirrezabal-Telleria et al. 2011). In particular, the utilization of biphasic media, in which an organic solvent plays an important role as an F extraction agent, shows good results (Weingarten et al. 2010; Gürbüz et al. 2012; Yang et al. 2012; Rivas et al. 2013; Wang et al. 2015).

The presence of solid substrates and oligo and polysaccharides from hexoses as a result of incomplete hydrolysis further decrease the F yields. Thus, the overall kinetic mechanism describing the utilization of HW autohydrolysis liquors for F production is difficult to assess based on theoretical considerations, when the operations are carried out in biphasic media. An empirical assessment based on the response surface method (RSM) leads to realistic and optimized results.

The present work deals with the optimization of F production from birch wood via acid hydrolysis in mono or biphasic media, in the course of which the principle of RSM will be applied for yield maximization. Wood autohydrolysis will be assessed by a kinetic model to obtain the best conditions for F production. MIBK will serve as organic solvent in the biphasic acid hydrolysis.

Materials and methods

All percentage data are wt%, if not otherwise indicated.

Raw material and analysis: Birch wood (*Betula alba*) was collected locally (Ourense, NW Spain), chipped, air dried, homogenized, and stored at room temperature. Wood samples for autohydrolysis assays were ground in a Willey mill (Retsch SM1, Verder Scientific Inc., USA) to pass a 3 mm sieve. Samples for analytical determinations were further ground in a Willey mill equipped with a 0.5 mm sieve (Polymix® PX-MFC 90 D, Kinematica AG, Switzerland). The contents of extractives, moisture, and ash were determined according to TAPPI T-264-cm-97 and T211 om-02. Extractive-free samples were subjected to quantitative acid hydrolysis with 72% and 3% H₂SO₄ (TAPPI T-249-em-85), respectively, and the unhydrolysed residue was recovered by filtration and oven-dried (Klason lignin). Hydrolysates were filtered through 0.45 µm cellulose acetate membranes and assayed by HPLC (Agilent 1200 Series) equipped with RI and UV detectors. One aliquot of hydrolysate was submitted for analysis of organic acids and furans by HPLC (300×7.8 mm BioRad Aminex HPX-87H column, eluted with 0.6 ml min⁻¹ of 3 mM H₂SO₄ at 50°C). The second aliquot was neutralized with barium carbonate and assayed for monosaccharides (glucose, xylose, mannose, galactose, and arabinose) using a CARBOsep CHO-682 column operated at 80°C with 0.4 ml min⁻¹ of deionized water. The experimental results are listed in Table 1.

Autohydrolysis and analysis of products: Autohydrolysis was carried out in a 0.6 l Parr reactor (Parr Company, Illinois, USA) stirred at 150 rpm, while the liquid-to-solid ratio (L/S-R) was 8 kg kg⁻¹, under non-isothermal conditions to the final temperature T_f, i.e. 190, 200,

Table 1: Wood composition, expressed as weight percent on oven-dry basis (o.d.b).

Component	%±SD
Cellulose	35.4±0.7
Xylan	21.5±0.5
Galactan	1.4±0.1
Arabinan	0.4±0.1
Mannan	2.1±0.1
Acetyl groups	5.4±0.2
Klason lignin	22.2±0.9
Extractives	5.1±0.1
Uronic acids	2.4±0.2
Ash	0.4±0.1

205, 210, 215, 220, or 230°C. The heating and cooling profiles of the treatments were recorded and fitted to empirical equations for modeling. The withdrawn samples were analyzed by the methods described below. The composition of autohydrolysis liquors was determined by HPLC analysis of samples without and with quantitative posthydrolysis (performed with 4% H₂SO₄ for 20 min). Concentrations of poly and oligosaccharides and bound OAc were measured on the basis of the concentration increments of monosaccharides and acetic acid (AA) resulting from the coupled quantitative posthydrolysis step. Samples were assayed for monosaccharides, furans, and organic acids by the same HPLC method employed in the analysis of the liquid phase from the quantitative acid hydrolysis. Uronic acids were determined spectrophotometrically at 520 nm according to Blumenkrantz and Asboe-Hansen (1973), which is based on the formation of a chromogen between *m*-hydroxyphenyl and uronic acids in concentrated H₂SO₄. The content of non-volatile compounds

(NVC) was measured by oven-drying liquor aliquots at 105°C until they reached constant weight.

Furfural (F) production via autohydrolysis liquors in mono or biphasic systems:

Autohydrolysis liquors were supplemented with 1% H₂SO₄ and heated in a 0.6 l stainless steel Parr reactor (stirred at 400 rpm), without or with MIBK (see below). Heating followed the standard temperature profile of the reactor. Both aqueous (Aq) and organic (Or) phases were analyzed for monosaccharides, organic acids, and furans by HPLC (Aminex HPX-87H column) under the conditions described above. The general scheme for analysis and processing followed in this work is summarized in Figure 1.

Empirical modeling: F production in biphasic systems was optimized by the response surface methodology (RSM). The set of experiments corresponds to an optimized, incomplete, factorial, centered experimental design with minimal dead volume. The independent variables and their respective variation ranges are: temperature (T) 160–180°C, reaction time under isothermal conditions (t) 30–90 min, and volume ratio of organic phase to aqueous phase (Or/Aq-R) 0.5–2.0 (see Table 2). In the course of calculations, the above-mentioned parameters were converted into normalized dimensionless variables, i.e. T (x₁), t (x₂), and Or/Aq-R (x₃), and the variation ranges (-1, 1) are defined as follows:

$$x_1 = 2[T(^{\circ}\text{C}) - 170] / (180 - 160) \quad (1)$$

$$x_2 = 2[t(\text{min}) - 60] / (90 - 30) \quad (2)$$

$$x_3 = 2[Or / Aq - R (v/v) - 1.25] / (2 - 0.5) \quad (3)$$

Table 2 also includes these dimensionless operational variables.

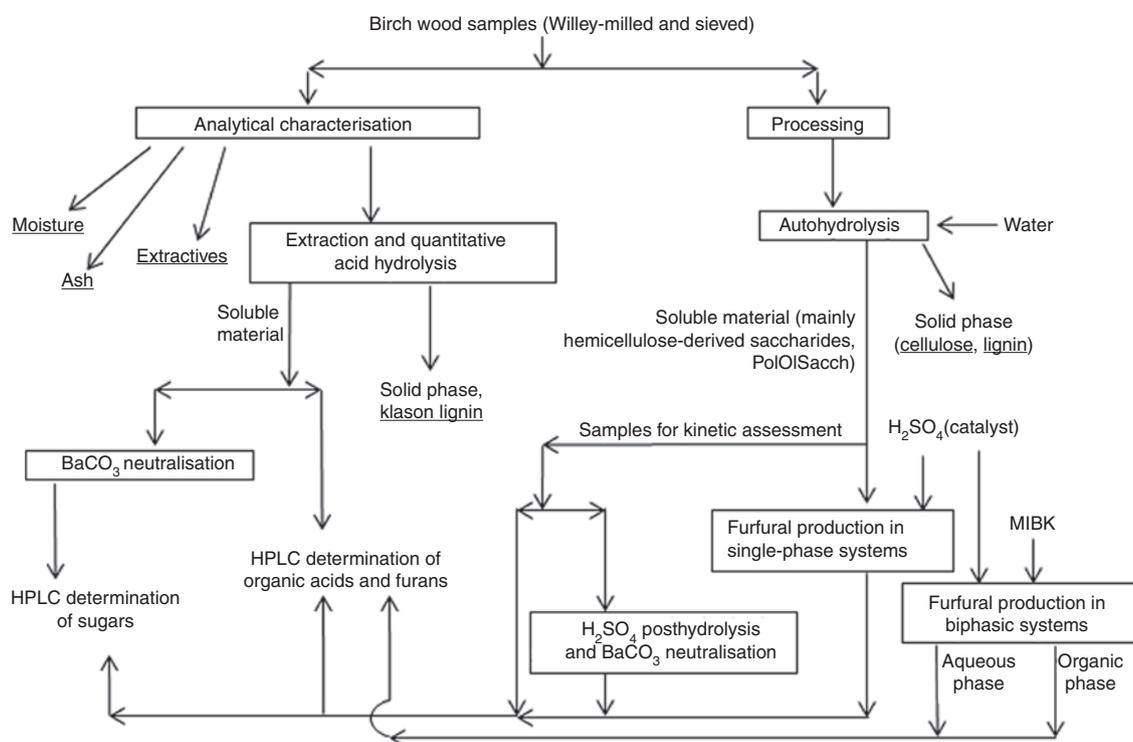
**Figure 1:** General procedure for analysis and processing followed in this study.

Table 2: Operational conditions defining the experiments in the biphasic MIBK/aqueous system, expressed in terms of dimensional and dimensionless variables.

Exp. no.	Dimensional			Dimensionless		
	T (°C)	t (min)	Or/Aq-R (v/v)	T (x_1)	t (x_2)	Or/Aq-R (x_3)
1	160	60	0.5	-1	0	-1
2	160	30	1.25	-1	-1	0
3	160	90	1.25	-1	1	0
4	160	60	2	-1	0	1
5	170	30	0.5	0	-1	-1
6	170	90	0.5	0	1	-1
7	170	60	1.25	0	0	0
8	170	60	1.25	0	0	0
9	170	60	1.25	0	0	0
10	170	30	2	0	-1	1
11	170	90	2	0	1	1
12	180	60	0.5	1	0	-1
13	180	30	1.25	1	-1	0
14	180	90	1.25	1	1	0
15	180	60	2	1	0	1

Nomenclature: Or/Aq-R, volume ration between the organic and aqueous phases.

Results and discussion

Autohydrolysis: kinetic modeling and selection of operational conditions

The average composition listed in Table 1 confirms the dominance of the glucuronoxylan fraction, as well as the presence of a small amount of arabinosyl groups (which are also potential substrates for F production) esterified with OAc groups. Mannose and galactose are also part of polysaccharides. The overall amount of hemicelluloses, including substituents, accounted for 30.8% of the raw material [oven-dry basis (o.d.b)]. The compositional data determined in this work are in the range reported for birch species *Betula verrucosa* (Patt et al. 2006) and *B. pendula* (Helmerius et al. 2010; Borrega et al. 2011; Testova et al. 2014).

The kinetic modeling of heteroxylan autohydrolysis has been reported for a number of woods, including *Eucalyptus globulus* Labil. (Garrote and Parajó 2002), birch (Borrega et al. 2011), *Acer saccharum*, and *Populus tremuloides* (aspen) wood (Mittal et al. 2009). Some reported calculation schemes assume a set of series and parallel reactions, in which xylan (denoted as X_n , either considered as a single polymer or formed by two fractions with different reactivities) is converted in xylose-containing oligomers [eventually, with different average degrees of polymerization (DP)], which are hydrolyzed into xylose.

This sugar is dehydrated into F, which acts as a substrate for further reactions. In some cases, the arabinosyl groups linked to xylan (Ar_n) are still present as xylooligosaccharide substituents ($ArOl$), and give rise to arabinose (Ara) upon hydrolysis and both xylose (Xyl) and Ara are dehydrated into F. Simultaneously, acetyl groups in xylan (OAc_n) are still present in oligomers ($OAcOl$), and yield AA upon hydrolysis.

The optimal generation of the pentoses and polysaccharides made up of pentoses was estimated (data not shown) and the best interpretation of experimental data was achieved with the set of reactions shown in Figure 2: xylan is assumed to contain a susceptible fraction X_{ns} (i.e. a part of it is not reactive under the tested conditions). The susceptible fraction is calculated as a regression parameter by extrapolation of the 1st order decay of xylan at an infinite reaction time. X_{ns} is converted sequentially into oligomers with high molecular weight (XOl_H), low molecular weight (XOl_L), Xyl, F, and decomposition products (decPr). Additional F generation from XOl_L and F consumption by reaction with xylose had to be included in the model for improved fitting. As previously described by Parajó et al. (2004) and Kumar and Wyman (2008), XOl_L can be directly converted to F in hydrothermal processes in high yields, whereas reactions between F and either

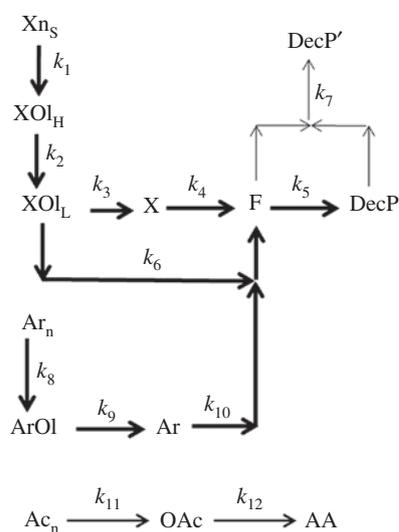


Figure 2: Kinetic mechanism considered for wood autohydrolysis. Nomenclature: X_{ns} : xylan susceptible to hydrolysis; XOl_H and XOl_L : high and low molecular weight xylooligosaccharides, respectively; X, xylose; F, furfural; Ar_n , arabinosyl units present in hemicelluloses; $ArOl$, arabinosyl groups in soluble saccharides; Ar, arabinose; Ac_n , acetyl groups in polymeric hemicelluloses; OAc, acetyl groups linked to soluble saccharides; AA, acetic acid; DecP and DecP', decomposition products. Thick arrows correspond to productive reactions leading to furfural production; thin arrows indicate furfural-consuming reactions or AA generation.

xylose or xylose-to-F intermediates have been discussed in literature (Zhang et al. 2014). F can also be consumed by resinification reactions so that very different types of F-derived products can be expected. The hydrolysis of arabinosyl units linked to xylan or oligosaccharides and the subsequent dehydrogenation to AA from OAc groups may also occur.

The reactions in Figure 2 are irreversible, pseudo-homogeneous, and obey 1st order kinetics with an Arrhenius-type temperature dependence:

$$k_i = k_{oi} \exp\left(-\frac{Ea_i}{R \cdot T}\right) \quad (4)$$

where k_i (i : 1–12) corresponds to the kinetic coefficients, k_{oi} is for pre-exponential factors, and Ea_i for activation energies. The set of differential equations directly derived from the kinetic model were solved numerically by the 4th order Runge-Kutta method (Garrote and Parajó 2002; Yáñez et al. 2009; González et al. 2011). The fitting results are presented in Table 3, and the correspondence between experimental and calculated concentration values are presented in Figure 3a and b.

The proportion of reactive xylan under the tested conditions (measured by the “susceptible fraction” α), was 0.88 g g⁻¹, close to the results reported by Parajó et al. (2004) for *Eucalyptus* wood (0.855 g g⁻¹) and corn cobs (0.865 g g⁻¹), and by Yáñez et al. (2009) for *Acacia dealbata* (0.875 g g⁻¹).

The concentration profiles determined for both xylan and OAc groups were compatible with the predicted exponential decrease (Figure 3a and b), reaching values of 3.7 and 0.4 g l⁻¹, respectively, under the severest conditions.

Table 3: Results obtained for the susceptible fractions (α), preexponential factors (k_{oi}), activation energies (Ea_i), and R² (see Figure 2 for nomenclature).

	Ln k_{oi} (k_{oi} in h ⁻¹)	Ea_i (kJ mol ⁻¹)	R ²
k_1	19.9	65.6	0.995
k_2	23.4	63.6	0.982
k_3	21.2	78.3	0.971
k_4	25.9	95.9	0.838
k_5	15.2	104.2	0.931
k_6	9.9	95.0	0.896
k_7	22.2	79.3	0.868
k_8	15.0	124.7	0.892
k_9	28.9	98.7	0.978
k_{10}	24.6	90.5	0.821
k_{11}	10.3	28.2	0.989
k_{12}	40.3	153.3	0.988

Susceptible fraction: $\alpha=0.88$ g susceptible xylan per g xylan.

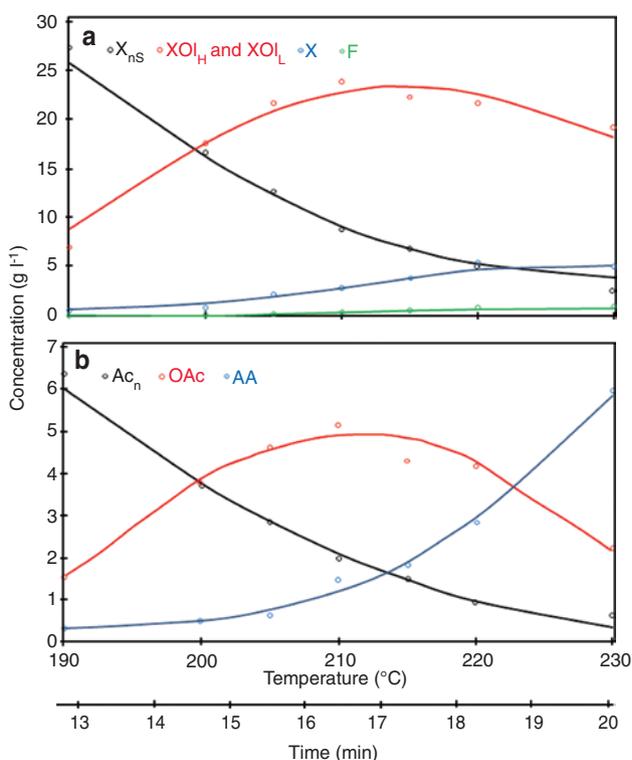


Figure 3: Experimental and calculated concentration profiles for susceptible xylan (X_{ns}) and reaction products. XO_{IH} , high molar mass soluble saccharides; XO_{L} , low molar mass soluble saccharides; X, xylose; F, furfural.

The activation energies and the preexponential factors were near the ones reported for *Eucalyptus globulus* by Parajó et al. (2004). Arabinan shows a comparatively high susceptibility to hydrolysis leading to total conversion under harsh conditions.

Xylooligosaccharides (including the ones of low and high DPs) and xylose are the major potential substrates for F production. The kinetic model predicted a maximum xylooligosaccharide concentration of 23.5 g l⁻¹ which is in the range reported in related studies (Garrote et al. 2008; Yáñez et al. 2009). In this work, these conditions were selected for further operation, which lead to maximum yield of the total F concentration, C5 sugars, and their oligomers and polymers.

The detailed analysis of the stock solution is listed in Table 4. The concentration of sugars and potential sugars, i.e. also the poly and oligosaccharides, which could be saccharified stoichiometrically are (in mmol l⁻¹): glucose 5.20, xylose 147.6, galactose 8.20, arabinose 2.35, and mannose 7.37. The identified compounds account for the 92.9% of nonvolatile dissolved compounds (34.6 g kg⁻¹ liquor). However, other nonvolatile components correspond to nonsaccharide products that could participate in unwanted

Table 4: Composition of *Betula alba* autohydrolysis liquors obtained under optimal conditions.

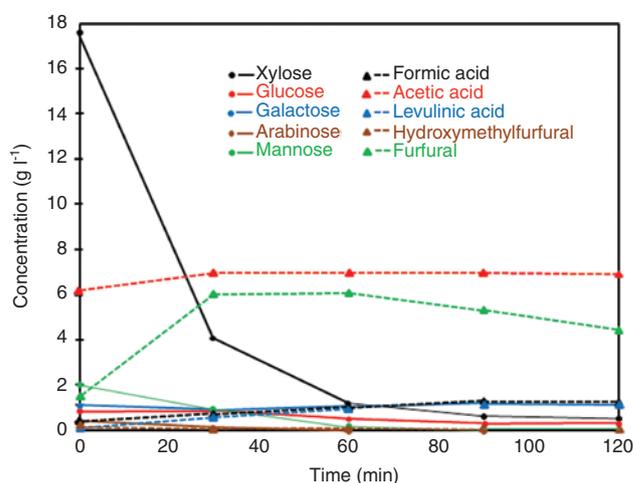
Component	Conc. (mmol l ⁻¹)
Glucose	1.22
Xylose	28.6
Galactose	2.85
Arabinose	2.35
Mannose	0.00
Acetic Acid	39.2
Formic Acid	4.68
Hydroxymethylfurfural	0.83
Furfural	8.01
Units in PolISacch:	
Glucosyl units	3.98
Xylosyl units	119.0
Galactosyl units	5.36
Arabinosyl units	0.00
Mannosyl units	7.37
Acetyl groups	71.2
Uranyl groups	8.73

PolISacch, Poly or oligosaccharides.

side reactions with F in subsequent reaction stages. The material balance shows that 80.5% of the pentosans in the raw material are recovered as F, pentoses, and higher molecular mass saccharides, accounting for about 97% of the solubilized pentosans; thus, decomposition reactions did not play an important role under these conditions.

Furfural production from autohydrolysis liquors in single-phase experiments

Figure 4 shows the concentration profiles determined when the autohydrolysis liquors were treated at 170°C in the presence of 1% H₂SO₄. The mixture of polymeric and oligomeric saccharides (PolISacch) was completely depleted during the heating up period, and a part of xylose (33.9% of the potential amount) was already converted at the beginning of the isothermal stage. Residual xylose (about 2% of the theory) was still present after 120 min of isothermal operation. At the beginning of the isothermal stage, 91.7% of the potential glucose remained in the reaction medium, in comparison to 29.8% after 120 min isothermal operation. Under these conditions, the rest of the sugars in the medium (mannose, galactose, and arabinose) were depleted. The different susceptibility of the various sugars to dehydration is clearly seen in accordance with the literature (Rivas et al. 2014). The dehydration of hexoses led to the formation of 5-hydroxymethylfurfural (HMF), but in low concentrations because of the low amounts of hexoses in the feed and by side

**Figure 4:** Concentration profiles determined for the potential sugars, furans, and organic acids operating under isothermal conditions at 170°C in media containing 1% H₂SO₄.

reactions. Both formic acid (FA) and levulinic acid (LA) are HMF rehydration products. The increase in AA concentration is ascribed to the hydrolysis of residual OAc groups linked to PolISacch. The concentration of F as the target product increased in the first 30–45 min of isothermal processing and then decreased owing to the side reactions.

The highest experimental F concentration (44.8% of the theory) was obtained after 60 min, a result that is in agreement with that in the literature (Sánchez et al. 2013; García-Domínguez et al. 2013, 2015), whereas harsher conditions resulted in lower F concentrations. The formation of humins under harsh conditions was evidenced by the darkening of reaction media.

Optimization of furfural production from autohydrolysis liquors in biphasic media

For F yield improvement, the process was also carried out in the presence of MIBK, which is a good extraction agent for F from aqueous media and allows an easy recover (Rivas et al. 2013; Zaitseva et al. 2014). F can be separated from MIBK by distillation, and the remaining MIBK can be reused (Zaitseva et al. 2014). Transferring F to the organic phase limits its consumption by the side reactions. Table 5 shows the compositional data in the aqueous and organic phases after the experiments listed in Table 2.

High sugar yields were achieved in most experiments, and F accumulated in the MIBK phase. The partition of a given reaction product *i* between the two phases was measured by the extraction ratio R_i , defined as the ratio of the concentrations of component *i* in organic and aqueous

Table 5: Concentrations of the reaction products present in the aqueous and organic phases.

Exp	Conc. in aqueous phase (g l ⁻¹)					Conc. in MIBK phase (g l ⁻¹)				
	FA	AA	LA	HMF	F	FA	AA	LA	HMF	F
1	0.313	4.899	0.165	0.171	1.724	0.248	3.268	0.262	0.221	12.494
2	0.414	4.317	0.139	0.129	0.624	0.158	2.395	0.111	0.157	4.950
3	0.436	4.352	0.293	0.193	0.825	0.271	2.472	0.228	0.223	6.782
4	0.505	3.174	0.409	0.173	0.552	0.156	1.912	0.110	0.210	4.274
5	0.449	5.478	0.417	0.183	1.799	0.215	3.277	0.486	0.217	12.385
6	0.844	5.487	0.851	0.116	1.867	0.345	3.153	0.511	0.139	13.036
7	0.447	5.014	0.605	0.175	0.910	0.204	2.339	0.311	0.206	6.979
8	0.666	4.527	0.687	0.195	0.886	0.266	2.523	0.315	0.173	6.986
9	0.865	4.591	0.606	0.178	1.286	0.226	2.929	0.343	0.185	6.764
10	0.465	3.556	0.216	0.181	0.599	0.184	2.086	0.172	0.224	4.713
11	0.399	3.373	0.385	0.155	0.623	0.225	2.006	0.279	0.182	4.761
12	0.682	5.044	0.910	0.056	1.593	0.389	2.892	0.231	0.065	12.379
13	0.818	4.788	0.691	0.141	0.904	0.333	2.934	0.365	0.162	6.845
14	0.531	4.153	0.820	0.025	0.807	0.349	2.378	0.455	0.031	6.512
15	0.365	3.587	0.490	0.083	0.610	0.240	2.055	0.257	0.094	4.549

FA, Formic acid; AA, acetic acid; LA, levulinic acid; HMF, hydroxymethylfurfural; F, furfural.

phases. According to the data in Table 5, the R_F values are in the range of 7–8. The percentage of F transferred to the organic phase is around 77%–78% in experiments with Or/Aq-R 0.5, 90%–91% with Or/Aq-R 1.25, and 93%–94% with Or/Aq-R 2. The HMF concentrations were similar in aqueous and organic phases (average R_{HMF} 1.17), whereas levulinic, formic, and acetic acids showed a higher affinity for the aqueous phase (average extraction ratios, 0.67, 0.49, and 0.56, respectively).

For optimization purposes, the following dependent variables were defined:

- y_1 : F molar yield, total mol F generated (in both phases) per 100 mol of potential pentoses
- y_2 : HMF molar yield, total mol HMF generated (in both phases) per 100 mol of potential hexoses
- y_3 : levulinic molar yield, total mol levulinic acid generated (in both phases) per 100 mol of potential hexoses

The results determined for these dependent variables are listed in Table 6. The maximum F molar yield ($y_1=74.9\%$) was obtained in experiment 11, performed at the longest time and largest Or/Aq-R ratio, whereas the selectivity (defined as mol of F per 100 mol of potential pentoses consumed) was 76.8%. The maximum HMF molar yield ($y_2=23.6\%$) was achieved in experiment 10 (performed at the intermediate temperature, shortest reaction time and higher Or/Aq-R), whereas the maximum LA molar yield ($y_3=56.5\%$) was reached in experiment 14 (performed at the highest temperature for the longest reaction time with an intermediate Or/Aq-R). The results confirm that the optimal conditions for HMF and F production are markedly

Table 6: Values of the dependent variables y_1 to y_3 calculated from the results listed in Table 5.

Exp	Dependent variables		
	y_1 (%)	y_2 (%)	y_3 (%)
1	58.8	10.5	12.0
2	50.3	12.2	11.3
3	68.7	17.7	23.5
4	67.2	22.2	25.6
5	59.0	10.9	26.9
6	61.9	6.9	45.0
7	71.1	16.2	40.5
8	71.0	15.4	44.0
9	71.9	15.3	42.1
10	74.0	23.6	22.8
11	74.9	19.4	38.4
12	57.5	3.3	41.7
13	69.9	12.9	46.7
14	66.1	2.4	56.5
15	71.7	10.2	40.9

different, in agreement with the literature (Rivas et al. 2014). Because LA is formed from HMF, harsh conditions were needed to reach its maximum concentration. In any case, the concentrations of HMF and LA were limited by the low amounts of hexoses in the autohydrolysis liquors.

Following the RSM approach, the independent and dependent variables were considered to be related by equations including 1st order, interaction, and 2nd order terms, according to:

$$y_j = b_{0j} + \sum_i b_{ij} x_i + \sum_i \sum_k b_{ikj} x_i x_k \quad (5)$$

where y_j (j : 1–3) stands for the dependent variables, x_i or x_k (i or k : 1–3, $k \geq i$) are the independent and dimensionless variables, and b_{0j}, \dots, b_{ikj} are the regression coefficients.

The coefficients obtained by regression analysis are listed in Table 7 including their statistical significance (based on a t -test), and statistical parameters measuring the correlation and significance of the equations (R^2 and F).

The model calculated for the F molar yield y_1 shows significant coefficients affecting linear, interaction, and 2nd order terms. Figure 5a shows the calculated dependence of y_1 on T and t for Or/Aq-R 2: values slightly above 75% were predicted for a range of experimental conditions defined by either prolonged reaction times and intermediate temperatures or short times and high temperatures. The maximum F molar yield (76.5%) was predicted for treatments lasting 56 min at 174°C and Or/Aq-R 2. Under the same conditions, the values predicted for y_2 and y_3 were 18.5 and 38.4%, respectively. The model prediction was close to the highest experimental F yield (74.9%, achieved in experiment 11, performed at 170°C for 90 min with Or/Aq-R 2). Under these conditions, the model predicted 75.6% yield, confirming its suitability for quantitative estimations.

Figure 5b and c show the surface responses describing the dependence of y_2 and y_3 on selected operational variables. Even if both y_2 and y_3 are of limited importance for the purposes of this study (because of the low amounts of hexoses and their oligomers), it can be highlighted that the maximum y_2 (24.4%) was predicted for 90 min operation at 160°C with Or/Aq-R 2 (which compares well with 23.6% obtained in experiment 10 under related conditions). Concerning y_3 ,

Table 7: Regression coefficients and statistical parameters obtained by data analysis.

Para-meter	Dependent variables (y)		
	y_1	y_2	y_3
b_{0j}	71.36 ^a	15.63 ^a	42.19 ^a
b_{1j}	2.505 ^c	-4.244 ^a	14.17 ^a
b_{2j}	2.298 ^c	-1.649 ^b	6.970 ^b
b_{3j}	6.326 ^a	5.467 ^a	0.266
b_{12j}	-5.546 ^b	-3.999 ^a	-0.590
b_{13j}	1.470	-1.216	-3.612
b_{23j}	-0.507	-0.057	-0.656
b_{11j}	-5.651 ^b	-3.998 ^a	-5.436
b_{22j}	-1.990	-0.341	-2.245
b_{33j}	-1.915	-0.068	-6.700 ^c
R^2	0.941	0.982	0.935
F exp	8.834	30.17	8.009

^{a, b, c}Significant coefficients at the 99, 95, and 90% confidence levels, respectively.

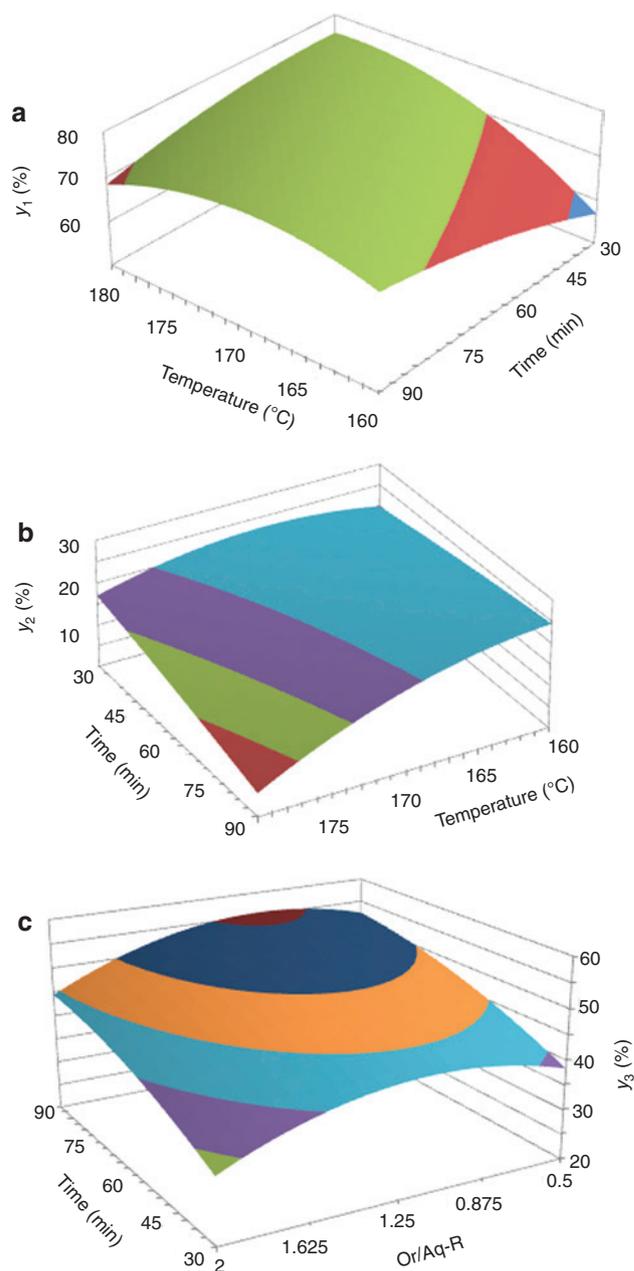


Figure 5: Response surfaces calculated for the dependent variables. (a) Dependence of y_1 on T and time at Or/Aq-R=2; (b) dependence of y_2 on T and time, at Or/Aq-R=2; (c) dependence of y_3 on time and Or/Aq-R at $T=180^\circ\text{C}$.

the maximum value (55.6%) was predicted by the model for 90 min operation at 180°C with Or/Aq-R 1.03. Again, this value is close to the best experimental y_3 (56.5%, reached in experiment 14, performed at the same temperature and reaction time, but at a slightly higher Or/Aq-R).

A number of articles on F production from biomass, xylan, or xylose in biphasic media have been published. Weingarten et al. (2010) reported a kinetic model for

xylose dehydration into F in a water-MIBK system with HCl as a catalyst, and estimated F yields of about 80%, in contrast with 30% yield in single phase operation. Rivas et al. (2013) employed MIBK as an extraction agent and H_2SO_4 as a catalyst for the dehydration of hemicellulosic saccharides from aqueous solutions derived from the autohydrolysis of *Pinus pinaster* wood, achieving 74.9% F yield together with HMF and LA as reaction coproducts. Yang et al. (2012) produced F from a number of feedstocks in a water-THF biphasic medium containing $AlCl_3 \cdot 6 H_2O$ and NaCl. The F yields from various substrates were 75% (xylose), 64% (xylan), 55% (corn stover), 38% (pine wood), 56% (switch grass), and 64% (poplar wood). Wang et al. (2015) obtained 78.1% F yield from xylan-type hemicelluloses with $SnCl_4$ as catalyst in a biphasic system made up of 2-methyl-THF and water.

Conclusions

Birch (*Betula alba*) wood is a good raw material for furfural production based on its comparatively high content of acetylated xylan. Performing consecutive steps of autohydrolysis (for hemicellulose solubilization and separation from lignin and cellulose) and acidic processing (with 1% H_2SO_4) for further furfural production) is a viable approach. Operating under selected conditions (60 min at 170°C in the presence of 1% H_2SO_4), the theoretical furfural yield was 44.8%. The results were further improved in presence of MIBK as organic phase, in which furfural is highly soluble. In a set of experiments, the production of furfural, HMF, and LA was assessed by the statistical response surface methodology. Theoretical furfural yields of about 75% were identified. The generation of HMF and LA is also possible from the hexoses present in autohydrolysis liquors.

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References

Agirrezabal-Telleria, I., Larreategui, A., Requies, J., Güemez, M.B., Arias, P.L. (2011) Furfural production from xylose using sulfonic ion-exchange resins (Amberlyst) and simultaneous stripping with nitrogen. *Bioresource Technol.* 102:7478–7485.

- Baktash, M.M., Ahsan, L., Ni, Y. (2015) Production of furfural from an industrial pre-hydrolysis liquor. *Sep. Purif. Technol.* 149:407–412.
- Blumenkrantz, N., Asboe-Hansen, G. (1973) New method for quantitative determination of uronic acids. *Anal. Biochem.* 54:484–489.
- Borrega, M., Nieminen, K., Sixta, H. (2011) Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. *Bioresource Technol.* 102:10724–10732.
- Borrega, M., Tolonen, L.K., Bardot, F., Testova L., Sixta H. (2013) Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping. *Bioresource Technol.* 135:665–671.
- Bozell, J.J., Petersen, G.R. (2010) Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green Chem.* 12:539–554.
- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E. (2014) Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *J. Chem. Technol. Biotechnol.* 89: 2–10.
- Choi, S., Song, C.W., Shin, J.H., Lee, S.Y. (2015) Biorefineries for the production of top building block chemicals and their derivatives. *Metab. Eng.* 28:223–239.
- Dalin Yebo (2015) Information retrieved from <http://www.dalinyebo.com/>. Last accessed, December 2015.
- De Jong, E., Higson, A., Walsh, P., Wellish, M. (2012). Value added products from biorefineries. IEA Bioenergy. Task 42: Biorefinery. Downloaded from: <http://www.ieabioenergy.com/wp-content/uploads/2013/10/Task-42-Biobased-Chemicals-value-added-products-from-biorefineries.pdf>. Last accessed, December 2015.
- Ebringerová, A., Hromádková, Z., Heinze, T. (2005) Hemicellulose. *Adv. Polym. Sci.* 186:1–67.
- García-Domínguez, M.T., García-Domínguez, J.C., Ferial, M.J., Gómez-Lozano, D.M., López, F., Díaz, M.J. (2013) Furfural production from *Eucalyptus globulus*: optimizing by using neural fuzzy models. *Chem. Eng. J.* 221:185–192.
- García-Domínguez, M.T., García-Domínguez, F., López, F., de Diego, C.M., Díaz, M.J. (2015) Maximizing furfural from wheat straw and *Eucalyptus globulus* by nonisothermal autohydrolysis. *Environ. Prog. Sustain. Energy.* 34:1236–1242.
- Garrote, G., Parajó, J.C. (2002) Non-isothermal autohydrolysis of *Eucalyptus wood*. *Wood Sci. Technol.* 36:111–123.
- Garrote, G., Yáñez, R., Alonso, J.L., Parajó, J.C. (2008) Coproduction of oligosaccharides and glucose from corncobs by hydrothermal processing and enzymatic hydrolysis. *Ind. Eng. Chem. Res.* 47:1336–1346.
- González, D., Santos, V., Parajó, J.C., 2011. Manufacture of fibrous reinforcements for biocomposites and hemicellulosic oligomers from bamboo. *Chem. Eng. J.* 167:278–287.
- Gorgoso-Varela, J.J., Afif-Khouri, E., Barrio-Anta, M., Rojo-Alboreca, A. (2008) Modelling diameter distributions of birch (*Betula alba* L.) and pedunculate oak (*Quercus robur* L.) stands in northwest Spain with the beta distribution. *Invest. Agr.: Sist. Recur. Forest.* 17:271–281.
- Gullón, P., González-Muñoz, M.J., van Gool, M.P., Schols, H.A., Hirsch, J., Ebringerová, A., Parajó, J.C. (2011) Structural features and properties of soluble products derived from *Eucalyptus globulus* hemicelluloses. *Food Chem.* 127:1798–1807.

- Gürbüz, E.I., Wettstein, S.G., Dumesic, J.A. (2012) Conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alkylphenol solvents. *ChemSusChem* 5:383–387.
- Helmerius, J., Vinblad von Walter, J., Rova, U., Berglund, K.A., Hodge, D.B. (2010) Impact of hemicellulose pre-extraction for bioconversion on birch kraft pulp properties. *Biores. Technol.* 101:5996–6005.
- Koch, S., Kindler, A. (2015) Production of furfural from xylose. *Pat. WO2015/087248*.
- Kumar, R., Wyman, C.E. (2008) The impact of dilute sulfuric acid on the selectivity of xylooligomer depolymerization to monomers. *Carbohydr. Res.* 343:290–300.
- Lange, J.P., van der Heide, E., van Buijtenen, J., Price, R. (2012) Furfural- a promising platform for lignocellulosic biofuels. *ChemSusChem* 5:150–166.
- Liu, H., Hu, H., Jahan, M.S., Ni, Y. (2015) Improvement of furfural production from concentrated prehydrolysis liquor (PHL) of a kraft based hardwood dissolving pulp production process. *J. Wood Chem. Technol.* 35:260–269.
- Mittal, A., Chatterjee, S.G., Scott, G.M., Amidon, T.E. (2009) Modeling xylan solubilization during autohydrolysis of sugar maple and aspen wood chips: reaction kinetics and mass transfer. *Chem. Eng. Sci.* 64:3031–3041.
- Nakagame, S., Dano, N., Obuchi, T., Hagiwara, S., Uchida, Y., Kisara, K., Sasaki, T. (2014) Method for manufacturing monosaccharides, oligosaccharides and furfurals from biomass. *US Patent 2014/0288298 A1*.
- Parajó, J.C., Garrote, G., Cruz, J.M., Domínguez, H. (2004) Production of xylooligosaccharides by autohydrolysis of lignocellulosic materials. *Trends Food Sci. Technol.* 15:115–120.
- Patt, R., Kordsachia, O., Fehr, J. (2006) European hardwoods versus *Eucalyptus globulus* as a raw material for pulping. *Wood Sci. Technol.* 40:39–48.
- Rivas, S., González-Muñoz, M.J., Santos, V., Parajó, J.C. (2013) Production of furans from hemicellulosic saccharides in biphasic reaction systems. *Holzforschung* 67:923–929.
- Rivas, S., González-Muñoz, M.J., Santos, V., Parajó, J.C. (2014) Acidic processing of hemicellulosic saccharides from pine wood: product distribution and kinetic modeling. *Bioresource Technol.* 162:192–199.
- Sánchez, C., Serrano, L., Andres, M.A., Labidi, J. (2013) Furfural production from corn cobs autohydrolysis liquors by microwave technology. *Industrial Crop. Prod.* 42:513–519.
- Teleman, A., Larsson, P.T., Iversen, T. (2001) On the accessibility and structure of xylan in birch kraft pulp. *Cellulose* 8:209–215.
- Testova, L., Chong, S.L., Tenkanen, M., Sixta, H. (2011) Autohydrolysis of birch wood. *Holzforschung* 65:535–542.
- Testova, L., Borrega, M., Tolonen, L.K., Penttilä, P.A., Serimaa, R., Larsson, P.T., Sixta, H. (2014) Dissolving-grade birch pulps produced under various prehydrolysis intensities: quality, structure and applications. *Cellulose* 21:2007–2021.
- Vila, C., Romero, J., Francisco, J.L., Santos, V., Parajó, J.C. (2012) On the recovery of hemicellulose before kraft pulping. *BioResources* 7:4179–4189.
- Vila, C., Santos, V., Parajó J.C. (2014) Manufacture of microcrystalline cellulose from wood using an environmentally friendly biorefinery method. *J. Wood Chem. Technol.* 34:8–19.
- Wang, W., Ren, J., Li, H., Deng, A., Sun, R. (2015) Direct transformation of xylan-type hemicelluloses to furfural via SnCl_4 catalysts in aqueous and biphasic systems. *Bioresource Technol.* 183:188–194.
- Weingarten, R., Cho, J., Conner, W.C., Huber, W. (2010) Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem.* 12:1423–1429.
- Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., Manheim, A., Eliot, D., Lasure, L., Jones, S. (2004) *Top Value Added Chemicals from Biomass – Vol. 1: Results of Screening for Potential Candidates from Sugars and Synthesis Gas*. Downloaded from: <http://www.nrel.gov/docs/fy04osti/35523.pdf>. Last accessed, December 2015.
- Yan, K, Wu, G., Lafleur, T., Jarvis, C. (2014) Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. *Renew. Sust. Energ. Rev.* 38: 663–676.
- Yáñez, R., Romaní, A., Garrote, G., Alonso, J.L., Parajó, J.C. (2009) Processing of *Acacia dealbata* in aqueous media: first step of a wood biorefinery. *Ind. Eng. Chem. Res.* 48:6618–6626.
- Yang, Y., Hu, C.W., Abu-Omar, M.M. (2012) Synthesis of furfural from xylose, xylan and biomass using $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ in biphasic media via xylose isomerization to xylulose. *ChemSusChem*, 5:405–410.
- Zaitseva, A., Laavi, H., Pokki, J.P., Uusi-Kyyny, P., Alopaeus, V. (2014) Isothermal vapor-liquid equilibrium and excess molar enthalpies of the binary mixtures furfural+methyl isobutyl ketone, +2-butanol and +2-methyl-2-butanol. *Fluid Phase Equilib.* 372:85–99.
- Zhang, Z., Du, B., Quan, Z.J., Da, Y.X., Wang, X.C. (2014) Dehydration of biomass to furfural catalyzed by reusable polymer bound sulfonic acid (PEG-OSO₃H) in ionic liquid. *Catal. Sci. Technol.* 4:633–638.