Kinetics of 5-Hydroxymethylfurfural Production from Monosaccharides in Media Containing an Ionic Liquid and a Solid Acid Catalyst

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Glucose and mannose, the major structural units found in softwood hemicelluloses, were used to produce 5-hydroxymethylfurfural (HMF) in the ionic liquid 1-butyl-3-methylimidazolium chloride, in the presence of a commercial zeolite (which acted as an acidic catalyst), and in the presence or absence of co-catalysts. Experiments were performed under diverse operational conditions, and the reaction kinetics were interpreted by a mechanism involving three major reactions (non-productive substrate conversion, HMF generation, and HMF decomposition). Activation energies were determined for the best reaction medium.

Keywords: 5-Hydroxymethylfurfural; Glucose; Hexoses; Ionic liquid; Mannose

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INTRODUCTION

Economic growth based on the intensive consumption of fossil resources is threatened by multiple issues, for example, their limited availability, price volatility, unstable supply, and environmental impact. The transition to a bio-economy in which specific needs are fulfilled from renewable resources provides a sustainable alternative to the current situation. In this context, the manufacture of platform chemicals from lignocellulosic biomass is attracting the interest of the scientific community.

Lignocellulosic materials contain polysaccharides made up of hexoses and pentoses. Cellulose (made up of glucose units) and softwood hemicelluloses (mainly made up of glucose and mannose) can be easily converted into the corresponding monosaccharides (for example, by prehydrolysis or autohydrolysis-posthydrolysis) and further dehydrated to yield 5-hydroxymethylfurfural (HMF). This compound has applications in the manufacture of chemicals (2,5-furandicarboxylic acid, 2,5-bis (hydroxymethyl) tetrahydrofuran, and levulinic acid), biofuels (2,5-dimethylfuran, 2-methylfuran, and alkanes), and medicine (Rosatella *et al*. 2011; Dutta *et al.* 2013). Some of the above compounds have been identified as the important chemicals from biomass (Werpy and Petersen 2004; Bozell and Petersen 2010).

The manufacture of HMF from polysaccharide-containing raw materials, purified polysaccharides, biomass hydrolyzates, and monosaccharides (considered model compounds) has been traditionally performed in acidic aqueous media, but the yields are often limited by side reactions leading to unproductive substrate conversion (for example, to yield fragmentation or condensation products) and HMF consumption (for example, rehydration reactions yielding equimolecular amounts of formic and levulinic acids or condensation products yielding humins). Thus, HMF production has been performed in non-aqueous media, including ionic liquids (ILs).

Ionic liquids are salts with melting points near ambient temperature. The special chemical, physical, and technological properties of ILs (*e.g.*, negligible vapor pressure, non-flammability, low toxicity, chemical and thermal stability, and solvation capability) define their "green" character and foster a number of applications as reaction media and separation processes (Peleteiro *et al*. 2015). Exhaustive information on the properties and utilization of representative ILs as solvents for synthesis and catalysis can be found in the review by Hallett and Welton (2011). In particular, imidazolium-based ILs have been widely employed for processing carbohydrates. One example is 1-butyl-3-methylimidazolium chloride ([bmim]Cl), which has favorable behavior as a solvent for furan production from biomass, biomass-derived products, and fractions. In this field, the review by Zakrzewska *et al.* (2011) provides extensive information on HMF production in ILs.

Dehydrating hexoses into HMF in [bmim]Cl with good yields requires catalysts. Of the wide variety of possible catalysts, solid acid catalysts provide the advantage of easy separation of the reaction media, allowing its direct reutilization in further reaction cycles, which is beneficial for sustainable conversion technologies. A number of solid acid catalysts have been used for furan production, including cation exchange resins, heteropolyacids, lignin-derived materials, and zeolites. Acidic porous solid catalysts are highly attractive due to the potential for combined acidic catalysis and shape-selective catalysis (Zhang *et al*. 2017). In addition, zeolites have many catalytic sites and high thermal stability, meeting the desired conditions for HMF production (Rinaldi and Schüth 2009).

This work deals with the kinetics of HMF production from glucose and mannose in [bmim]Cl media using a commercial zeolite as a catalyst. Additional experiments were carried out in the presence of a selected co-catalyst to increase both the reaction rate and HMF yield. The results were interpreted on the basis of a simplified kinetic model, which includes the consumption of the considered substrates by productive and non-productive reactions and HMF degradation. This research provides key information to assess the manufacture of HMF from softwood hemicellulose hydrolyzates.

EXPERIMENTAL

Materials

The solvent (1-butyl-3-methylimidazolium chloride), was purchased from Sigma-Aldrich (St. Louis, MO, USA), and the glucose and mannose standards were purchased from Scharlab (Barcelona, Spain) and Fluka (Bucharest, Romania), respectively. Other standards of assayed compounds including a possible intermediate (fructose), the target product (HMF), and possible rehydration products (levulinic and formic acids) were purchased from Sigma-Aldrich. The zeolite CBV-400 was purchased from Zeolyst International (Conshohocken, PA, USA). The co-catalysts H_2SO_4, $FeCl_3·6H_2O$, LiCl, WCl_6, and $SnCl_2$ were purchased from Prolabo (Llinars del Vallés, Spain), Merck Spain (Madrid, Spain), Fluka, and Sigma-Aldrich, respectively. $CrCl_3·6H_2O$, which was also used as a catalyst, was purchased from Panreac (Castellar del Vallés, Spain).

Reaction

The IL was molten and vacuum-dried to constant weight before being used in experiments. Dry [bmim]Cl samples were heated to the target temperature, and then mixed with the catalyst (eventually, with the considered co-catalyst) and the glucose or mannose substrate. All experiments were performed at the same substrate to solvent ratio (15 g [bmim]Cl/g sugar). The zero time was set when the substrate was added to the media. The reaction time was considered as an operational variable, and the longest reaction time considered was fixed for each set of operational conditions (see below). At preset reaction times, samples from the reaction media were withdrawn, diluted, and assayed for composition. Experiments and analysis were performed in duplicate, and the average values are reported.

Analytical Methods

Monosaccharide (glucose or mannose) and HMF in the reaction media were determined by high performance liquid chromatography (HPLC) using an Agilent 1260 instrument (Santa Clara, CA, USA) fitted with Refractive Index (RI) and Diode Array (DA) detectors (wavelength, 280 nm), as well as with an Aminex HPX-87H column. Because fructose is a reaction intermediate that is co-eluted with mannose in the above column, selected samples were assayed for monosaccharides by high performance anion-exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD) using an ICS3000 instrument (Dionex, Sunnyvale, CA, USA) equipped with a 250 × 4 mm CarboPac PA-1 column in combination with a 50 × 4 mm CarboPac PA-1 guard column (from Dionex, Sunnyvale, CA, USA). For better quantitation, peak deconvolution was carried out using Fityk software (Wojdyr 2010).

RESULTS AND DISCUSSION

Kinetics of HMF Production from Monosaccharides: General Aspects

The acidic processing of glucose in aqueous media follows a complex kinetic mechanism involving productive reactions (generation of isomers and/or intermediates and subsequent production of HMF from them) and parasitic reactions (including substrate fragmentation and/or reversion, HMF consumption by reactions with itself and/or with intermediates and/or substrate and/or other reactive species present in the reaction media, and HMF rehydration to yield levulinic and formic acids). The overall mechanism is still subjected to debate, and further details can be found in recent studies (Van Putten *et al*. 2013; Rasmussen *et al*. 2014). For practical reasons, simplifications to the above model are necessary for performing kinetic studies. For example, the glucose decomposition rate has been evaluated using a single lumped reaction without considering the individual reactions yielding various products, whereas additional reactions were proposed to incorporate the formation of HMF (Van Putten *et al*. 2013). Individual reactions have been interpreted on the basis of either first-order or power law kinetics. For example, Ramli and Amin (2016) considered a simplified mechanism involving four first-order reactions: glucose consumption by two reactions (leading, respectively, to HMF and undesired reaction products), and HMF consumption by two reactions (rehydration into formic and levulinic acids, and formation of humins). In comparison, little information is available on HMF production from glucose in ionic liquid media. Qi *et al*. (2010) considered the generation of HMF in [bmim]Cl catalyzed with chromium ions and determined the activation energy of the first-order reaction responsible for the overall glucose consumption, but no further kinetic discussion regarding HMF formation or decomposition was provided. Zhang *et al*. (2014) reported on the kinetics of HMF production from glucose in three alkylimidazolium chloride ionic liquids (including [bmim]Cl) catalyzed with chromium ions, in a study dealing with three reactions (glucose isomerization into fructose, fructose consumption to yield HMF, and fructose conversion into humins). The reaction of glucose followed second-order kinetics, and the HMF was generated through a first-order reaction. Hu *et al*. (2014) investigated the production of HMF from glucose in media catalyzed with zeolites under conditions leading to maximum HMF yields in the vicinity of 50%, and the calculated first-order coefficients for the overall glucose consumption, without quantitative kinetic assessment on HMF generation or decomposition. No additional studies dealing with the kinetic modeling of HMF generation in ionic liquids have been reported.

The mechanism considered in this study for HMF formation from glucose and mannose was based on the above ideas. Under the experimental conditions employed here, the rates of the reactions involving intermediates were comparatively fast, and no significant amounts of fructose were detected in the media. The experimental data were interpreted in terms of glucose consumption, HMF generation, and HMF decomposition. However, material balances showed that the glucose consumption could not be interpreted just on the basis of HMF formation, so non-productive substrate consumption was considered. Finally, no significant amounts of levulinic acid were found in the media, confirming that HMF rehydration did not occur. Notably, the amount of water in the media was very low in all cases, coming just from monosaccharide dehydration into HMF, and in some cases, from the hydrated salts employed as co-catalysts. In summary, the kinetic analysis performed in this work is based on the following premises: a) glucose (or mannose) is dehydrated into HMF according to a reaction governed by a kinetic coefficient denoted k_G in the case of glucose, and k_M in the case or mannose; b) glucose (or mannose) is consumed by non-productive reactions to yield undesired products according to a reaction governed by a kinetic coefficient denoted k_G' in the case of glucose, and k_M' in the case of mannose; c) HMF is consumed by a reaction with a kinetic coefficient k_{HMFG} or k_{HMFM}; and d) all coefficients follow an Arrhenius-type dependence on temperature. With these hypotheses, the differential equations describing the concentration profiles of substrate and HMF in reactions using glucose as a substrate are as follows,

$$-dC_G/dt = k_G\, C_G + k_G'\cdot C_G{}^2 \qquad (1)$$

$$dC_{HMF}/dt = k_G\cdot C_G - k_{HMFG}\cdot C_{HMF} \qquad (2)$$

where t is the reaction time (min), and C_G and C_{HMF} are the molar concentrations of glucose and HMF (mmol/L), respectively.

Equations 3 and 4 using mannose as a substrate follow the same expressions, denoting the mannose concentration as C_M, and replacing the G by M in the subscripts of Eqs. 1 and 2. The considered reactions are summarized in Fig. 1.

$$-dC_M/dt = k_M\, C_M + k_M'\cdot C_M{}^2 \qquad (3)$$

$$dC_{HMF}/dt = k_M\cdot C_M - k_{HMFM}\cdot C_{HMF} \qquad (4)$$

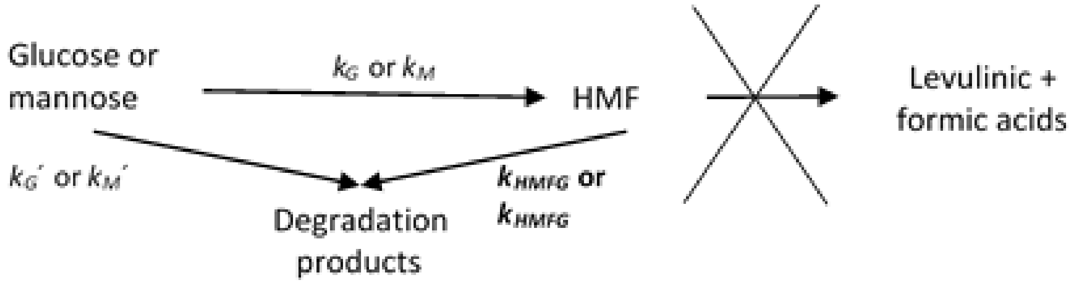

Fig. 1. Reaction mechanism employed for kinetic modeling

HMF Production from Glucose or Mannose in Media Containing Zeolite CBV-400

Acidic zeolites have been used as catalysts for the hydrolysis or hydrolysis-dehydration of cellulose, as they include Brønsted acid sites (proton donor) that allow the generation of reducing sugars and/or HMF. The zeolite CBV-400 employed in this study is characterized by a SiO_2/Al_2O_3 5:1 mole ratio, moderate acidic properties, a large porous structure, and a surface area of 730 m^2/g; it has been used for cellulose processing in ionic liquid media (Tan *et al*. 2011; Abou-Yousef and Hassan 2014).

To assess the ability of zeolite CBV-400 to catalyze HMF production from glucose and mannose, preliminary experiments (data not shown) were performed at temperatures and catalyst charges within ranges performed in literature. These results confirmed that obtaining good HMF yields at practical reaction times entailed operation at temperatures in the vicinity of 160 °C and catalyst charges of at least 6.67 g/100 g IL. The best results obtained in this stage of the study using glucose or mannose as substrates are shown in Fig. 2a and Fig. 2b. The calculated concentrations were obtained from the values determined for the kinetic parameters k_G, k_G', k_M, k_M', k_{HMFG}, and k_{HMFM} by regression of experimental data under the considered hypotheses.

The analysis of experimental data led to the following conclusions: a) the best fit was obtained considering first order for the consumption of substrates by productive reactions, and second order for non-productive reactions; b) this hypothesis led to the set of kinetic coefficients listed in Table 1; c) the proposed model gave a close reproduction of experimental data, as shown in Figs. 2a and 2b (see regression coefficients in Table 1); d) the maximum HMF concentration obtained from glucose was 46.5 mmol/L (which was achieved in the experiment with a zeolite charge of 10 g/100 g IL); e) the maximum HMF concentration obtained from mannose was 12.6 mmol/L after 15 min (which was achieved in the experiment with a zeolite charge of 10 g/100 g IL).

The values determined for the various kinetic coefficients justify the experimental trends observed in Fig. 2a and 2b on a quantitative basis. For each substrate, increasing the catalyst charge from 6.67 g/100 g IL to 10 g/100 g IL resulted in faster consumption kinetics by both the productive and non-productive reactions, but the coefficient governing the HMF-consuming reaction was fairly constant with the catalyst charge for a given substrate. In comparative terms, the catalyst charge had a greater effect on the coefficients governing the non-productive consumption of substrates than to the ones governing the productive dehydration of monosaccharides into HMF.

In comparison with mannose, the better performance of glucose as a substrate is justified by both its faster conversion into HMF and its more favorable balance between the coefficients governing the productive and non-productive glucose conversions. Additionally, the relative importance of non-productive substrate consumption reactions was higher for mannose in experiments performed at the lowest catalyst charge assayed, but reached similar values for glucose and mannose in assays at the highest catalyst charge.

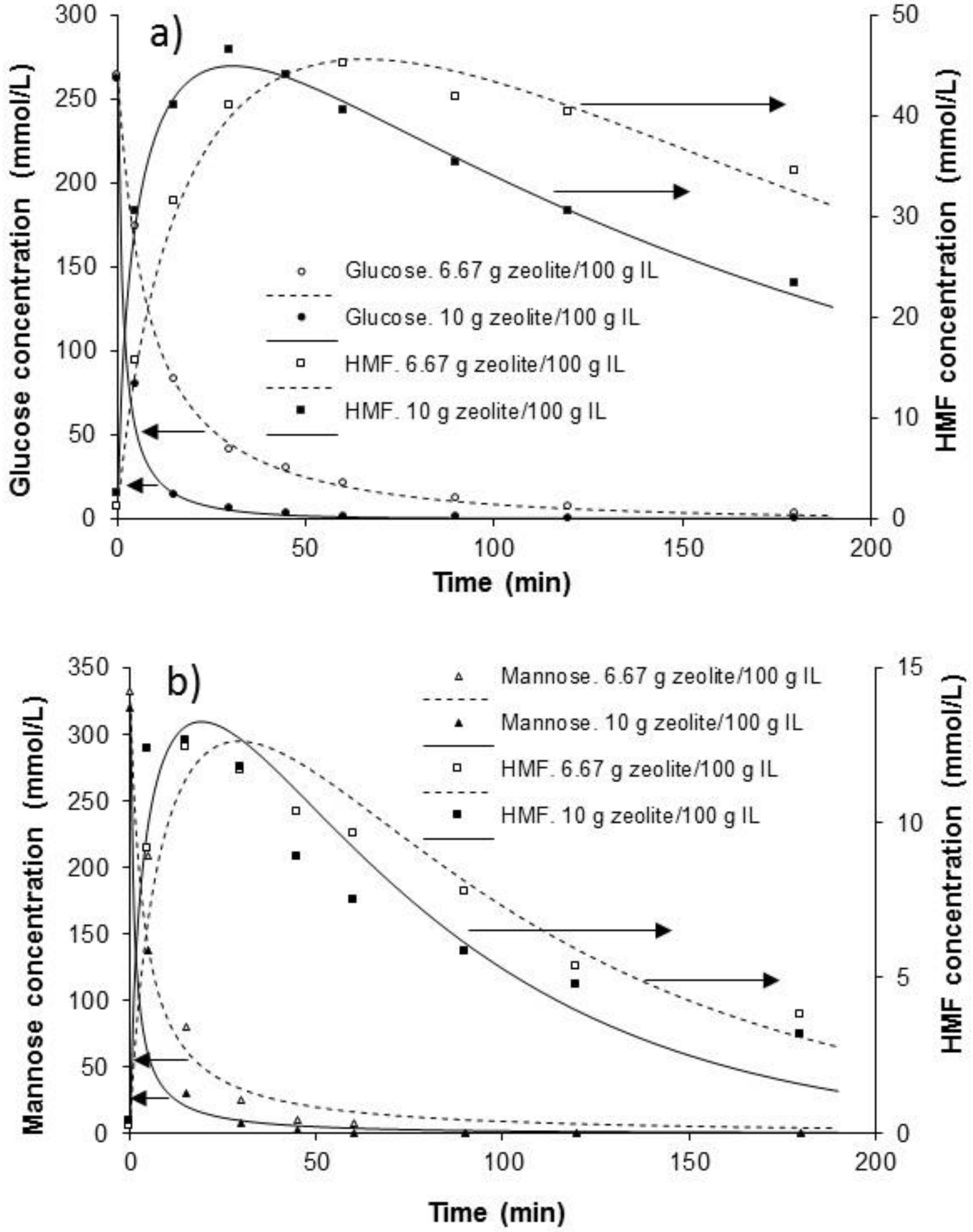

Fig. 2. Experimental and calculated concentration profiles for the substrates (a, glucose; b, mannose) and HMF in experiments performed at 160 °C in the presence of zeolite CBV-400 at the charges indicated in the legend (see Table 1 for further details)

Table 1. Kinetic Coefficients Calculated from the Data Shown in Fig. 2

Experiment	Substrate	Catalyst Charge (g/100 g IL)	Kinetic Coefficients			Regression Coefficients (R^2) for Concentration Profiles	
			$k_G \cdot 10^2$ or $k_M \cdot 10^2$ (min^{-1})	$k_G´$ 10^4 or $k_M´$ 10^4 (L $mmol^{-1}$ min^{-1})	$k_{HMFG} \cdot 10^3$ or $k_{HMFM} \cdot 10^3$ (min^{-1})	Substrate (glucose or mannose)	HMF
1	Glucose	6.67	1.42	4.46	5.37	0.995	0.992
2	Glucose	10	5.11	26.2	5.42	0.986	0.996
3	Mannose	6.67	0.68	8.12	18.0	0.939	0.921
4	Mannose	10	1.62	26.8	19.2	0.925	0.904

HMF Production from Glucose in Media Containing Zeolite CBV-400 and Co-Catalysts

To improve the kinetics and HMF yields of the reactions using glucose as a substrate, additional experiments were performed using the zeolite CBV-400 at the lowest charge considered in the previous set of experiments (6.67 g/100 g IL) in the presence of selected co-catalysts. This operational procedure followed the idea proposed by Abou-Yousef and Hassan (2014), who investigated the furans production from cellulose in the ionic liquid 1-ethyl-3-methylimidazolium chloride in media containing both a zeolite and metal chlorides as co-catalysts. According to these authors, the addition of alkali metal chlorides enhances the liberation of HCl gas and accordingly accelerates the dehydration step, increasing the rate of HMF generation, which is also valuable for obtaining HMF from hexoses. In a related study, Tan *et al*. (2011) employed [bmim]Cl/zeolite/$CrCl_2$ for manufacturing HMF from cellulose.

In this study, the conversion of glucose into HMF was assayed in [bmim]Cl containing the CBV-400 zeolite and one of the following co-catalysts: sulfuric acid, LiCl, and four chlorides of transition metals (WCl_6, $SnCl_2$, $FeCl_3$, or $CrCl_3$). These catalysts (and the operational conditions to be assayed) were selected from reported studies. Sulfuric acid was chosen as a co-catalyst on the basis of the results reported by Chidambaram and Bell (2010) for the dehydration of glucose in acid-catalyzed [bmim]Cl: among the various acids (H_2SO_4, CF_3SO_3H, CH_3SO_3H, CF_3COOH, HNO_3, HCl, and H_3PO_4), sulfuric acid showed the highest catalytic activity. Lithium halides were employed by Binder and Raines (2009) for sugar dehydration in N,N-dimethylacetamide, as well as by Abou-Yousef and Hassan (2014) for cellulose conversion in the reaction system mentioned above. Chlorides of Fe, Sn, or W have been employed as catalysts for HMF manufacture from sugars in ionic liquids, in the absence of zeolites (Zhao *et al*. 2007; Hu *et al*. 2009; Chan and Zhang 2009; Zhou *et al*. 2015). Finally, chromium chlorides are known to be good catalysts for HMF production from aldohexoses (including glucose and mannose) in ionic liquids, including [bmim]Cl (Zhao *et al*. 2007; Li *et al*. 2009; Qi *et al*. 2010; Peleteiro *et al*. 2014; Zhang *et al*. 2014; Peleteiro *et al*. 2015; Zhou *et al*. 2015).

The operational conditions considered in this set of experiments are listed in Table 2, and Table 3 shows the experimental data obtained about the concentrations of glucose and HMF. These results were fitted to the kinetic model in Fig. 1 to yield the kinetic coefficients in Table 4, which provided a satisfactory regression of experimental data (see values of the statistical parameter R^2 in Table 4). The ability of the proposed model to provide a quantitative and generalized interpretation of data is confirmed by the close interrelationship between experimental and calculated data, as confirmed in Fig. 3.

Table 2. Operational Conditions Employed for HMF Production from Glucose in [bmim]Cl/Zeolite/Co-catalyst Systems

Experiment	Co-catalyst	Concentration (g/100 g IL)	Temperature (°C)
5	H_2SO_4	0.36	160
6	LiCl	0.33	160
7	LiCl	0.17	160
8	WCl_6	0.33	145
9	$SnCl_2$	0.42	160
10	$FeCl_3\cdot6H_2O$	0.60	160
11	$CrCl_3\cdot 6H_2O$	0.33	145
12	$CrCl_3\cdot 6H_2O$	0.33	160

Table 3. Glucose and HMF Concentrations Obtained in Experiments 5 to 12 in Table 2 using Different co-catalysts

Experiment	Time (min)									
	0	3	5	10	15	20	25	30	45	60
	Glucose Concentration (g/L)									
5	48.79	19.17	10.45	4.58	2.72	1.72	1.29	0.87	0.83	0.40
6	52.64	32.01	23.15	12.95	9.54	7.58	6.01	4.89	3.11	2.16
7	52.22	29.79	21.48	11.66	8.02	6.15	4.86	3.93	2.24	0.31
8	44.82	14.76	7.88	3.68	1.84	1.20	0.94	0.49	0.00	0.00
9	52.30	33.40	21.74	10.43	5.99	3.32	1.77	1.15	0.61	0.40
10	42.81	18.39	10.66	3.98	2.52	1.81	1.34	1.09	0.01	0.00
11	55.49	17.09	10.23	7.91	3.51	1.55	0.97	0.70	0.61	0.45
12	50.95	3.81	1.11	0.55	0.56	0.70	0.53	0.29	0.11	0.06
	HMF Concentration (g/L)									
5	0.32	2.62	3.60	4.65	4.91	4.98	4.91	4.92	4.57	4.20
6	0.09	1.69	2.62	4.07	4.69	4.96	5.18	5.33	5.30	5.15
7	0.18	2.13	2.88	4.23	4.82	5.18	5.39	5.49	5.67	5.36
8	0.83	4.66	5.46	6.01	5.93	5.73	5.55	5.35	4.82	4.48
9	0.11	5.59	10.49	14.95	16.38	16.83	16.84	16.81	15.95	15.17
10	0.11	2.92	3.99	4.74	5.20	5.25	5.16	4.90	4.21	3.63
11	2.58	21.97	25.31	27.77	28.22	28.41	28.48	28.54	28.00	27.56
12	6.14	29.20	29.74	29.83	29.35	29.21	28.85	28.25	27.11	26.40

The results obtained in experiments 5, 6, 7, 8, and 10, using sulfuric acid or chlorides of Li, W, or Fe as co-catalysts, were poor (maximum HMF concentrations 5.0 g/L to 6.1 g/L, corresponding to 11.6% to 14.2% molar conversion of glucose into HMF, at 11.9% to 14.7% selectivities) and below the values expected from data reported for operation in [bmim]Cl and the cited catalysts in the absence of zeolites (which varied in the conversion range of 20.0% to 61.4%) (Hu *et al*. 2009; Li *et al*. 2009; Chidambaram and Bell 2010). The values of the kinetic coefficients listed in Table 4 highlight the reasons for which the maximum HMF concentrations were lower than expected. Sulfuric acid enabled a fast conversion of glucose into HMF, but also increased the kinetic coefficient governing the non-productive glucose consumption, and HMF decomposition was more favored than in other cases. Experiments 6 and 7, performed in the presence of LiCl, were mainly affected by the slow generation of HMF from glucose. Experiment 8, performed in the presence of W ions, was highly affected by a fast non-productive glucose consumption reaction. In experiment 10, the presence of $FeCl_3$ resulted in an increased rate of the productive glucose consumption, but also the kinetics of the other two parasitic reactions was improved with an unfavorable overall balance.

Slightly better results were obtained in experiment 9, using $SnCl_2$ as a catalyst (16.8 g HMF/L, corresponding to 39.2% molar conversion at 40.3% selectivity). Compared with the assays mentioned above, this co-catalyst improved the productive consumption of glucose and decreased the non-productive one, with a value of the kinetic coefficient describing the HMF decomposition in the lower range. The ability of Sn ions to catalyze the dehydration of glucose into HMF in IL media has been justified on the basis of their ability to stabilize specific reaction intermediates, including the formation of a five membered-ring chelate structure of the Sn atom with the two neighboring hydroxyl groups in glucose (Hu *et al*. 2009).

Table 4. Values Determined for the Kinetic Coefficients and R^2

	Kinetic Coefficients			R^2	
Experiment	$k_G \cdot 10^2$ (min^{-1})	$k_G' \cdot 10^4$ ($L\ mmol^{-1}\ min^{-1}$)	$k_{HMFG} \cdot 10^3$ (min^{-1})	Glucose	HMF
5	4.37	19.9	12.4	0.9953	0.9904
6	2.20	7.34	10.6	0.9976	0.9963
7	2.58	9.34	8.06	0.9957	0.9951
8	6.74	28.0	12.3	0.9973	0.9832
9	7.98	4.59	8.23	0.9928	0.9817
10	5.42	21.9	14.1	0.9908	0.9918
11	27.0	5.44	1.41	0.9962	0.9849
12	72.6	11.0	3.16	0.9980	0.9894

The best results (29.5 g HMF/L to 30.4 g HMF/L, corresponding to 68.5% to 70.6% molar conversion at 69.6% to 71.3% selectivity) were achieved in experiments 11 and 12, in the presence of $CrCl_3$ as a co-catalyst at 145 °C or 160 °C. Both experiments provided the highest rates of productive glucose decomposition and the best ratio between the parameters measuring the productive and non-productive consumption reactions. The molecular-level details justifying the unique reactivity of chromium ions in IL (including the formation of five ion pairs of the ionic liquid leading to the formation of two noninteracting square-planar substructures) have been identified in literature (Pidko *et al*., 2010).

Based on this finding, additional experiments were performed to provide a deeper assessment on HMF production from glucose and mannose in the presence of zeolite CBV-400 and $CrCl_3$.

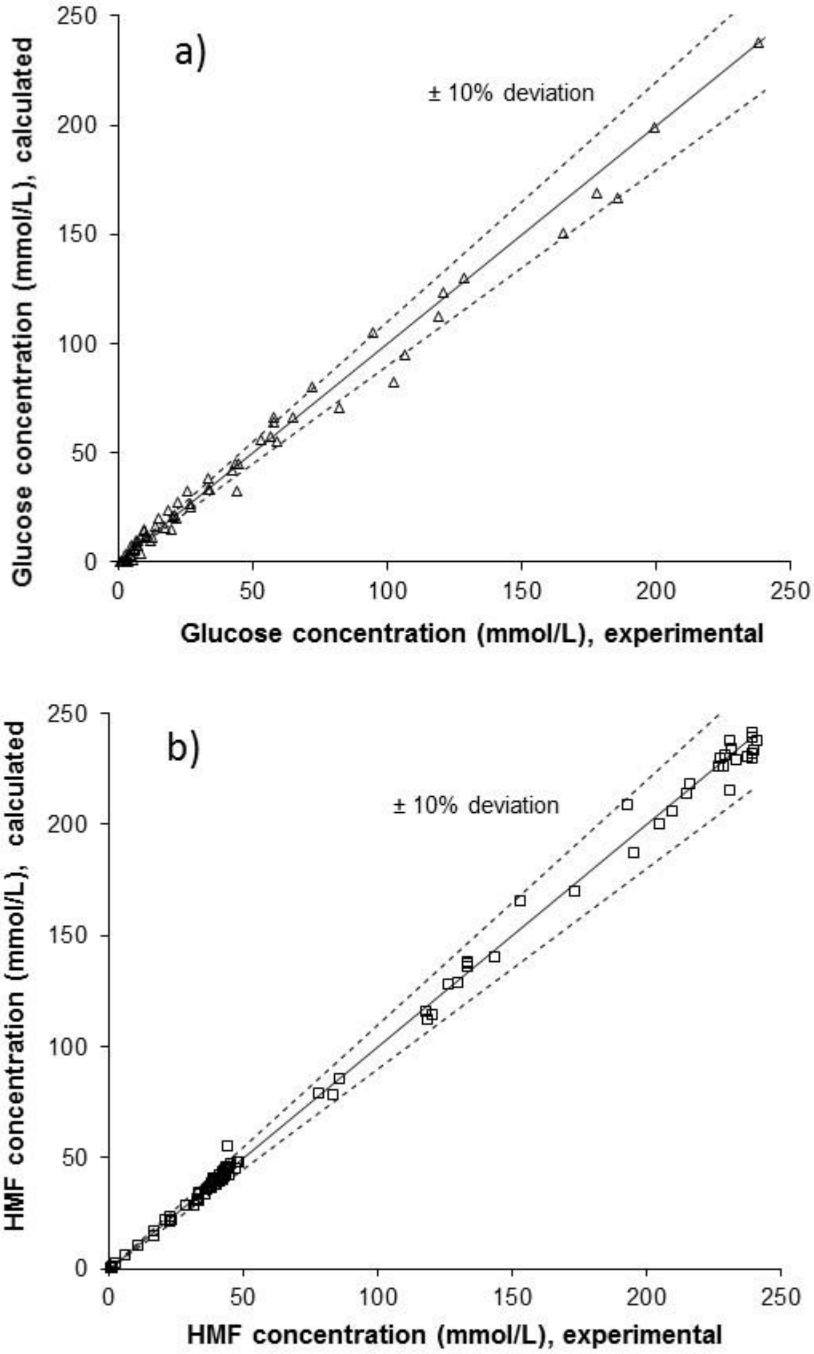

Fig. 3. Experimental and calculated concentrations of glucose and HMF for experiments 5 to 12 in Tables 2, 3, and 4

Production of HMF from Glucose and Mannose in Media Containing Zeolite CBV-400 and $CrCl_3$

Two additional experiments (13 and 14) were performed at 160 °C using 0.20 g $CrCl_3 \cdot 6H_2O$/100 g IL and 0.47 g $CrCl_3 \cdot 6H_2O$/100 g IL separately to explore (in combination with experiment 12, performed with 0.33 g $CrCl_3 \cdot 6H_2O$/100 g IL) the effects of the catalyst charge. Figure 4 shows the experimental and calculated concentration profiles (including the ones determined for experiment 12, for comparative purposes), and Table 5 lists the kinetic and statistical parameters resulting from data analysis. The most important finding was the high HMF concentration (31.4 g/L) achieved after 5 min in experiment 14, which improved the optimal result obtained in experiment 12 in terms of both concentration and reaction time, owing to the higher values of the k_G / $k_G{}'$ and the more favourable balance between the values of these coefficients and the one measuring the HMF decomposition. However, the improvement obtained when the catalyst charge was increased from 0.33 g $CrCl_3 \cdot 6H_2O$/100 g IL (conditions of experiment 12) up to 0.47 g $CrCl_3 \cdot 6H_2O$/100 g IL (conditions of experiment 14) was considered not enough to justify the increased need of catalyst, and the charge employed in experiment 12 was employed in further experiments.

Table 5. Values Determined for the Kinetic Coefficients and R^2 in the Additional Experiments Performed to Assess the Production of HMF from Glucose at 160 °C in the Presence of Zeolite CBV-400 and $CrCl_3 \cdot 6H_2O$

	Kinetic Coefficients			R^2	
Experiment/(Co-catalyst Charge) (g/100 g IL)	$k_G \cdot 10^2$ (min^{-1})	$k_G{}' \cdot 10^4$ (L $mmol^{-1}$ min^{-1})	$k_{HMFG} \cdot 10^3$ (min^{-1})	Glucose	HMF
13/(0.20)	33.8	5.5	2.50	0.9947	0.9922
14/(0.47)	109.0	13.1	3.62	0.9996	0.9992

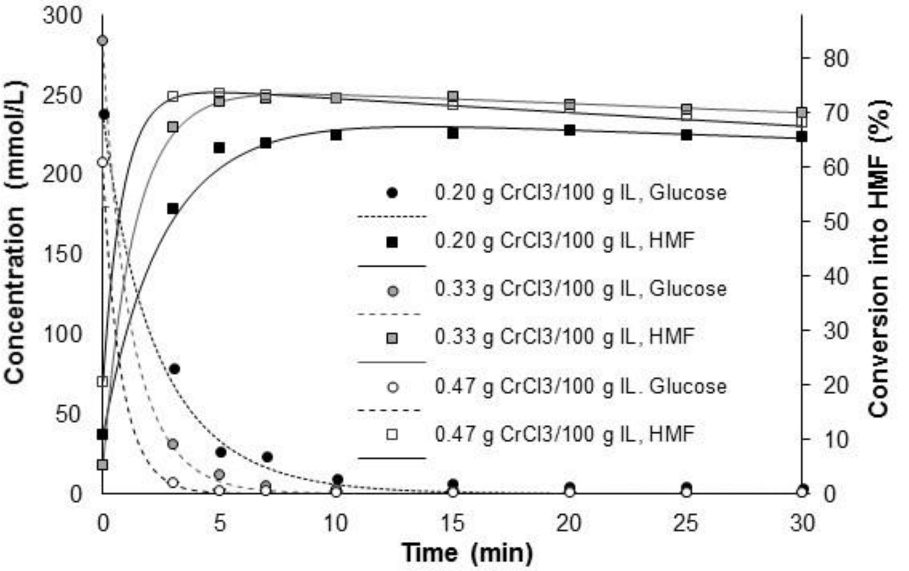

Fig. 4. Experimental and calculated results obtained in experiments 12, 13, and 14, performed to assess the effects of the co-catalyst charge on HMF production from glucose at 160 °C

To calculate the activation energies under the above operational conditions and to check their suitability for HMF production from mannose, new experiments (15 to 22) were performed to cover the desired temperature range (140 °C to 160 °C, see Table 6). Concerning the behavior of glucose as substrate, experiments 15 to 17 (together with experiments 11 and 12) enabled the calculation of the kinetic coefficients involved in Eqs. 1 and 2 for each experiment. Similar maximum HMF concentrations (30.0 g/L to 31.2 g/L, corresponding to 71.2% to 74.0% selectivity and 69.7% to 72.1% molar yield) were obtained in this set of experiments at reaction times in the range 10 min to 30 min.

The effect of temperature (in the same range mentioned before) on HMF production from mannose was assessed in experiments 18 to 22 in Table 6. The maximum HMF concentrations (27.8 g/L to 29.1 g/L, corresponding to 65.7% to 68.1% selectivity and 64.6% to 67.7% molar yield) were slightly below the ones determined for glucose, and were reached at comparatively short reaction time (3 min to 15 min). Again, the proposed model showed an excellent ability to reproduce the experimental results obtained at each temperature using mannose or glucose as substrates, as deduced from the regression coefficients in Table 6 and observed in Fig. 5a and Fig. 5b. Figure 6 confirmed an Arrhenius-type dependence of all the kinetic parameters on temperature, which allowed the calculation of the activation energies listed in Table 7.

Table 6. Values Determined for the Kinetic Coefficients and R^2 in the Additional Experiments Performed to Assess the Production of HMF from Glucose or Mannose in the Presence of Zeolite CBV-400 and $CrCl_3 \cdot 6H_2O$ at Different Temperatures

Experiment	Temp. (°C)	Kinetic Coefficients			R^2	
a) Experiments with glucose						
		$k_G \cdot 10^2$ (min^{-1})	$k_G' \cdot 10^4$ ($L\ mmol^{-1}\ min^{-1}$)	$k_{HMFG} \cdot 10^3$ (min^{-1})	Glucose	HMF
15	155	60.1	9.02	2.39	0.9993	0.9982
16	150	35.3	4.43	1.69	0.9990	0.9978
17	140	19.3	3.50	1.01	0.9904	0.9896
b) Experiments with mannose						
		$k_M \cdot 10^2$ (min^{-1})	$k_M' \cdot 10^4$ ($L\ mmol^{-1}\ min^{-1}$)	$k_{HMFM} \cdot 10^3$ (min^{-1})	Mannose	HMF
18	160	143.7	29.1	3.98	0.9997	0.9955
19	155	74.9	22.2	2.70	0.9999	0.9913
20	150	62.8	14.1	2.32	0.9992	0.9966
21	145	43.9	10.9	1.82	0.9994	0.9954
22	140	27.0	9.36	1.20	0.9997	0.9912

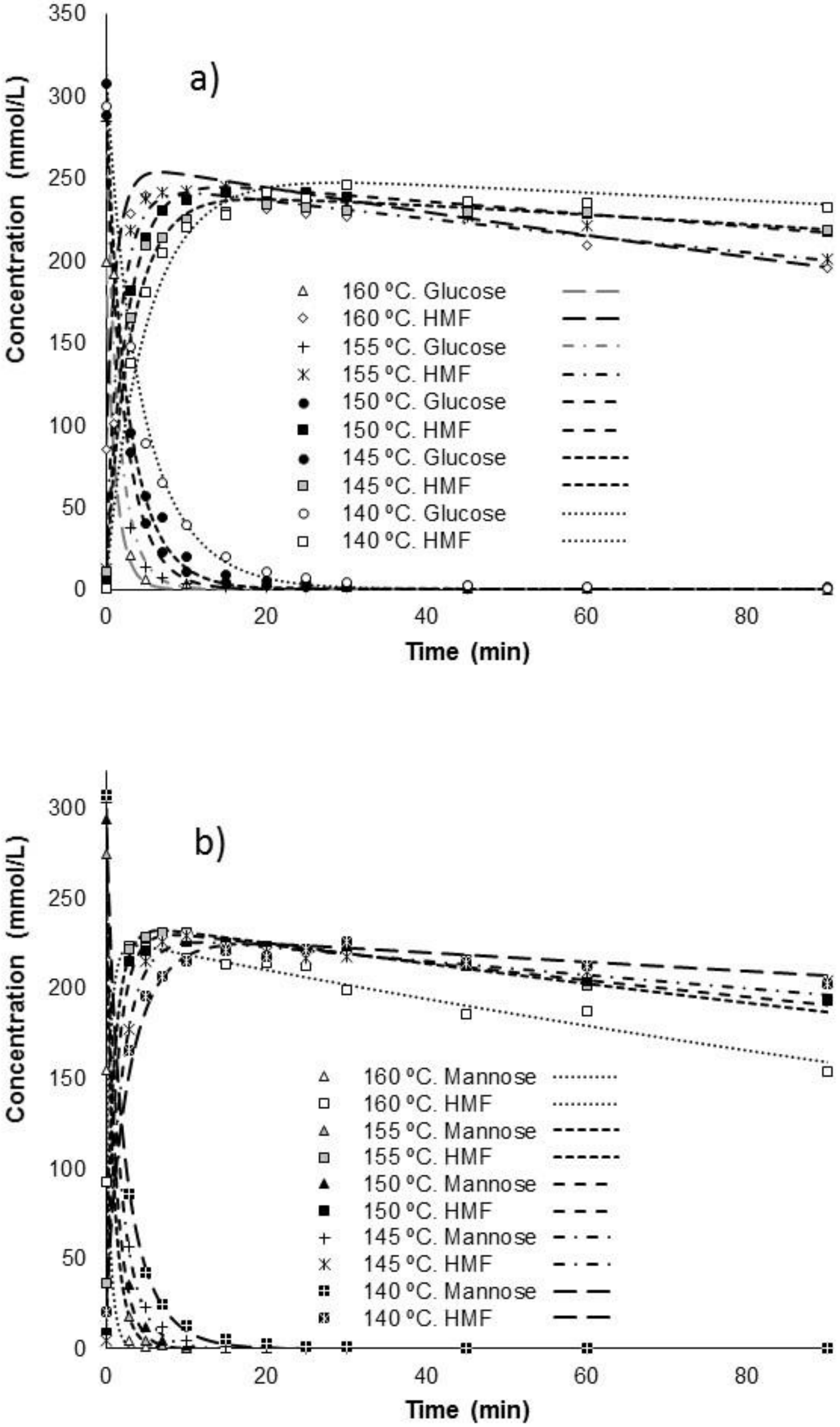

Fig. 5. Experimental and calculated concentration profiles for experiments 11 and 12 and experiments 15 to 22 in Table 6, performed to allow the calculation of the activation energies of the parameters involved in Eqs. 1 through 4.

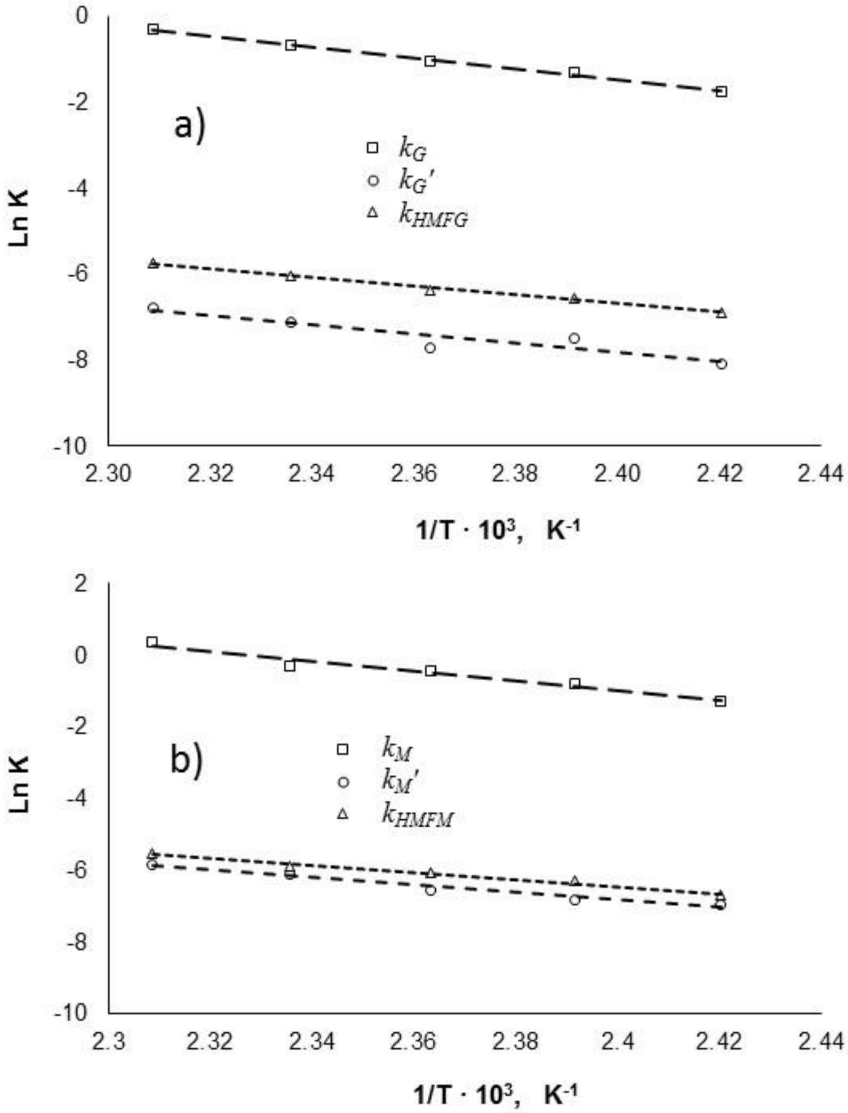

Fig. 6. Arrhenius plots for the kinetic parameters involved in Eqs. 1 through 4 for the conversion of (a) glucose or (b) mannose

Table 7. Results Obtained for the Activation Energies of the Various Reactions Involved in the Kinetic Mechanism Considered in this Study

	k_G or k_M		$k_G´$ or $k_M´$		k_{HMFG} or k_{HMFM}	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
Glucose	104.7	0.9948	88.8	0.8686	83.8	0.9937
Mannose	115.3	0.9697	88.5	0.9697	83.0	0.9764

CONCLUSIONS

1. Glucose and mannose, two hexoses that are model compounds for softwood hemicellulose hydrolyzates, were suitable substrates for HMF production in media containing [bmim]Cl and either an acidic zeolite or both zeolite and a selected co-catalyst.
2. Operating in the presence of the zeolite CBV-400 as the only catalyst, the conversion of mannose and glucose into HMF proceeded according to a first order kinetics for HMF generation and consumption, and to a second order reaction for non-productive substrate consumption.
3. Among the various co-catalysts tested, chromium salts led to the best HMF yields.
4. Operation in media containing zeolites and chromium salts led to maximum HMF molar yields of 72.1% and 67.7% from glucose and mannose, respectively.
5. The activation energies of the reactions involved in the HMF generation from glucose and mannose were 104.7 kJ/mol and 115.3 kJ/mol respectively, 88.8 kJ/mol and 88.5 kJ/mol for non-productive glucose and mannose consumption reactions, and 83.8 kJ/mol and 83.0 kJ/mol for HMF consumption reactions.

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