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Short communication

Manufacture of furfural in biphasic media made up of an ionic liquid and a co-solvent

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ABSTRACT

Xylose was converted into furfural operating in a medium containing the acidic ionic liquid (AIL) 1-butyl-3-methylimidazolium hydrogen sulfate, in the presence of toluene as a co-solvent. No catalytic species different from the AIL were needed for furfural production from xylose. Operating at 100–140 °C for 15–480 min in media containing 10 g xylose/100 g AIL and 2–4 g toluene/g (AIL + xylose), most furfural generated in the AIL phase was transferred to the co-solvent, limiting the losses caused by undesired side reactions. Operating under optimal conditions (140 °C for 240 min using 4.4 g toluene/g initial AIL phase), xylose was almost completely consumed, and furfural was obtained at 73.8% of the stoichiometric yield.

1. Introduction

The integral benefit of lignocellulosic materials is needed for designing efficient biorefineries. One of the possible ways of getting profit from xylan-containing biomass (such as hardwoods, straws and many agricultural wastes or byproducts) is the production of xylose. This pentose sugar can be easily obtained by mild, selective, acidic processing of suitable feedstocks by prehydrolysis or autohydrolysis–posthydrolysis. These technologies also yield a solid phase enriched in cellulose and lignin, which can be further processed in biorefineries to yield a scope of end products.

Xylose can be employed for multiple purposes (including biotechnological transformation into solvents, chemicals or fuels; or chemical modification into a number of compounds, including furfural). Furfural has been identified as one of the top 30 chemicals derived from biomass in a report commissioned by the US Department of Energy (Werpy and Petersen, 2004), which was further updated (Bozell and Petersen, 2010). Even if furfural is directly employed in industry (for example, as a solvent, or as an extraction agent), its role as a platform chemical is gaining importance, since it can serve as a starting material for the sustainable production of a number of bio-based chemicals (International Furan Chemicals, 2015), including furan derivatives, green fuels and coupling products.

The conversion of xylose ($C_5H_{10}O_5$) into furfural ($C_5H_4O_2$) involves the loss of three water molecules (stoichiometric yield, 0.64 g furfural/g xylose). However, the kinetic mechanism is complex and still subjected to debate. In general, in the presence of an acidic catalyst, xylose can undergo retroaldol fragmentation reactions, or give intermediates (whose chemical nature is under discussion) (Antal et al., 1991; Aida et al., 2010; Nimlos et al., 2006). The intermediates can be decomposed into furfural and/or give undesired reactions with other compounds present in the medium. On the other hand, furfural can be decomposed (for example, by rehydration or resinification reactions).

As a result of the complex kinetic mechanism, the practical furfural yields obtained in a single reaction stage are usually far below the stoichiometric one. In order to improve the furfural yield, a number of approaches have been proposed in literature, including the utilization of non-aqueous media (to avoid rehydration) and/or biphasic media (in which furfural is transferred to the co-solvent before undergoing condensation reactions).

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Ionic liquids (ILs) are considered as green reaction media (Harmer and Sun, 2001) owing to characteristics such as non-volatility, non-toxic character, thermal stability and recyclability, which make them attractive media for performing green catalytic reactions (Hallett and Welton, 2011). In particular, a number of imidazolium-containing ILs has been employed to carry out the conversion of xylose into furfural, frequently in the presence of acidic catalysts (including Brönsted acids, Lewis acids, and solid acid catalysts) (da Costa Lopes and Bogel-Lukasik, 2015; Zakrzewska et al., 2011). Chromium halides have been reported to behave as efficient catalysts for furfural production from xylose, which proceeds *via* isomerization of xylose into an intermediate (xylulose), and dehydration of the latter into furfural (Binder et al., 2010).

In the past few years, growing attention has been paid to the utilization of acidic ionic liquids (AILs) owing to their ability to act as both a reaction media and a catalyst (Brandt et al., 2011). It can be noted that AILs utilization allows simpler operational schemes, since no stages of catalyst recovery have to be implemented, and other possible issues related to the catalysts (for example, environmental hazards) are avoided.

This work deals with the production of furfural from xylose operating in biphasic media made up of a Brönsted AIL (1-butyl-3-methylimidazolium hydrogen sulfate, denoted [bmim][HSO_4]) and an organic co-solvent (toluene). The effects of the major experimental variables (temperature, reaction time and solvent to co-solvent volume ratio) were assessed in order to define the operational conditions leading to the optimal furfural yield.

2. Materials and methods

2.1. Materials and reaction in biphasic media

The chemical products employed and their suppliers were as follows: [bmim][HSO_4], xylose, formic acid, and furfural were purchased from Sigma–Aldrich, and toluene from Riedel-de Haën. All products were used as received.

Experiments were carried out in sealed, stirred glass tubes immersed in a thermostatized bath at 100–140 °C. The tubes were prepared by mixing [bmim][HSO_4], xylose and toluene at the desired proportions (xylose to [bmim][HSO_4] mass ratio = 1:10; toluene to ([bmim][HSO_4] + xylose) mass ratio in the range 2:1–4:1), and immersed in the bath. Zero time was set when xylose was completely dissolved in [bmim][HSO_4]. The reaction was stopped at the desired reaction time (in the range 15–480 min) by cooling in an ice bath, and the phases were recovered using a separatory funnel. Samples from the AIL and co-solvent phases were immediatly diluted with distilled water at the desired proportions (10 g water/g AIL phase and 6 g water/g co-solvent, respectively), homogenized, filtered through 0.45 μm nylon membranes and assayed for composition.

2.2. Analytical methods

Diluted samples from the AIL and co-solvent phases were assayed by HPLC for furfural, xylose and organic acids using an Agilent 1100 instrument fitted with refractive index (RI) and diode array (DA) detectors, and with an Aminex HPX-87H column (Bio-Rad, Life Science Group, Hercules, CA). Operation was carried out using the following conditions: mobile phase, 5 mM H_2SO_4; flow, 0.6 mL/min; temperature, 50 °C. All compounds were analyzed from the signal of the RI detector. Additionally, organic acids and furfural were also assayed using the signal from the DA detector (wavelengths: 210 nm for organic acids and 280 nm for furans). Fig. 1 shows representative chromatograms recorded with the DAD and IR detectors.

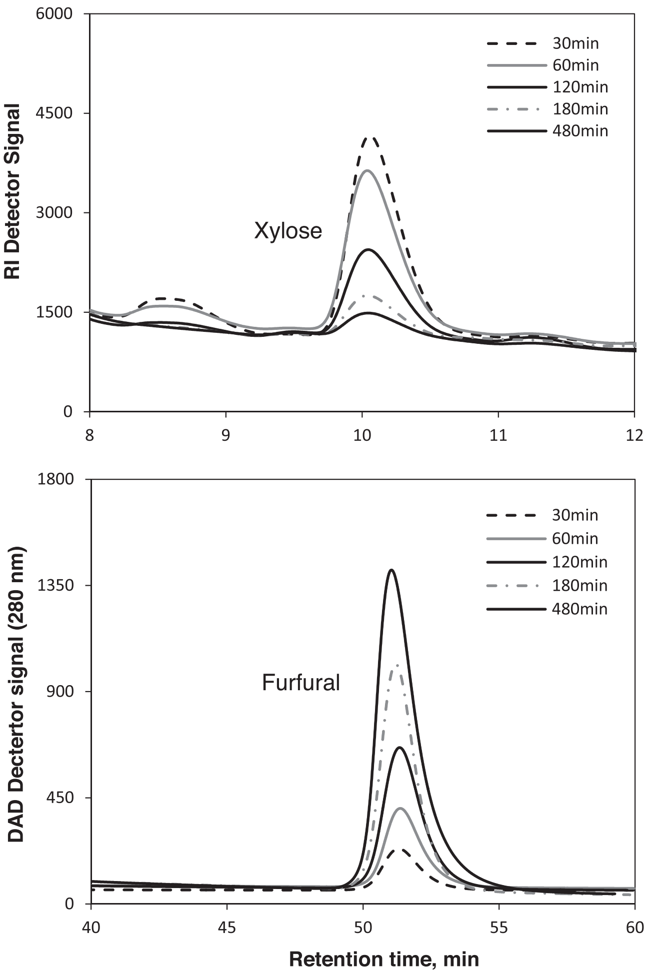

Fig. 1. Chromatograms recorded with the IR and DAD detectors in representative experiments.

3. Results and discussion

3.1. Effects of temperature and time on xylose consumption and product generation

Preliminary experiments (data not shown) were performed in absence of toluene, to assess the catalytic activity of the AIL. Total xylose consumption was observed under a broad range of experimental conditions below 140 °C, but the xylose conversion into furfural was always below 37%, confirming the importance of undesired side reactions leading to non-productive consumption of substrate and/or intermediates. In order to improve the experimental results, the reaction was carried out in the presence of toluene, which presents a favorable partition coefficient for furfural respect to [bmim][HSO_4]. Immiscible solvents have been employed as extracting agents for furfural from a variety of different reaction media, including ionic liquids. In particular, toluene has been used to improve the furfural yields from xylose obtained in media containing acid-catalyzed 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium chloride (Lima et al., 2009,2011).

A preliminary set of experiments of furfural production in the system xylose/[bmim][HSO_4]/toluene was carried out at 100 °C for 30–240 min using 2 g toluene/g (AIL + xylose) (see Table 1). A preliminary analysis of results confirmed the suitability of

Table 1
Experimental data regarding xylose (X) consumption and generation of formic acid (FA) and furfural (F) in toluente (T) and IL phases

a) Experiments performed at 100 °C

		Concentration, g/kg dissolution			Relative F amount		Conversion (%)	
T (°C)	t (min)	X	FA	F_{total}	In IL phase	In *T* phase	X	F
100	30	24.67	0.00	1.92	1.30	0.62	75.33	3.00
100	60	15.23	0.47	2.49	1.05	1.45	84.77	3.90
100	120	17.49	0.37	5.12	1.65	3.46	82.51	7.99
100	180	13.63	0.54	4.66	1.77	2.89	86.37	7.27
100	240	16.01	0.69	6.73	2.25	4.48	83.99	10.51
120	30	11.34	0.00	4.55	1.85	2.70	88.66	7.11
120	60	8.17	0.78	6.76	2.13	4.63	91.83	10.56
120	120	4.31	0.41	11.96	3.47	8.49	95.70	18.69
120	180	5.91	0.61	17.82	5.10	12.72	94.09	27.84
120	240	6.91	0.86	25.75	7.67	18.08	93.09	40.23
120	480	2.26	0.00	29.76	8.05	21.71	97.74	46.51
140	15	23.45	0.00	13.18	3.39	8.30	76.55	17.30
140	30	4.22	0.00	14.71	3.13	11.58	95.78	22.98
140	60	3.69	0.00	28.52	7.94	20.58	96.31	44.57
140	120	0.50	0.65	34.83	9.54	25.30	99.50	54.43
140	240	0.36	0.88	39.55	10.16	29.39	99.64	61.80
140	360	1.04	0.75	36.18	11.37	24.81	98.96	56.54
140	480	1.01	0.13	38.54	8.22	30.31	98.99	59.69

toluene as an agent for furfural extraction, as well as the ability of ([bmim][HSO_4]) to keep its catalytic activity in the presence of the co-solvent. Formic acid (FA) was the only organic acid found in the media, always at low concentrations (0–0.88 g/kg solution), revealing the limited importance of this type of furfural-consuming reactions under the conditions tested. Operating at 100 °C, 84% of the initial xylose was consumed after 240 min, but just 10.5% of the initial substrate was converted into furfural. Under these conditions, most furfural appeared in the co-solvent phase (6.73 g/kg, in comparison with 2.25 g/kg in the AIL phase). Keeping in mind the expected kinetic pattern (which includes the formation of intermediates from xylose, formation of furfural from intermediates, and multiple undesired side-reactions consuming substrate, intermediates and/or furfural), it can be concluded that the operational conditions were not severe enough, in a way that the results did not show if the substrate was preferently converted into intermediates or into condensation products. Operating at 120 °C (see Table 1), near 90% xylose consumption took place after 30 min, conditions under which the xylose conversion into furfural was just 7.1%. After 480 min, the xylose consumption increased up to near 98%, whereas the xylose conversion into furfural boosted up to 46.5%. Considering the behavior of the system between along this period, it can be seen that the incremental xylose conversion into furfural was much higher than the incremental xylose consumption, confirming the presence of important amounts of reaction intermediates in the media during the early reaction stages (enabling the generation of considerable amounts of furfural when most xylose was consumed). This finding reveals that the limited furfural concentrations achieved in the experiment at 100 °C were due, at least in part, to incomplete conversion of intermediates into furfural.

Looking for further improvements in furfural production, new experiments were performed at 140 °C (see Table 1). The results confirmed the major experimental trends described above: more than 76 and 95% of the initial xylose was consumed after 15 and 30 min, respectively, with limited furfural generation (17.3 and 23% conversion, respectively); whereas prolonging the reaction up to 240 min resulted in almost complete substrate consumption and improved furfural generation (61.8% xylose conversion into furfural), a finding that confirms the production of furfural from reaction intermediates. Longer reaction times resulted in decreased furfural concentrations, owing to the comparatively higher incidence of furfural-consuming reactions. Since the formic acid concentration remained low even under these operational conditions, the furfural consumption can be ascribed to resinification reactions (leading to the production of humins and/or precipitates, a fact evidenced by the darkening of the reaction media).

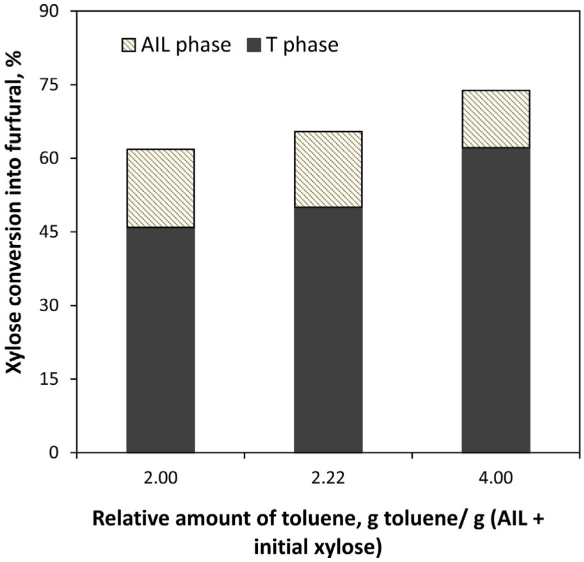

Fig. 2. Dependence of the xylose conversion into furfural on the relative amount of toluene present in IL and co-solvent phases.

3.2. Effect of the relative amount of co-solvent

On the basis of the furfural yield increase obtained when the reaction media was supplemented with 2 g toluene/g (AIL + initial xylose), additional experiments were performed with increased amounts of co-solvent (2.42 or 4.4 g toluene/g initial AIL phase). In these experiments, temperature and reaction time were fixed in the optimal values determined above (140 °C and 240 min). The results (see Fig. 2) show that furfural was mainly present in the organic phase, and that the furfural yield increased with the toluene charge. Using the highest toluene proportion assayed, the xylose conversion into furfural reached 73.8% of the stoichiometric value.

Extensive literature has been reported on the production of furfural from commercial xylose, xylan or xylan-containing biomass using ionic liquids; and providing an exhaustive overview on this wide topic is out of our scope. Although the literature results are difficult to compare owing to differences in the experimental protocols (and particularly, in the substrate charge, which is has a strong influence on furfural yield), some representative data are summarized in the next sentences. Furfural has been produced from pure xylose using alkylimidazolium ionic liquids (such as 1-ethyl-3-methylimidazolium chloride, denoted [emim]Cl, or 1-butyl 3-methylimidazolium chloride, denoted [bmim]Cl) catalyzed with acids, leading to furfural yields in the range 10.3–82.2% (Lima et al., 2009; Sievers et al., 2009; Peleteiro et al., 2014; Zhang et al., 2013; Wu et al., 2014), even if it has to be remarked that the latter result (considerably higher than the average) was obtained operating at a very low substrate charge (38.3 mg xylose/2 g of ionic liquid) (Zhang et al., 2013). Alternatively, the catalytic ability of selected AIL may avoid the utilization of externally-added catalysts, facilitating the recovery and recycling of chemicals. Following this approach, Lima et al. (2009) achieved 62% xylose conversion into furfural in [emim]HSO_4. Interesting results have been reported for biphasic systems: for example, furfural was produced from xylose at 44% yield in [bmim]Cl–toluene using H_2SO_4 as a catalyst; whereas (in an approach related to the one presented in this study, but based on a different AIL), the dehydration of commercial xylose into furfural in [emim]HSO_4–toluene was performed at 33–84% furfural yield (Lima et al., 2009).

4. Conclusions

The conversion of xylose into furfural using the acidic ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate as both a reaction medium and a catalyst resulted in product yields below 37%. The results were significantly improved when toluene was incorporated to the reaction media as a co-solvent, since the furfural generated in the AIL phase was transferred to the co-solvent, limiting the importance of undesired side reactions taking place in the AIL phase. Under conditions of intermediate severity, a significant part of the substrate was converted into reaction intermediates, which reacted further to yield furfural. The highest furfural yield (corresponding to 73.8% of the stoichiometric amount) was obtained operating at 140 °C for 240 min using 4.4 g co-solvent/g initial AIL phase.

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References

Aida, T.M., Shiraishi, N., Kubo, M., Watanabe, M., Smith, R.L., 2010. Reaction kinetics of D-xylose in sub- and supercritical water. J. Supercrit. Fluid 55, 208–216.
Antal, M.J., Leesomboon, T., Mok, W.S., Richards, G.N., 1991. 3. Mechanism of formation of 2-furaldehyde from D-xylose. Carbohydr. Res. 217, 71–85.
Binder, J.B., Blank, J.J., Cefali, A.V., Raines, R.T., 2010. Synthesis of furfural from xylose and xylan. ChemSusChem 3, 1268–1272.
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.
Brandt, A., Ray, M.J., To, T.Q., Leak, D.J., Murphy, R.J., Welton, T., 2011. Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid–water mixtures. Green Chem. 13, 2489–2499.
da Costa Lopes, A.M., Bogel-Lukasik, R., 2015. Acidic ionic liquids as sustainable approach of cellulose and lignocellulosic biomass conversion without additional catalysts. ChemSusChem 8, 947–965.
Hallett, J.P., Welton, T., 2011. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. Chem. Rev. 111, 3508–3576.
Harmer, M.A., Sun, Q., 2001. Solid acid catalysis using ion- exchange resins. Appl. Catal. A 221, 45–62.
International Furan Chemicals B.V, Applications of Furfural. In: http://www.furan.com/furfural_applications_of_furfural.html (accessed April.15).
Lima, S., Neves, P., Antunes, M.M., Pillinger, M., Ignatyev, N., Valente, A.A., 2009. Conversion of mono/di/polysaccharides into furan compounds using 1-alkyl-3-methylimidazolium ionic liquids. Appl. Cata. A: Gen. 363, 93–99.
Lima, S., Antunes, M.M., Pillinger, M., Valente, A.A., 2011. Ionic liquids as tools for the acid-catalyzed hydrolysis/dehydration of saccharides to furanic aldehydes. ChemCatChem 3, 1686–1706.
Nimlos, M.R., Qian, X., Davis, M., Himmel, M.E., Johnson, D.K., 2006. Energetics of xylose decomposition as determined using quantum mechanics modeling. J. Phys. Chem. A 110, 11824–11838.
Peleteiro, S., Garrote, G., Santos, V., Parajó, J.C., 2014. Conversion of hexoses and pentoses into furans in an ionic liquid. Afinidad 567, 202–206.
Sievers, C., Musin, I., Marzialetti, T., Olarte, M.B., Agrawal, P.K., Jones, C.W., 2009. Acid-catalyzed conversion of sugars and furfurals in an ionic liquid phase. ChemSusChem 2, 665–671.
Werpy, T., Petersen, G.R., 2004. Top Value Added Chemicals from Biomass - Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Report from Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL), Retrieved at: http://www.nrel.gov/docs/fy04osti/35523.pdf
Wu, C., Chen, W., Zhong, L., Peng, X., Sun, R., Fang, J., Zheng, S., 2014. Conversion of xylose into furfural using lignosulfonic acid as catalyst in ionic liquid. J. Agric. Food Chem. 62, 7430–7435.
Zakrzewska, M.E., Bogel-Lukasik, E., Bogel-Lukasik, R., 2011. Ionic liquid- mediated formation of 5- hydroxymethylfurfural- A promising biomass- derived building block. Chem Rev. 111, 397–417.
Zhang, L., Yu, H., Wang, P., Dong, H., Peng, X., 2013. Conversion of xylan, D-xylose and lignocellulosic biomass into furfural using $AlCl_3$ as catalyst in ionic liquid. Bioresour. Technol. 130, 110–116.