Furfural from corn stover hemicelluloses. A mineral acid-free approach†

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Furfural was obtained from corn stover hemicelluloses by a microwave-assisted, green and heterogeneously catalyzed two-step cascade process as follows: first step, hydrothermal fractionation of corn stover hemicelluloses, and second step, hydrolysis/dehydration of soluble hemicellulosic sugars over niobium phosphate to yield furfural at moderate temperatures (<200 °C), with both steps being performed in water. Furfural yields of up to 23 mol% with respect to the starting raw biomass were reached.

Introduction

The increasing demand for energy and fuels, while easily available petroleum resources are diminishing, and the need to reduce greenhouse gas levels in the atmosphere have drawn attention to lignocellulosic biomass (LCB) as a major source of carbon. In this context, agricultural residues, such as corn stover, represent a highly sustainable worldwide resource[1] for the production of bio-platform molecules. In particular, furfural is a biomass-derived industrial feedstock of growing interest, with an annual production volume of more than 200 000 tonnes.[2] This versatile intermediate is used in many fields, such as oil refining, pharmaceutical, and agrochemical industries,[3] and for the development of new generation of biofuels and bioplastics, as well as jet or diesel fuel range alkanes to serve as gasoline blendstock.[2,4,5] Furfural is industrially synthesized from lignocellulosic materials (corncobs, oat hulls, cottonseed hull bran, almond husks, bagasse *etc.*) that are rich in pentosans in either batch or continuous reactors, using mineral acids (H$_2$SO$_4$ or HCl) as catalysts[6] and large amounts of steam as stripping agent.[5] The use of such acids results in several issues, especially in terms of operational

safety, equipment corrosion and waste disposal, derived from acid neutralization. Moreover, in industrial practice, this process operates at quite low yields (~50% of the theoretical), with 0.73 kg of furfural per kg of pentosan being the highest possible theoretical yield.[4]

Novel greener processes should thus be developed that address the major drawbacks of furfural production. A viable alternative is solid catalysts, which avoid equipment corrosion problems, avoid production of waste and allow both easy separation from liquid streams and reusability. In order to achieve good contact between biomass sugars and the solid catalyst, deconstruction of the solid LCB into more hydrophilic products is required.[7] To this end, water can itself promote soluble oligosaccharide formation by autohydrolysis, taking advantage of hydronium ions from both water and *in situ*-generated compounds, such as acetic acid, uronic and phenolic acids, which catalyze hemicellulose depolymerization.[8] Further processing of these hemicellulosic sugars with a solid catalyst would then be desirable.

Extensive studies on xylose dehydration have been performed with the objective of simplifying the initial matrix (raw biomass) for furfural production. Among these, biphasic systems,[3,9,10] allowing simultaneous separation of furfural from the aqueous medium, are preferred over monophasic aqueous[11,12] and non-aqueous[13,14] systems.

Even though several studies have been performed on this subject, furfural production from raw, whole biomass with solid catalysts has not received that much attention. This study hence focuses on valorizing corn stover hemicelluloses (due to its high xylan content[15]) to yield furfural by a two-step cascade process. The first step consists of the solubilization of the hemicellulosic fraction of corn stover by autohydrolysis. During the second step, hydrolysis and dehydration reactions take place over niobium phosphate (NbP), an excellent solid acid. Throughout the process, microwave (MW) dielectric heating was employed, as it reaches the temperature set point efficiently, while diminishing degradation products.[16] Several aspects of green chemistry characterize this approach: the use of water as the sole solvent, the avoidance of highly polluting

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catalysts such as mineral acids, and saving of time and energy due to MW heating.[17]

To the best of our knowledge, such an approach (autocatalyzed fractionation of raw waste biomass, followed by heterogeneously catalyzed hydrolysis/dehydration of the as-obtained hemicellulosic hydrolysates over NbP) has not been proposed before for the production of furfural from raw biomass. This novel approach allows subsequent exploitation of the unaltered cellulose and lignin fractions. Furthermore, it is the first time that NbP has been used in the presence of biomass hydrolysates, as it has previously only been used in the presence of model sugars. In this respect, a recent paper on xylose dehydration to furfural in biphasic system using this catalyst was published.[18] NbP is an amorphous and water-tolerant solid acid that has both Brønsted and Lewis acidity,[19] the former being slightly predominant, according to Bassan *et al.*[20] This solid acid is not a naturally available compound, but it is easily formed by addition of phosphoric acid to a solution containing pentavalent Nb ions.[21] It is not commercially available yet, due a to lack of market demand, but its production appears to be easy to scale up according to a niobium manufacturer (Companhia Brasileira de Metalurgia e Mineração, CBMM). Additionally, niobium is the 33rd most abundant element in the Earth's crust, so it is a plentiful resource.[22] It is both nontoxic and physiologically inert, hence it is found in many medical devices.[23]

Results and discussion

Corn stover solubilization by autohydrolysis

Recent studies on pure hydrothermal conversion of biomass claim that close to 100% solubilization of hemicelluloses can be obtained at temperatures from 180 to 200 °C, while cellulose would need temperatures beyond 200 °C.[24] MW-assisted autohydrolysis treatments of corn stover, leading to hemicellulose fractionation, were then performed over a temperature interval from 180 °C to 200 °C and over times varying from 10 to 30 minutes. The progress of such autohydrolysis fractionation was mainly followed by IR spectroscopy of the solid residues produced and HPLC analysis of the liquid fractions obtained.

The severity of the autohydrolysis treatments increases with increasing time and temperature,[8] resulting in biomass solubilization percentages of up to 49%. Further increasing severity of treatments only leads to changes in liquid product distributions while keeping the solubilization percentage the same. Hydrolysates obtained by these treatments contain mostly xylose oligomers. Furfural yields obtained by autohydrolysis are low at these reaction conditions and they increase with increasing temperature up to 190 °C; further increasing temperature to 200 °C results in decreased furfural yields. Regarding yields of monomeric xylose, a maximum is observed at 180 °C and 30 minutes of reaction, then concentrations decrease due to dehydration to furfural and/or condensation reactions between xylose and furfural.

Table 1 MW assisted autohydrolysis of 5 wt% slurries of corn stover[a]

T (°C)	Time (min)	Solubilization (wt%)	Y_{Xy} (mol%)	Y_{Fur} (mol%)
180	10	42	2.9	1.4
180[b]	10	28	1.2	0.8
180	15	47	6.2	4.5
180	20	49	7.1	4.6
180	30	49	7.3	5.9
190	20	49	3.9	7.1
200	20	49	0.9	5.5

[a] Reaction conditions: 500 mg biomass in 10 mL of distilled water subjected to MW heating. [b] Test performed in a conventionally heated autoclave.

Acetic acid is also released during autohydrolysis from the cleavage of acetyl groups in hemicelluloses, lowering the pH of the reaction medium to 4.5 in most cases.

MW heating enhances the autohydrolysis process, as observed by a comparative test performed in a conventionally heated stainless steel Parr autoclave (see Table 1). The solubilization percentage obtained after 10 minutes of reaction at 180 °C was lower than 30%. As a consequence, longer reaction times are necessary when using conventional heating in order to achieve a similar solubilization percentage. Clear differences exist between conventional and MW heating. In the former, heat transfers slowly by conduction and convection processes (long induction periods are observed before reaching the temperature set point), while during MW heating, all components in the mixture heat simultaneously at a rate governed by their MW absorptivity. In this regard, Monteil-Rivera *et al.*[25] have measured the MW absorptivity of cellulose, xylan and lignin and have stated that carbohydrates are better absorbers than lignin, thus leading to their preferential heating and/or degradation. In line with these results, MW heating promotes rapid corn stover fractionation, probably due to a fast and preferential heating of the carbohydrate fraction at a temperature that is still low for significant cellulose degradation.

The obtained solid residues have IR spectra with diminished intensity of the peaks ascribed to the stretching vibration of the C=O (1734 cm^{-1}) and C–O (1243 cm^{-1}) of the acetyl ester units in hemicelluloses, as observed in Fig. 1. The decrease in these bands is indicative of the dissolution of hemicellulose.[26] It is evident that by increasing the severity of treatment, the spectra of the solid residues more resemble that of cellulose with the addition of the characteristic features of lignin.

In the inset of Fig. 1, the spectrum h, obtained from subtracting the mildest autohydrolysis treatment from the spectrum of the raw material, displays the main features removed from raw corn stover. The obtained spectrum is quite similar to the spectrum of reference xylan (i), but it shows an increased absorption of the bands ascribed to the acetyl groups at 1734 and 1243 cm^{-1} (C=O and C–O stretching vibrations) that seem to be present in higher amounts in corn stover hemicelluloses. The differences in the region of 2850–2900 cm^{-1} can also be ascribed to CH$_3$ *sym* ν vibrations
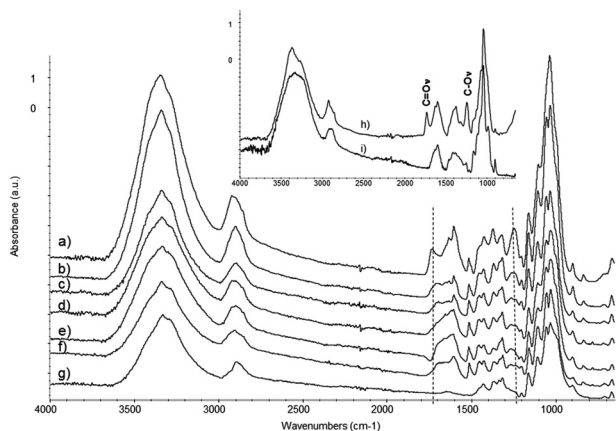
Fig. 1 FT-IR spectra of the solid residue obtained after autohydrolysis of corn stover at different conditions: (a) raw corn stover, (b) autohydrolysis at 180 °C for 10 min, (c) autohydrolysis at 180 °C for 15 min, (d) autohydrolysis at 180 °C for 20 min, (e) autohydrolysis at 180 °C for 30 min (f) autohydrolysis at 200 °C for 20 min, (g) cellulose. Inset: (h) subtraction a−b, (i) reference xylan from birchwood.

in a C–CH$_3$ group due to acetyls.[27] Rather small amounts of lignin were also removed from the raw material, as suggested by the weak peak at 1325 cm^{-1} in spectrum h, characteristic of skeletal vibrations of phenol rings.[28] Moreover, a slight peak at 832 cm^{-1}, comparable to noise, is observed. This peak also corresponds to the lignin spectrum and was clearly observed in the subtraction spectrum of the highest severity treatment (not shown). A slight decrease in this peak is also evident from a closer look at spectrum f, meaning that higher amounts of lignin were solubilized at these severe conditions.[8,26]

From the autohydrolysis treatments performed, the mildest conditions were hence selected (180 °C for 10 minutes) due to potentially good hemicellulose solubilization, minor sugar degradation, as well as insignificant lignin and cellulose fractionation, all occurring in the absence of externally added proton acids.

Preliminary thermogravimetric analyses under nitrogen atmosphere (not shown) of raw corn stover and the mildest autohydrolyzed residue, as well as the Van Soest characterization, confirm the removal of 86% hemicelluloses from corn stover with the mildest treatment, leaving cellulose and lignin practically untouched. However, for the clarity of comparisons in the following section, total hemicellulose conversion is assumed.

The suitability of the autohydrolysis process for biomass fractionation has been extensively reviewed from the biorefinery viewpoint and it has been considered a viable alternative.[29] However, an adequate severity of autohydrolysis treatment must be selected in order to maximize solubilization of hemicellulosic sugars, while still obtaining a solid residue prone to valorization either by thermochemical or biochemical routes. Specifically in the case of corn stover, optimized liquid hot water flow pretreatment has been reported to maximize solubilization of the hemicellulose fraction as soluble oligosaccharides. Controlling the pH of this process minimizes

complete hydrolysis to monosaccharides and subsequent sugar degradation.[30] On the other hand, the far-from-green acid hydrolysis of corn stover (1 wt% H$_2$SO$_4$) has been reported to yield up to 82% xylose.[31] It should be noted that hydrolysis of agricultural wastes such as corn stover proceeds faster than hydrolysis of woods, so sugar degradation products are easily obtained.[32] In the present study, the focus was on selecting hydrolysates with minor amounts of degradation products, since these will be in contact with the solid catalyst in the second stage of the proposed process.

Dehydration of hemicellulosic sugars over NbP

In the second stage of the process, the obtained hydrolysates from the autohydrolysis step were subjected to further hydrolysis and dehydration reactions over NbP to yield furfural. Our group previously characterized this material and it presents both terminal POH and NbOH groups. The former lead to a slightly stronger Brønsted acidity than NbOH sites. Lewis acidity is also present in this catalyst and is assigned to coordinatively unsaturated Nb^{+5} sites.[19]

Before evaluating the activity of NbP on such a complex system as corn stover hydrolysates, dehydration tests on pure xylose aqueous solutions (5 wt%) were performed with MWs as the heating source, since they provide selective heating for chemical transformations and result in energy saving and better yields in a short time.[17] This was clearly confirmed by our group through poplar sawdust valorization to levulinic acid,[16] where reaction times were lowered from one hour with conventional heating to 15 minutes when using MWs, leading to even better yields. Similarly short reaction times and temperatures ranging from 150 to 180 °C were therefore evaluated for xylose dehydration over NbP, and these results are presented in Table 2.

Good furfural yields and selectivities up to 52% were obtained using pure water as solvent. The best reaction conditions for xylose dehydration over NbP are 160 °C and 30 minutes. A control test without catalyst at these conditions displayed a net decrease in xylose conversion (from 82 to 15%), as well as in furfural yield (from 43 to 4%). These results highlight the remarkable activity of this heterogeneous catalyst, even though the presence of water as solvent promotes

Table 2 Xylose dehydration reactions over NbP[a]

Run	T (°C)	Time (min)	X_{Xy} (mol%)	Y_{Fur} (mol%)	S (mol%)
1	150	15	44	23	49
2	160	15	63	31	49
3	160	30	82	43	52
4	170	15	83	42	50
5	180	5	80	38	48
6	180	10	83	40	47
7	160[b]	30	15	4	23
8	100[b]	120	3	0	0
9	100	120	7	2	33

[a] Reaction conditions: 250 mg of xylose in 5 mL of distilled water; catalyst to xylose wt ratio, $R = 0.8$; subjected to MW heating. [b] Control reactions without catalyst.
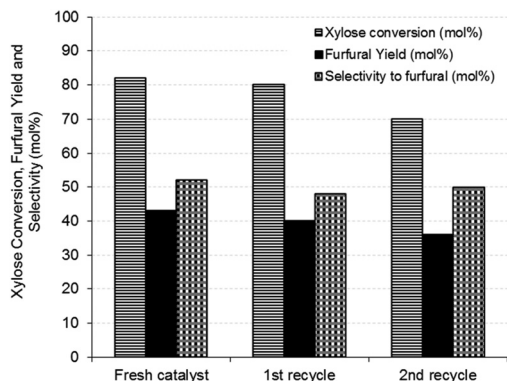
Fig. 2 Recyclability tests of NbP during xylose dehydration at 160 °C for 30 min.

Fig. 3 Reactions performed with 5 mL of corn stover hydrolysates (obtained from autohydrolysis at 180 °C and 10 min) over NbP (overall catalyst/biomass wt ratio = 0.8) subjected to MW heating.

furfural degradation reactions such as fragmentation, resinification and condensation reactions. The latter take place between furfural and xylose intermediates and cause furfural yields to decrease.

Recyclability of the spent catalyst was evaluated after two recycles under the best reaction conditions, as observed in Fig. 2.

Yields of furfural remained high, decreasing only around 5% after the second recycle. Selectivity was maintained in all three runs and xylose conversion was lowered in the second recycle. It should be noted that the spent catalysts had changed color from white to brown and their IR spectra (not shown) displayed two new weak peaks at ~1730–1700 cm^{-1} and 1620 cm^{-1}, which can possibly be ascribed to a C=O stretching vibration due to carbonyl groups in humins[33] deposited on the catalyst surface and adsorbed water, respectively. In spite of this, the spent catalysts displayed good activity after two recycles, setting a good baseline for reusability.

NbP is a truly heterogeneous catalyst that presents Brønsted and Lewis acid sites.[19] Specific studies on the role of Brønsted and Lewis acidity on xylose dehydration have demonstrated the need for a high ratio of Brønsted to Lewis acid sites for the selective conversion of xylose into furfural.[11,14] On one hand, Lewis acid sites decrease furfural selectivity by catalyzing condensation reactions to form insoluble humins, as observed with zeolite HY.[11] On the other hand, true Lewis acid sites selectively catalyze isomerization of aldoses to ketoses obtaining high yields.[34] Further dehydration of such ketose (either pentose or hexose) already in the furanose form then results in rapid conversion to the furaldehyde. This reaction pathway has usually been proposed at low temperatures (≪150 °C), and xylulose (ketopentose) has been detected and quantified as the reaction intermediate.[12,13]

In this regard, a probe test to evaluate true Lewis acid sites on NbP was carried out at l00 °C over a two hour reaction (Table 2, run 9), obtaining 7% xylose conversion and 2% yield of furfural, while the control reaction did not yield any furfural with only 3% conversion (Table 2, run 8). Although these yields are quite low, they suggest the presence of true Lewis acid sites on NbP,[35] which can catalyze, to a small extent,
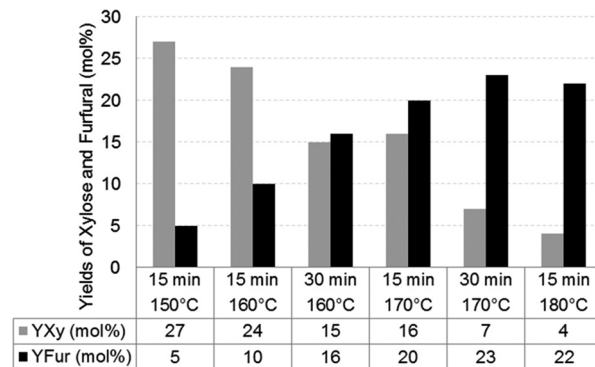
xylose isomerization with subsequent furfural formation. At such low temperatures, single Brønsted acids have not been able to catalyze xylose dehydration to furfural.[36] This is also in agreement with quantum mechanical calculations suggesting that single Brønsted acids promote furfural formation by a direct intramolecular rearrangement resulting from protonation of xylose at the O2 hydroxyl group, which is significant at temperatures between 150 and 200 °C.[37]

Finally, the performance of NbP was evaluated on real corn stover hydrolysates. These hydrolysates contain hemicellulose derived carbohydrates, mainly xylose oligomers, unidentified extractives and minerals. From theoretical calculations assuming total hemicellulose removal, the pentosan units subjected to dehydration account for ~90 mmol L^{-1} and from these only ~3% is detected as monomeric xylose.

During furfural production from biomass, pentosan units present in the system first undergo hydrolysis to monomeric pentoses which further dehydrate, losing three molecules of water, to yield furfural.[5]

As observed in Fig. 3, the lower reaction temperatures employed in this study result in high xylose concentrations but low furfural yields. Our group previously reported a similar behavior[38] when working with sucrose and inulin, thus confirming that hydrolysis reactions over NbP in aqueous medium proceed faster than dehydration reactions. By increasing reaction temperatures higher furfural yields were achieved after 15 minutes of reaction. In the case of xylose (see Table 2), the best selectivity and furfural yields were obtained at 160 °C after 30 minutes of reaction time, but with corn stover hydrolysates the best reaction conditions are 170 °C and 30 minutes, which result in 23% yield of furfural from corn stover. This yield is only slightly better than the one obtained at 180 °C, but we believe that this decrease in temperature can lead to less degradation of reactants and products, and thus less carbon deposits on the catalyst. It should be noted that single autohydrolysis tests at 180 °C over 30 minutes (Table 1), lead to quite low yields of furfural, showing that the acids released during autohydrolysis are not able to autocatalyze this reaction and that NbP does increase furfural yields from corn stover

Table 3 Recent studies on furfural production from corn residues

Reaction conditions	Catalyst	Solvent	Molar yield	Ref.
Xylose, 100 °C, 4 h	$CrCl_2$	DMA-LiBr	56%	36
Xylan, 140 °C, 2 h	$CrCl_2$, HCl	[EMIM]Cl	25%	
Corn stover 140 °C, 2 h	$CrCl_2$, HCl	[EMIM]Cl	22%	
Xylan, 200 °C, 2 min[MW]	$CrCl_3 \times 6H_2O$	[C4mim]Br	63%	44
Corn stalk, 200 °C. 3 min			23%	
Xylose, 250 °C, 5 min	TiO_2–ZrO_2	Water	34%	45
Corn stalk, 200 °C. 3 min			10%	
Xylan, 170 °C, 2.5 min[MW]	$AlCl_3$	[BMIM]Cl–water	85%	6
Corncob, 160 °C, 3 min	$AlCl_3$		19%	
Corncob, 160 °C, 3 min	$AlCl_3$/$CrCl_3$		27%	
Xylose, 160 °C, 30 min[MW]	$NbOPO_4$	Water	42%	[a]
Corn stover, 170 °C, 30 min		(in 2 stages)	23%	

MW = Microwave heating. [a] This work, with overall catalyst/biomass wt. ratio, R = 0.8.

hydrolysates. It is worth noting that although higher temperatures were used with corn stover hydrolysates, furfural yields were lower than those obtained with xylose solutions. This can be ascribed to the complexity of this matrix, containing not only xylo-oligomers, which NbP seems to effectively hydrolyze, but also extractives and mineral ions (ashes). For instance, the corn stover used in this study contained a very high amount of ashes, most likely stemming from soil remaining in biomass. It has been claimed that soil has a high neutralizing capacity, diminishing performance of dilute acid hydrolysis.[39] For the rest, preliminary IR characterizations of the spent catalysts show a potentially lower organic matter deposition on catalysts used with corn stover hydrolysates, which is quite promising.

The furfural yields obtained here are still low, mainly because of water (the greenest solvent) promoting furfural degradation, as has been observed with most catalytic systems[3,9–14] needing simultaneous furfural separation. However, the good hydrolysis activity of NbP, even at lower temperatures, and its higher dehydration activity at higher temperatures (see Fig. 3) make this solid acid very appropriate for this process. In order to improve yields in an eco-friendly manner, the authors envisage coupling this approach with furfural stripping with nitrogen,[40] which allows high furfural purity in the stripped stream and N_2 recycling with few post-treatment steps.

Recent studies performed on furfural production from corn residues (see Table 3) show how the different catalytic systems often suffer when subjected to reactions with real biomass or even xylan. In our case, raw biomass hydrolysates contained mostly xylo-oligomers, minor amounts of monomeric xylose and high amounts of unidentified extractives and minerals (ashes). The latter have been demonstrated to reduce the hydrogen ion activity on dilute-acid hemicellulose hydrolysis, accounting for a neutralizing capacity as high as 17.3 mg of H_2SO_4 per gram of dry corn stover.[41] Moreover, these ion salts released from biomass during fractionation might promote side reactions, diminishing furfural selectivity,[42] or even cause

catalyst deactivation by exchange of protons on the catalyst with such cations in solution.[14] Nonetheless, NbP proved to be active in both hydrolysis and dehydration reactions even in the presence of these unidentified compounds, while decreasing furfural yields to a minor extent compared to other catalytic systems. Furthermore, the process proposed follows the main principles of green chemistry: using water as solvent, avoiding the use of polluting reagents and the formation of residues needing to be disposed of. The high point is that the solid residue (cellulose and lignin) produced in the first autohydrolysis stage constitutes a future raw material for the production of platform chemicals (like HMF, levulinic acid, *etc.*) and lignin upgrading products, as it has been reported that fractionated cellulose and lignin derived from such mild treatments as autohydrolysis are practically not degraded and allow further valorization.[43]

Experimental

Details on experimental procedures and calculations are provided in the ESI.† Briefly, corn stover used in this study was collected from San Piero a Grado, Pisa (Italy). It consisted only of leaves and stems and is composed of 24.4 wt% hemicellulose, 42.2 wt% cellulose and 12.5 wt% lignin. This material contains high amounts of extractives and ashes which account for 11.5 and 9.5 wt%, respectively, and was used in the hydrothermal conversion as a whole without pretreatment. The composition of the dry corn stover and the selected autohydrolyzed residue was evaluated by the Van Soest methodology.[46] All reagents were used as received for HPLC calibration and, in the case of xylose, also as a model compound. Xylan from birchwood was used as a reference compound for IR characterization. Niobium phosphate ($NbOPO_4$, NbP) ADF25 (surface area 180 m^2 g^{-1}) was supplied by CBMM and was treated at 255 °C for 6 h under high vacuum and its effective acidity resulted in 0.33 meq g^{-1}.[47]

MW-assisted non-catalytic and catalytic tests were performed using a commercially available mono-mode microwave unit (CEM Discover S-class system) comprised of a calibrated external infrared sensor. Temperature control is achieved by a P.I.D. controller by adjusting the MW power (see ESI† for a typical temperature profile). During every run, the MW reactor was set to dynamic mode with an initial MW power of 150 W. Initial reaction time ($t = 0$) was taken when the temperature set point was reached. Autohydrolysis tests were carried out in a 35 mL reactor and catalytic tests in a 10 mL one, both comprising a magnetic stirrer. Catalytic recycle tests were performed with prior acetone washings of spent catalysts (see ESI†). A comparison autohydrolysis test was also performed in a Parr reactor as explained in ESI.† Reproducibility of repeated autohydrolysis and catalytic runs resulted within 5%.

Products present in the aqueous solutions were quantitatively analyzed by HPLC (Perkin Elmer Flexar) equipped with RI detector using a PolyporeCA column eluted with 5 mM H_2SO_4.

The solid fraction obtained from the first autohydrolysis stage was characterized with Spectrum One FTIR system (Perkin Elmer, Wellesley, MA) comprised of a universal ATR (Attenuated Total Reflection) accessory provided with a ZnSe surface. These spectra were normalized at a peak position near 1510 cm^{-1} as referenced by Chundawat et al.[1]

Conclusions

This work provides a solid basis for a simple and green valorization of the hemicellulosic fraction of corn stover, leaving cellulose and lignin readily utilizable for further processing, either by thermochemical or other routes.

This MW-assisted, two-stage cascade process, using only corn stover and water in the presence of niobium phosphate (NbP) as catalyst, leads to good furfural yields.

During the first stage of the process, corn stover was hydrothermally fractionated to obtain soluble hemicellulosic sugars and a solid residue containing cellulose and lignin. A mild autohydrolysis treatment was selected so as to produce the least sugar degradation products in this stage. A positive effect of MW dielectric heating on biomass solubilization was observed during this stage.

In the second step of the process, the obtained hemicellulosic sugars (mostly oligomers) were hydrolyzed and dehydrated over NbP to obtain up to 23% furfural yield. This is a very promising result, taking into account the use of whole raw biomass in pure water and a heterogeneous catalyst.

The activity of NbP in water was also evaluated for xylose dehydration, yielding up to 43% furfural at 160 °C over 30 minutes of reaction time. The spent catalyst was re-used in two more recycling tests, while still obtaining high furfural yields.

Further studies are in progress for the optimization and subsequent exploitation of the residual cellulose and lignin fractions here obtained, which evaluate more severe conditions for cellulose valorization.

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