Conversion of hexoses and pentoses into furans in an ionic liquid

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Conversión de hexosas y pentosas en furanos empleando un líquido iónico

Conversió de hexoses i pentoses en furans emprant un líquid iònic

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RESUMEN

Se estudia la reacción de azúcares que aparecen como unidades estructurales de las hemicelulosas de maderas resinosas (manosa, glucosa, galactosa, xilosa y arabinosa) en un medio conteniendo el líquido iónico cloruro de 1-butil-3-metilimidazolio ([Bmim]Cl) y el catalizador $CrCl_3$. La reacción se orientó hacia la producción de furanos (hidroximetilfurfural a partir de hexosas y furfural a partir de pentosas). La reacción se llevó a cabo empleando una proporción de sustrato fija (10 g /100 g [Bmim]Cl) y una limitada cantidad de catalizador (0.5 g $CrCl_3 \cdot 6H_2O$/100 g [Bmim]Cl). Se establecieron los efectos de la temperatura y del tiempo de reacción sobre la producción de los compuestos deseados. Se identificaron las condiciones óptimas para la producción de furanos a partir de los distintos sustratos, y se comparan los resultados con datos bibliográficos de estudios relacionados.

Palabras clave: furfural, hexosas, hidroximetilfurfural, líquido iónico, pentosas.

SUMMARY

Sugars appearing as structural units in softwood hemicelluloses (mannose, glucose, galactose, xylose and arabinose) were processed in media containing the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and $CrCl_3$ as a catalyst. Experiments were directed to the production of furans (hydroxymethylfurfural and furfural from hexoses and pentoses, respectively). Operation was performed at a fixed substrate loading (10 g /100 g [Bmim]Cl) using a low catalyst charge (0.5 g $CrCl_3 \cdot 6H_2O$/100 g [Bmim]Cl). The effects of temperature and reaction time on the production of the target products were assessed. The optimal conditions for furan production were identified, and the furan yields were evaluated comparatively to the ones reported in related studies.

Keywords: Furfural; hexoses; hydroxymethylfurfural; ionic liquid; pentoses.

RESUM

S'estudia la reacció de sucres que apareixen com a unitats estructurals de les hemicel·luloses de fustes resinoses (manosa, glucosa, galactosa, xilosa i arabinosa) en un medi que conté el líquid iònic clorur de butil -3 - metilimidazoli ([Bmim] Cl) i el catalitzador CrC_3. La reacció es va orientar cap a la producció de furans (hidroximetilfurfural a partir de hexoses i furfural a partir de pentoses). La reacció es va dur a terme emprant una proporció de substrat fixa (10 g/100 g [Bmim]Cl) i una limitada quantitat de catalitzador (0.05 g $CrCl_3 \cdot 6H_2O$/100 g [Bmim]Cl). Es van establir els efectes de la temperatura i del temps de reacció sobre la producció dels compostos desitjats. Es van identificar les condicions òptimes per a la producció de furans a partir dels diferents substrats, i es van comparar els resultats amb dades bibliogràfiques d'estudis relacionats.

Mots clau: furfural, hexoses, hidroximetilfurfural, líquid iònic, pentoses.

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INTRODUCTION

Softwood hemicelluloses are mainly made up of two types of polysaccharides: acetylated glucomannan containing galactose substituents (in which mannose, glucose and galactose appear as structural units), and heteroxylan (mainly made up of xylose and arabinose structural units). When softwoods are subjected to appropriate hydrolysis treatments (for example, prehydrolysis or autohydrolysis-prehydrolysis), the hemicelluloses present in the raw materials can be converted into a mixture of hemicellulose-derived sugars (mannose, glucose, galactose, xylose and arabinose).(1) Among other possible applications, these hemicellulose-derived sugars are potential starting materials for the manufacture of furans (hydroxymethylfurfural from hexoses and furfural from pentoses).

Hydroxymethylfurfural (HMF) and furfural are platform chemicals for the manufacture of a number of intermediates and chemicals. HMF has been identified as a promising platform compound serving as a bridge between carbohydrate chemistry and petroleum-based chemistry, (2) whereas furfural has been considered as one of the top value added chemicals from biomass.(3)

Ionic liquids (ILs) are considered “green chemicals” owing to their physical, chemical, and technological properties. A number of ILs can been employed for furan manufacture from sugars, including 1-butyl-3-methylimidazolium chloride ([Bmim]Cl).(4) ILs-based transformation of hexoses into hydroxymethylfurfural (HMF) has been reported using a numbers of substrates, including fructose (the most favourable one), glucose and mannose. Oppositely, galactose was reported not to be a suitable source of HMF when operating in media containing chloride ions.(5) On the other hand, furfural has been produced from xylose in media containing ILs.

This work deals with the production of furans (furfural or HMF) from model compounds (including hexoses and pentoses) that could be obtained from softwood hemicelluloses by selective hydrolysis. Reaction was carried out in media made up of an ionic liquid ([Bmim]Cl) in the presence of a catalyst ($CrCl_3$). The effects of temperature and time on both substrate consumption and product distribution were assessed, in order to quantify the maximum achievable furan yields. This information is of basic importance to assess the possible manufacture of furans from softwood hemicellulose hydrolyzates.

MATERIALS AND METHODS

Materials

1-Butyl-3-methylimidazolium chloride, xylose, arabinose, galactose, glucose, mannose, furfural and HMF were purchased from Sigma-Aldrich. Chromium (III) chloride 6- hydrate was purchased from Panreac (Barcelona, Spain).

Reaction in [Bmim]Cl-$CrCl_3$ media

[Bmim]Cl was molten, dried, heated to the target temperature (in the range 100 - 160 °C) and mixed with $CrCl_3·6H_2O$ at a charge of 0.5 g /100 g [Bmim]Cl. The catalyst loading was fixed in this value based on preliminary experiments (data not shown) performed to identify the minimum catalyst loading enabling sugar consumption and furan generation at acceptable rates. Once the catalyst was dissolved, the considered sugar was added to the medium at a loading of 10 g/100 g [Bmim]Cl under stirring. Zero time corresponded to substrate addition. At preset reaction times, samples from the reaction media were withdrawn, diluted immediatly with distilled water (at a mass ratio of 20 g water/g sample), homogenized, and assayed for composition.

Analytical methods

Individual monosaccharides (glucose, xylose, mannose, galactose, and arabinose) and furans (furfural and HMF) in the reaction media were quantitated using an Agilent 1100 instrument fitted with Refractive Index (RI) and Diode Array (DA) detectors (wavelength, 280 nm), as well as with an Aminex HPX-87H column.

RESULTS AND DISCUSSION

Conversion of commercial hexoses

Experiments were performed to assess the production of HMF from hexoses making part of softwood hemicelluloses (galactose, glucose and mannose) in the presence of a chromium catalyst, which has been found suitable for causing the dehydration of selected aldohexoses.(5,6)

Preliminary experimental results (data not shown) proved that galactose was not a suitable substrate for HMF production in [Bmim]Cl-$CrCl_3$ media under the range of conditions tested. This finding is in agreement with the scarce conversion reported in a study carried out with [Emim]Cl - $CrCl_3·6H_2O$,(5) which was justified by the formation of an intermediate (tagatose) that is not efficiently dehydrated into HMF. On this basis, the only suitable HMF sources in softwood hemicellulose hydrolyzates are glucose and mannose.

Glucose conversion into HMF in [Bmim]Cl-$CrCl_3$ media has been carried out in literature,(7) operating with 10 g glucose/100 g [Bmim]Cl supplemented with 25 mol $CrCl_3·6H_2O$/100 mol glucose. The maximum HMF conversion achieved in this study was near 65%. In this work, we have considered a much more reduced catalyst loading, an idea already applied by Li et al.(8) to the conversion of fructose in acid-catalyzed [Bmim]Cl media. Figures 1a and 1b show the experimental concentration profiles determined for glucose and HMF at 100-160 ºC. Glucose was totally consumed after 20-30 min at 140 or 160 ºC, whereas about 30 min were needed to convert 90% of the initial glucose in the experiment at 120 ºC. Under the mildest conditions assayed, about 16% of the initial glucose was still present in the reaction medium after 180 min. Following a typical mechanism, HMF behaved as a reaction intermediate: in the first reaction stages, the HMF concentration increased markedly with the reaction time, and then decreased. This variation pattern was evident at reaction times shorter than 180 min in experiments performed at 140 or 160 ºC (see Figure 1b), and was confirmed in the experiment carried out at 120 ºC by extending the reaction time up to 600 min. In comparison, the maximum HMF concentration was achieved after 600 min at 100 ºC. These findings are compatible with a typical mechanism involving consecutive reactions of glucose dehydration into HMF and HMF consumption by parasitic reactions (including HMF rehydration). The maximum HMF concentrations were 43.1 - 44.3 g/L (corresponding to 65.0 - 66.8% glucose conversion into HMF), and were achieved at 120 or 140 ºC after 120 or 10 min, respectively (see Figure 1b).

Even though the conversion of mannose into HMF in ILs such as [Emim]Cl and [Bmim]Cl has been considered in literature,(5,9) to our knowledge, no data have been reported for the same reaction in [Bmim]Cl-$CrCl_3$ media.

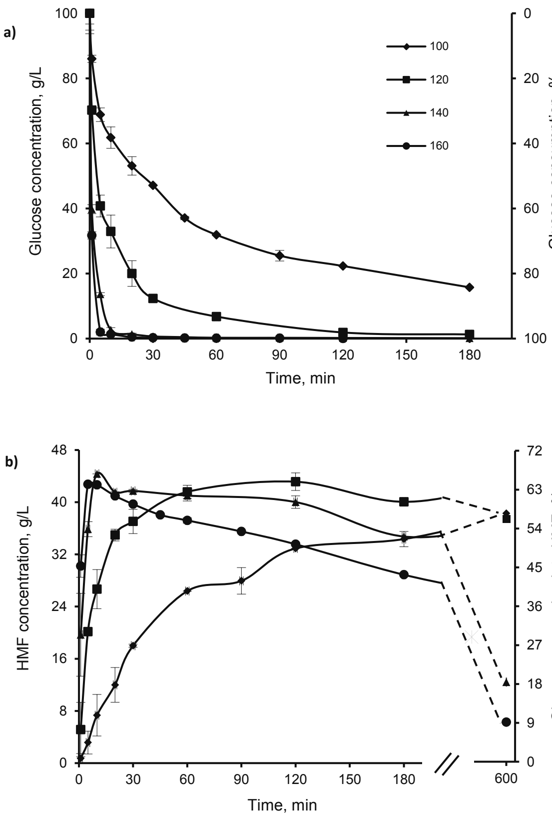

Figure 1. *a) Effects of temperature and time on glucose consumption; b) HMF concentration profiles obtained using glucose as a substrate.*

Since the structural features of the ILs play a significant role on the dehydration rates of monosaccharides,(9) selected experiments were performed to assess the maximum HMF yield achievable from mannose, covering the operational range of practical interest (temperatures in the range 100 - 160 °C and reaction times up to 10 h) operating in media containing 0.5 g $CrCl_3$/100 g [Bmim]Cl. Complete mannose conversion was achieved after 2 h, 60 min or 10 min operating at 120, 140 or 160 °C, respectively (see Figure 2a). Figure 2b shows the HMF concentrations and the corresponding conversions achieved in the various experiments. The general variation pattern observed in Figures 2a and 2b is similar to the one previously described for glucose, and consistent with the typical mechanism for hexose decomposition. The maximum HMF average concentration (41.4 g/L, corresponding to 62.4% mannose conversion) was obtained at 120 °C after 2 h.

In comparison, HMF concentrations near 37 g/L (about 55% mannose conversion into HMF) were achieved operating at 140 or 160 °C for 10 - 30 min. Harsher conditions resulted in the generation of humins, as it was evidenced by the development of a brownish color(10) and by the formation of solids. These results are in the range reported for HMF production from mannose in [Emim]Cl-$CrCl_3$ media (56% conversion).(5) In comparison, the mannose conversion into HMF achieved using [Bmim]Cl-H_2SO_4 media was below 5%.(9)

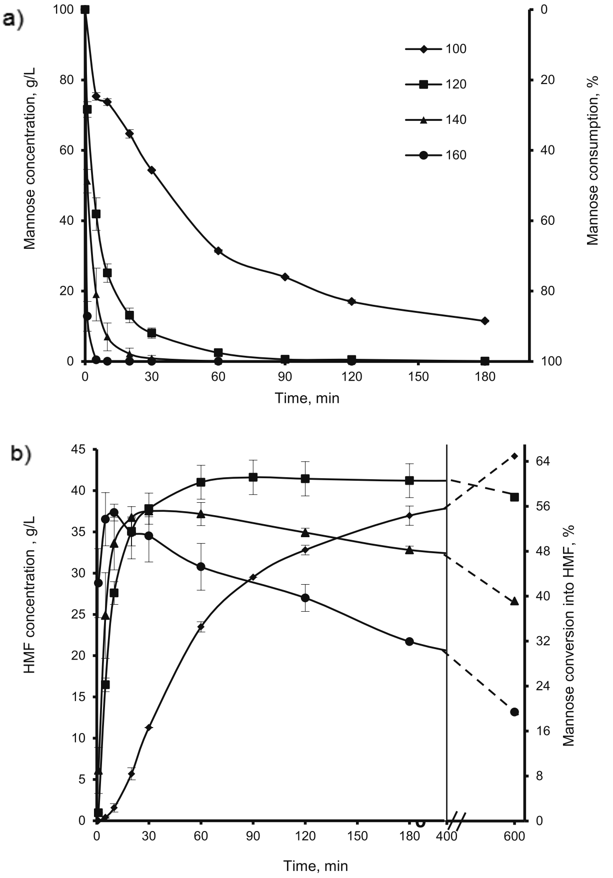

Figure 2. *a) Effects of temperature and time on mannose consumption; b) HMF concentration profiles obtained using mannose as a substrate.*

Conversion of commercial pentoses

Xylose, the structural unit present in xylan, is known to yield furfural upon dehydration, following a mechanism closely related to the one described for hexoses. However, scarce information is available on the utilization of ILs for this purpose. [Bmim]Cl media have been used for furfural production from xylose,(11) but the catalyst type ($AlCl_3$), the substrate concentration (lower than in our case) and the heating method (microwave irradiation) were different from the ones employed in this study.

The concentration profiles determined for xylose (see Figure 3a) confirmed the higher comparative susceptibility to dehydration respect to glucose or mannose. According to the variation patterns observed in Figure 3b, furfural behaved as a reaction intermediate, which was generated from xylose, and was consumed by parasitic reactions. This reaction scheme led to the formation of both soluble degradation products and black insoluble solids.(12) In the experiment at 100 °C, some furfural generation was still taking place after 180 min; whereas the furfural concentration profiles determined at 120 - 160 °C presented well defined maxima at reaction times in the range 5 - 45 min. The highest average furfural concentrations (29.6 - 29.8 g/L, corresponding to about 50% xylose conversion into furfural) were achieved operating at 120-160 °C for 5 - 30 min. Higher xylose conversions into furfural (up to 82.2%) were achieved in [Bmim]Cl-$AlCl_3$ media operating with microwave heating at low substrate loadings, which improved the furfural yield; whereas Sievers et al.(9) reported 13% xylose conversion into furfural operating in [Bmim]Cl-H_2SO_4 at 120 °C for 90 min with 5 g substrate/100 g [Bmim]Cl.

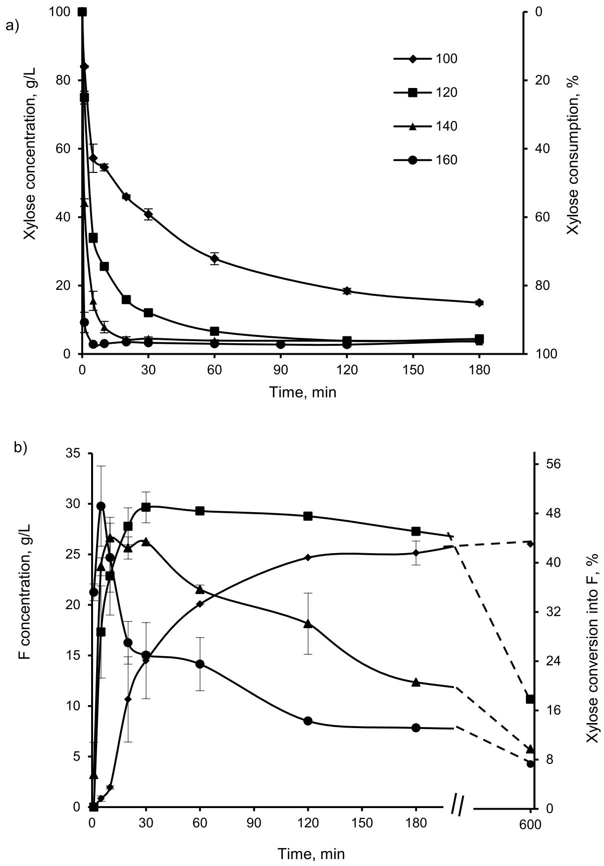

Figure 3. *a) Effects of temperature and time on xylose consumption; b) Furfural concentration profiles obtained using xylose as a substrate.*

Softwood hemicelluloses contain arabinose units, which are potential substrates for furfural production. To our knowledge, no studies have been reported on the dehydration of arabinose into furfural. The experimental data in Figure 4a show that 59.3 - 100% of arabinose was consumed after 180 min at the considered temperatures. Total arabinose consumption was achieved after 30 min at 160 ºC and 120 min at 140 ºC, whereas more than 600 min were needed to deplete the substrate at lower temperatures. The furfural concentration profiles followed the same general pattern (generation and further decomposition) discussed for xylose (see Figure 4b). In comparative terms, the furfural conversions determined for arabinose were poorer than the ones observed for xylose. The maximum arabinose conversion into furfural (15.5%, corresponding to an average concentration of 9.40 g/L) was obtained at 160 ºC after 5 min.

Furan yields achievable from pine wood hemicellulose hydrolyzates

Assuming that mixtures of hemicellulose-derived sugars could be converted in furans in amounts corresponding to the sum of the individual contributions of the various monosaccharides (neglecting interactions), the data obtained in this work allow the direct calculation of the furan yields that could be achievable from hydrolysis media of defined composition. As an example, the data reported for the composition of hydrolyzates obtained by autohydrolysis-posthydrolysis of *Pinus pinaster* wood (González-Muñoz et al., 2012), can be first converted in hexose yields (11.68, 3.39, and 2.54 kg/100 kg oven-dry wood for mannose, glucose, and galactose, respectively), and in pentose yields (4.71 and 1.29 kg/100 kg oven-dry wood for xylose and arabinose, respectively). Choosing suitable operational conditions for furan production in the [Bmim]Cl-$CrCl_3$ medium, the yields of HMF and furfural can be obtained from Figures 1 – 4, and the furan yields can be calculated on the basis of the individual contributions of the various sugars after stoichiometric conversion (0.70 g HMF/g hexose and 0.64 g furfural/g pentose). For example, working under the optimal conditions for HMF production from mannose and glucose (120 ºC, 2h), the HMF yield from pine hemicelluloses would be 6.69 kg/100 kg oven-dry wood. These operational conditions would also result in furfural production, but at a poorer yield owing to the lower proportions of the potential substrates (xylose and arabinose) and to their comparatively high lability.

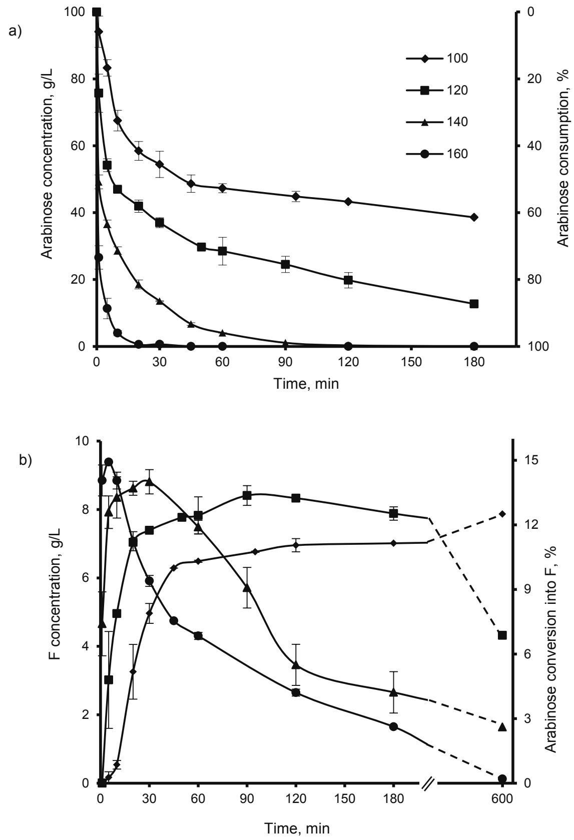

Figure 4. *a) Effects of temperature and time on arabinose consumption; b) Furfural concentration profiles obtained using arabinose as a substrate.*

CONCLUSION

The potential of commercial hexoses and pentoses as substrates for furan production was assessed in media containing the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) in the presence of a catalyst. Galactose did not behave as a suitable substrate for HMF production, whereas the effects of temperature and time on the HMF yields from glucose and mannose were assessed. Under optimal operational conditions, the HMF was obtained from glucose and mannose accounted for 66.8%

and 62.4% of the stoichiometric amounts, respectively. On the other hand, the production of furfural from xylose and arabinose in the same reaction media was studied. In comparative terms, the furfural yield from xylose about 50% of the stoichiometric value) was higher than the one from arabinose (15.5%). On the basis of the experimental results, it was concluded that pine hemicelluloses could be converted into HMF at a maximum yield of 6.69 kg/100 kg oven-dry wood.

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REFERENCES

1. González-Muñoz, M. J.; Alvarez, R.; Santos, V. and Parajó, J. C. *Wood Sci. Technol.*, **46**: 271 (2012).
2. Zhu, S.; Tong, Y.; Lu, Y. and Wu, Y. *Bioresources* **7**: 3 (2012).
3. Werpy T. and Petersen, G. Eds. Volume I - Results of Screening for Potential Candidates from Sugars and Synthesis Gas, T.A. U.S. Department of Energy (DOE), Golden, CO; Rep. DOE/GO-102004-1992 (2004)
4. Maki-Arvela, P.; Anugwom, I.; Virtanen, P.; Sjoholm, R. and Mikkola, J. P. *Ind. Crops Prod.* **32:**175 (2010)
5. Binder, J. B.; Cefali, A.V.; Blank J. J. and Raines, R. T. *Energy Environ. Sci.* **3**:765 (2010)
6. Zhao, H.; Holladay, J. E.; Brown, H. and Zhang, Z. C. *Science* **316**:1597 (2007).
7. Cao, Q.; Guo, X.; Yao, S.; Guan, J.; Wang, X.; Mu, X. and Zhang, D. *Carbohyd. Res.* **346**:956 (2011).
8. Li, C.; Zhao, Z. K.; Wang A.; Zheng, M. and Zhang, T. *Carbohyd. Res.***345**:1846 (2010).
9. Sievers, C.; Musin, I.; Marzialetti, T.; Olarte, M. B.; Agrawal, P. K. and. Jones, C. W. *ChemSusChem* **2**:665 (2009).
10. Kuster, B. F. M. *Starch/Staerke* **42**:314 (1990).
11. Zhang, L.; Yu, H.; Wang, P.; Dong, H. and Peng, X. *Bioresour. Technol.* **130**:110 (2013).
12. Zhang, L.; Yu, H and Wang, P. *Bioresour. Technol.* **136**:515 (2013).