LEVULINIC ACID PRODUCTION FROM WASTE BIOMASS

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The hydrothermal conversion of waste biomass to levulinic acid was investigated in the presence of homogeneous acid catalysts. Different cheap raw materials (poplar sawdust, paper mill sludge, tobacco chops, wheat straw, olive tree pruning) were employed as substrates. The yields of levulinic acid were improved by optimization of the main reaction parameters, such as type and amount of acid catalyst, temperature, duration, biomass concentration, and electrolyte addition. The catalytic performances were also improved by the adoption of microwave irradiation as an efficient heating method, allowing significant energy and time savings. The hydrothermal conversions of inulin and wheat straw were carried out in the presence of niobium phosphate, which up to now have never been employed in these reactions. The preliminary results appeared to be in need of further optimization.

Keywords: Biomass; Levulinic acid; Niobium phosphate; Acid catalysis; Microwave irradiation

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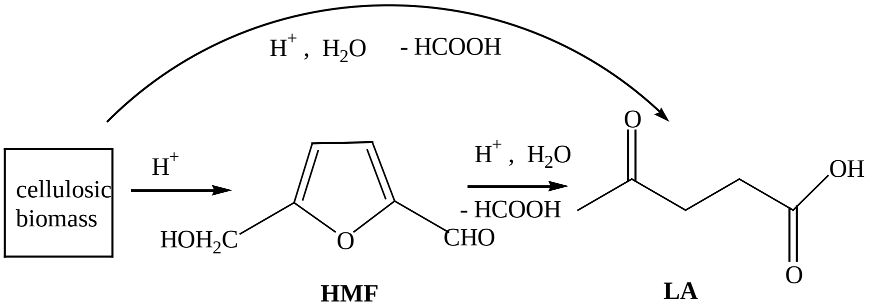
INTRODUCTION

The progressive depletion and price fluctuation of fossil resources are promoting a shift from fossil to renewable materials in the feedstock for the production of energy, fuels, and chemicals. Nowadays, only about 5% of all the produced chemicals derive from renewable resources. On the other hand, lignocellulosic biomass, hitherto underutilized, can be converted into value-added chemicals by acid hydrothermal treatment (Corma et al. 2007; Rackemann and Doherty 2011). This route represents a sustainable solution to increasing demand of these chemicals, allowing security of supply, and bringing economic advantage, in particular when cheap raw materials, agricultural waste, or residue are employed as substrates. The selection of the biomass feedstock is of paramount importance from both techno- and socio-economical points of view. Waste streams with a low or even negative value, such as agricultural wastes, are preferred, because their employment for chemical transformations does not compete with food production.

The key challenge is in finding ways to successfully abstract simple and defined chemical building blocks from the biomass. In this context, the selective syntheses of levulinic acid (LA) and 5-hydroxymethyl-2-furaldehyde (HMF) from hexoses or hexoses-derived molecules by acid hydrothermal conversion has gained increasing attention (Klaas and Schoene 2009) (Scheme1).



Scheme 1. Biomass conversion to levulinic acid in the presence of acid catalysts

HMF is the product of the acid-catalyzed dehydration of cellulosic biomass at mild temperature. It is a platform molecule, serving as an intermediate for the production of pharmaceuticals, fine chemicals, and furan-based polymers, which have recently been proposed as a biorenewable replacement for PET plastic (Taarning 2008). LA is the product of the subsequent rehydration of HMF, with formic acid co-produced in equimolar amount in this reaction (Girisuta 2007). LA is a versatile intermediate and is one of the United States Department of Energy's (DOE's) top 12 bioderived feedstocks (Manzer 2006). It can be used as solvent, antifreeze, food flavouring agent, intermediate for pharmaceuticals, and for plasticizers synthesis (Cha and Hanna 2002; Bozell et al. 2000).

In particular, LA can be hydrogenated to become γ-valerolactone, a sustainable liquid for the production of energy and chemicals (Horváth et al. 2008; Raspolli Galletti et al. 2012; Braca et al. 1991). γ-valerolactone is the centre of a cascade processes for the production of liquid fuels involving different smart approaches, as reported in a number of recent papers (Serrano-Ruiz et al. 2010; Guerbuez et al. 2011; Lange et al. 2010).

In spite of its great potential as a basic platform chemical, LA has never been produced in significant volume. The reason is probably that LA production was mainly studied in the early 1950s, when expensive precursors were employed. The yields were low and the equipment for separation and purification was lacking (Corma et al. 2007). The maximum theoretical yield of LA from hexoses and cellulose are 64.5 wt % and 71.5 wt % respectively, due to the co-production of formic acid. In the results published or patented so far, LA yields of up to about two thirds of the theoretical yield have been claimed (Rackemann and Doherty 2011). In fact, the yield is significantly lowered due to the formation of soluble polymeric by-products and undesired black solids, called humins, which can cause the clogging of the reactor.

The Biofine Process represents one of the most celebrated technologies currently claimed for LA industrial production (Hayes et al. 2006). Many feedstocks (such as paper, wood, and other ligno-cellulosic material) have been claimed as starting materials. This process involves the use of dilute sulphuric acid as a catalyst, and it takes place in two separate hydrolysis reactors. In the first step biomass and sulphuric acid solution are mixed and continuously supplied to a small diameter tubular reactor that operates at a temperature within the range of 210 to 220 °C and a pressure of 25 bar. The residence time in this first reactor is 12 seconds, in order to depolymerize the polysaccharides into their soluble monomers (e.g. hexoses, pentoses, HMF). The outflow mixture is then fed to the second continuously stirred tank reactor that operates at a lower temperature and pressure (190 to 200 °C, pressure 14 bar).

To the best of our knowledge, the first commercial-scale plant for the conversion of lignocellulosic biomass to LA was built in Caserta, Italy (Hayes et al. 2006). At the beginning, this plant adopted the Biofine technology. This was wet up with the two reactors configuration using local tobacco chops or paper mill sludge as feedstock. The process with tobacco chops highlighted many disadvantages of the Biofine approach for this raw material, in particular due to the complete clogging of the first reactor, which has smaller diameter, by deposition of salts and humins. Thus, University of Pisa has been engaged in order to improve the process (Fugalli et al. 2008). In this context, we now report our results in the acid hydrothermal conversion of different renewable resources to directly yield LA, employing homogeneous and heterogeneous acid catalysts. In this process, both traditional heating and microwave-assisted catalytic conversion have been investigated. The different substrates were reacted under similar reaction conditions, in order to compare their performances and thus evaluate the feasibility of their catalytic conversion, focused on levulinic acid production.

EXPERIMENTAL

Materials

All chemicals and commercial catalysts were purchased from Aldrich and used as received. Inulin from Dahlia tubers (Fluka) with M_n ca. 5000 was used as received. Niobium phosphate (NbP) ADF25 (surface area 180 m^2/g) was supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração). NbP was treated at 255°C for 6 h under high vacuum (5 Pa) and its effective acidity resulted 0.33 meq/g (Raspolli Galletti et al. 2012). Poplar sawdust, wheat straw, tobacco chops, and olive tree pruning were collected from local farms. Paper mill sludge was purchased from SCA Packaging Italia S.p.A. (Lucca, Italy). All the above raw materials were air-dried and milled using a laboratory hammer mill (Retsch) to produce particles smaller than 0.5 mm in diameter, homogenized in a single lot and stored until used. Before the catalytic reactions these raw materials were dried under vacuum (0.5 mm Hg) at 60 °C up to constant weight. The composition of the dry feedstocks is reported in Table 1. Deionized water was applied to prepare the various solutions.

Table 1. Composition of the Dry Feedstocks (wt %)

Dry feedstock	Cellulose Wt %	Hemicelluloses wt %	Lignin wt % Acid soluble	Klason	Ash wt %
Poplar sawdust	57.6	14.1	3.1	14.9	0.8
Olive tree pruning	39.4[a]	16.1	2.3	16.8	3.5
Wheat straw	39.2	25.6	3.8	19.1	5.6
Tobacco chops [b]	25.0	3.7	0.2	4.7	21.0
Paper sludge	57.1	8.1	1.8	15.8	7.1

[a]Including extractive hexoses [b]Calcium content: 4.2 wt %; magnesium content: 2.1 wt %.

Catalytic Experiments

The process was carried out in a 300 mL mechanically stirred Parr 4560 autoclave equipped with a P.I.D. controller 4843, an electrical heating system, and an internal temperature control device. In a typical procedure, the powdered biomass, added with NbP, was inserted in the autoclave under inert atmosphere. Then the autoclave was closed, evacuated up to 0.5 mm Hg, and added with the proper amount of water (containing the proton acid and, if necessary, the electrolyte) introduced inside by suction. Finally the autoclave was pressurized with nitrogen to 30 bar, and sufficient temperature ramping time was allowed before the reaction step at the proper temperature. After the reaction, the reactor was rapidly cooled to room temperature, degassed, and the reaction mixture was analyzed.

Microwave reactions were conducted using a commercially available mono-mode microwave unit (CEM Discover S-class system) in a 50 mL microwave tube containing a Teflon stirrer bar. The vial was purged with nitrogen and capped. Then the reaction mixture was transferred into the microwave unit and the sealed vessel irradiated at a fixed temperature of 200 °C. At the end of each experiment, the reactor was rapidly cooled to room temperature and the reaction mixture was analyzed.

Analytical Procedures

HMF, LA, and the other reaction products formed were identified by a GC (Hewlett-Packard 5980), equipped with a Phenomenex Zebron-Wax Plus column (30m x 0.32 mm x 0.50 μm), interfaced to a Hewlett-Packard 5995A spectrometer. The products present in aqueous solution were quantitatively determined by HPLC (Perkin Elmer Flexar) equipped with refractive index detector. 20 μL samples were loaded into a PolyporeCA column (4.6 mm x 220 mm x 10 μm) and eluted with 0.5 mM H_2SO_4 at a flow rate of 0.5 mL/min. The column was maintained at 60 °C, and the calibration was carried out using commercial standards. The concentration of formic acid was determined using a gas-chromatograph Hewlett-Packard HP 6890 with a TCD detector and equipped with a 10 % FFAP packed column maintained at 100 °C.

Levulinic acid yield based on the weight of raw material was calculated as: Yield of levulinic acid (%) = Levulinic acid recovered after reaction (g)/ substrate (g) x 100.

Theoretical yield of levulinic acid (%) was calculated as: cellulose content(g) x 0.715/ substrate (g).

The composition of the raw substrates was performed according to the procedure of Van Soest et al. (1991).

FTIR spectra of the dried solid residues were obtained with a Perkin-Elmer Spectrum One spectrophotometer equipped with an attenuated total reflectance apparatus.

RESULTS AND DISCUSSION

Different precursors such as fructose, glucose, sucrose, starch, cellulose, and also cheap biomass, such as wood, wheat straw, cotton linters, sorghum grain kernels, and agricultural wastes have been used to produce LA (Rackemann and Doherty 2011). These different substrates have been reacted under different reaction conditions, making it difficult to compare their performances and thus evaluate the feasibility of their catalytic conversion to levulinic acid. When water insoluble biomass is processed, homogeneous acid catalysts generally appear more suitable in comparison to heterogeneous ones, considering their ability to deliver the active species into the solid or swelled biomass (Mehdi et al. 2008). H_2SO_4 is the most commonly used mineral acid, yet HCl, HBr, and H_3PO_4 have been also reported (Takeuchi et al. 2008).

Selected results obtained in the conversion of different raw substrates to LA in the presence of homogeneous acid catalysts, adopting various reaction conditions, are now reported in Tables 2 and 3.

Only trace amounts of HMF and of furfural (derived from hemicellulosic C-5 sugars) were ascertained under the adopted reaction conditions. On the contrary, the molar yield of formic acid, co-produced in equal molar amount with LA (Scheme 1), resulted always slightly lower than that of LA, probably due to its side reactions.

When olive tree biomass, obtained from pruning, was employed using HCl as catalyst, it yielded up to 66% of the theoretical yield with traditional heating at 200 °C (run 2, Table 2). This result is interesting because olive tree biomass is a type of renewable and cheap lignocellulosic residue, lacking alternative usages, whose disposal is necessary.

On the other hand, with the aim of developing a novel, commercially attractive process, the application of environmentally benign conditions and sustainable technologies for reduced energy demand plays a fundamental role. In particular, the combination of superheated water as green solvent with the use of microwave irradiation as an efficient heating method represents a real prospect for truly sustainable chemical processes. In fact, microwave-assisted processes involve significant energy (up to 85-fold) and time savings (Dallinger and Kappe 2007). In effect, when oil bath heating was replaced by microwave heating at the same temperature under sealed-vessel conditions (runs 3, Table 2), a significant reduction of the reaction time was possible, accompanied by a simultaneous increase of LA yield up to 71% of the theoretical yield (compare run 2 with run 3).

This result confirms that microwave heating is a proper route to heat the biomass aqueous slurry. In fact, the radiation penetrates into the slurry and it is uniformly absorbed, thus providing a very rapid and homogeneous heating, without wall or heat diffusion effects (the microwave energy passes through the walls of the vessel and heats only the reactants), and partial overheating is avoided. In addition, MW irradiation can lower the activation energy or increase the pre-exponential factor in the Arrhenius law due to an orientation effect of the polar species in an electromagnetic field, thus leading to a more effective and selective chemical reaction (Kappe 2004).

When poplar sawdust was used as substrate (runs 4-6, Table 2), the performances could be improved not only by adopting MW irradiation (run 6, Table 2), but also by performing the traditional heating in two steps: a pre-hydrolysis at lower temperature and a successive conversion step at 200 °C (run 5, Table 2). The effects of different pre-hydrolysis temperatures on the LA yield for poplar sawdust are reported in Fig. 1.

Table 2. LA Yield from Different Precursors (1.75 g) Carried Out in the Presence of Homogeneous Acid Catalysts in Water (24 mL)

Run	Raw material	Cellulose content (wt %)	Thermal treatment	Acid (meq)	Yield[a] (wt %)	Yield based on cellulose content (%)	Yield based on theoretical yield (%)
1	Olive tree pruning	39.4[b]	180 °C for 1 h	HCl 37 % 11.5	11.7	29.7	41.5
2	Olive tree pruning	39.4[b]	200 °C for 1 h	HCl 37 % 0.95	18.6	47.2	66.0
3	Olive tree pruning	39.4[b]	MW irr. 200 °C for 0.25 h	HCl 37 % 11.5	20.1	51.0	71.3
4	Poplar sawdust	57.6	200 °C for 1 h	HCl 37 % 11.5	21.3	37.0	51.8
5[c]	Poplar sawdust	57.6	200 °C for 1 h	HCl 37 % 11.5	29.3	51.0	71.3
6	Poplar sawdust	57.6	MW irr. 200 °C for 0.25 h	HCl 37 % 11.5	26.4	45.8	64.1
7	Paper sludge	57.1	200 °C for 1 h	H_2SO_4 98 % 8.3	15.4	27.1	37.9
8	Paper sludge	57.1	200 °C for 1 h	H_2SO_4 98 % 11.5	15.1	26.5	37.2
9	Paper sludge	57.1	200 °C for 1 h	HCl 37 % 8.3	21.8	38.2	53.5
10	Paper sludge	57.1	200 °C for 1 h	HCl 37 % 11.5	31.4	55.1	77.0
11	Paper sludge	57.1	MW irr. 200 °C for 0.25 h	HCl 37 % 11.5	31.7	55.5	77.6

[a] Yield based on weight of raw material. [b] Cellulose and extractive hexoses. [c] A pre-hydrolysis step was carried out at 120 °C for 2 h.

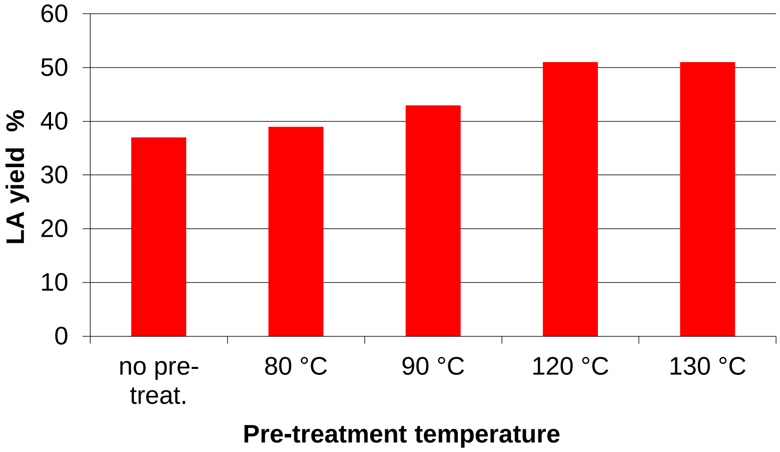


Fig. 1. Effect of poplar sawdust pre-treatment temperature on LA yield % based on cellulose content (Reaction conditions: poplar sawdust 1.75 g; HCl 37 % 0.95 mL, H_2O: 24 mL, pre-treatment for 2 h, then reaction at 200 °C for 1 h).

The pre-hydrolysis step solubilizes a fraction of the hemicellulosic component, making undissolved cellulose more accessible in the successive treatment at high temperature. A very recent characterization of poplar wood treated with dilute sulphuric acid for times ranging up to 20 minutes and at temperatures ranging from 120 to 150 °C made it possible to detect modification of the biomass structure at a molecular level, involving not only the dominant hydrolysis/depolymerization of hemicellulose, but also of holocellulose and lignin (Kobayashi et al. 2011). In comparison to MW irradiation, which needs the availability of the MW reactor, the adoption of the pre-hydrolysis step appears as a more immediate approach in order to improve the LA yields from raw biomass in a preliminary screening.

Diluted HCl always acted as a better catalyst in comparison with $H_2SO_{4.}$ In fact, in the presence of $H_2SO_{4,}$ significant deposition of humin solid by-products on the reactor walls was observed. Moreover, when the raw biomass had a significant content of calcium salts, as in the case of paper-mill cellulose wastes (runs 7 and 8, Table 2) or of tobacco chops (calcium concentration > 4 wt. %) (runs 15 and 16, Table 3), significant deposition of calcium sulphate was observed, even when working at lower H_2SO_4 concentrations. When higher H_2SO_4 concentrations were adopted, reactor clogging took place. On the contrary, under our optimized reaction conditions involving the use of HCl and limited times, the absence of salts precipitation and humins deposition was ascertained. HCl always afforded higher LA yields with respect to H_2SO_4 (compare runs 7 and 8 with 9 and 10 respectively).

It is remarkable that LA yields up to 77 % of the maximum theoretical yield were also obtained working on a negative value material such as paper mill sludge (run 8, Table 1). For some substrates, such as wheat straw and tobacco chops, the addition of a cheap electrolyte to the reaction medium, such as NaCl, increased the LA yield (compare run 10 with run 12, and run 14 with run 15). In fact, it is known that the addition of an electrolyte can increase the rate of the heterogeneous acid hydrolysis of cellulose to convert to glucose and then LA, while enhances the accessibility of the rest portion of the cellulose (Zaranyika and Madimu 1989). This salt effect has been explained by applying the Donnan's theory of membrane equilibria to the heterogeneous hydrolysis of the cellulose in dilute acid. The difference of concentration of H_3O^+ ions in the two phases can be minimized by the addition of an inert, diffusible salt. The addition of the electrolyte should result in an increase in the concentration of H_3O^+ ions in the cellulose phase, thus increasing its swelling and the rate of protonation of reaction sites. It has been reported that inorganic salts could also increase the hydrolysis rate of hemicellulose component during dilute acid pretreatment (Liu et al. 2009).

When water slurry of tobacco chops powder, containing 25 % w/w of cellulose, was employed as starting material, the actual yield of LA was about 83% of the theroretical yield, due to the combined effect of both the addition of the electrolyte and the pre-hydrolysis step at 120 °C (run 19, Table 3). This yield is the highest ever reported using a waste biomass in a batch process and, more in general, the yields reached with the different substrates are promising if compared with those that have been up to now reported in the literature (Doherty et al. 2011). In particular, a recent paper has studied the optimization of levulinic acid production from wheat straw using H_2SO_4 (Chang et al. 2007). Under the optimal conditions (209 °C, 37.6 min of reaction time, 3.5 wt % of acid concentration and 15.6 liquid/solid ratio) the reached yield based on the weight of raw material was 19.86 % , comparable with the 19.3 % value obtained by us in the presence of HCl 1.6 wt % (run 12 Table 3) adopting 1 h of reaction time. The use of this volatile acid catalyst enables the recovery of the produced LA by atmospheric/vacuum distillation and steam stripping, which can allow about 95% of the acid catalyst and water to be recycled (Doherty et al. 2011).

These results can be remarkable if the economics of the whole process are evaluated considering the possible exploitation of the solid residue, mainly due to lignin component. It has great potential for many applications: as a soil conditioner, as a free radical scavenger for antioxidation, as a low-density filler taking place of inorganic fillers, or as a component for biodegradable formulations.

On the other hand, if water-soluble carbohydrates are employed as substrates, heterogeneous acid catalysts appear preferable, offering the advantage of a very easy separation from the reaction products, allowing them to be easily recycled. Besides, they are environmentally friendly with respect to safety and corrosiveness. Up to now, only very few heterogeneous acid catalysts have been experimented for the conversion of carbohydrates to yield LA. Examples incude ion-exchange resins (Schraufnagel and Rase 1975), zeolites (Jow et al. 1987), pillared clays (Lourvanij and Rorrer 1994), nafion (Hegner et al. 2010), and solid superacid $S_2O_8^{2-}/ZrO_2-SiO_2-Sm_2O_3$ (Chen et al. 2011).

Table 3. LA Yield from Waste Precursors (1.75 g) Carried Out in the Presence of Homogeneous Acid Catalysts in Water (24 mL).

Run	Raw material	Cellulose content (wt %)	Thermal treatment	Acid (meq)	Yield[a] (wt %)	Yield based on cellulose content (%)	Yield based on theoretical yield (%)
12	Wheat straw	39.2	200 °C for 1 h	HCl 37 % 11.5	19.3	49.3	68.9
13	Wheat straw	39.2	MW irr. 200 °C for 0.25 h	HCl 37 % 11.5	20.6	52.5	73.5
14[b]	Wheat straw	39.2	200 °C for 1 h	HCl 37 % 11.5	21.7	55.3	77.4
15	Tobacco chops	25.0	200 °C for 1 h	H_2SO_4 98 % 8.3	3.0	12.0	16.8
16	Tobacco chops	25.0	200 °C for 1 h	H_2SO_4 98 % 11.5	3.7	14.8	20.7
17	Tobacco chops	25.0	200 °C for 1 h	HCl 37 % 11.5	5.2	20.8	29.1
18[b]	Tobacco chops	25.0	200 °C for 1 h	HCl 37 % 11.5	8.1	32.4	45.3
19[b, c]	Tobacco chops	25.0	200 °C for 0.5 h	HCl 37 % 11.5	15.0	59.0	82.5

[a] Yield based on weight of raw material. [b] NaCl (0.35 g) was added. [c]A pre-hydrolysis step was carried out at 120 °C for 2 h.

Niobium phosphate is a strong water-tolerant acid, proposed by our group more than ten years ago for the selective dehydration of fructose and inulin to HMF, carried out at a temperature of about 100°C (Carlini et al. 1999). This amorphous solid has strong Broensted acid sites and medium-strong Lewis acid sites at the surface, due to coordinatively unsaturated Nb^{+5} species (Armaroli et al. 2000).

Now, for the first time, the performances of this catalytic system for the direct synthesis of LA from biomass have been investigated, working at 200 °C, under traditional and microwave heating. The results obtained in the conversion of inulin solutions, a polyfructoside presents in roots and tubers of many plants and wheat straw slurries are reported in Table 4.

NbP was observed to be active in the conversion of inulin to yield LA under traditional heating for 1 h (run 17, Table 4). Yields about 20% w/w were achieved without appreciable formation of solid by-products. LA was the predominant monomer product, while the unique soluble monomer by-product ascertained in very low concentration was the intermediate HMF.

Also for this reaction, the use of MW irradiation (runs 21-24, Table 4) allowed a significant time saving accompanied with a simultaneous enhancement of the yield from 20 up to about 30% w/w, corresponding to 40 % of the theoretical yield. This preliminary investigation, carried out in slurry batch reactor, appears promising because many heterogeneous catalysts up to now investigated in the synthesis of LA generally required very long reaction times (15-25 h) to reach comparable yields (Schraufnagel and Rase 1975; Jow et al. 1987; Lourvanij and Rorrer 1994; Hegner et al. 2010).

Table 4. LA Yield in the Conversion of Inulin Aqueous Solutions and of Wheat Straw Slurries in the Presence of Niobium Phosphate (H_2O: 33 mL)

Run	Substrate (g)	Thermal treatment	Time (h)	NbP (g)	LA yield [a] (wt %)	HMF yield [a] (wt %)
20	Inulin (2)	200 °C	1	2	19.8	2.0
21	Inulin (2)	200 °C, MW irr.	0.25	2	28.1	2.4
22	Inulin (4)	200 °C, MW irr.	0.25	2	28.0	3.7
23	Inulin (4)	200 °C, MW irr.	0.1	2	5.7	0.8
24	Inulin (2)	200 °C, MW irr.	0.25	1	27.9	1.9
25	Wheat straw (2)	200 °C	1	2	9.7	0.4
26	Wheat straw (2)	200 °C, MW irr.	0.25	2	10.1	0.3
27	Wheat straw (2)	210 °C	1	2	9.6	0.4

[a] Yield % based on weight of starting substrate.

Remarkably, NbP was also observed to be active in the conversion of water slurries of wheat straw, with about 10% w/w yields based on the employed dry biomass (runs 25-27, Table 4). The obtained results can be compared with those obtained with homogeneous HCl under analogous thermal treatment conditions (compare runs 25 and 26 with runs 12 and 13 respectively): the expected superiority of homogeneous catalysis is well evident, catalytic performances resulting halved in the presence of NbP. Besides, working with the heterogeneous NbP, a significant drawback is that NbP remains englobed in the solid lignin residue, and it can be recovered and recycled only after suitable thermal treatment. Further research is necessary in order to optimize this step and improve these preliminary results.

CONCLUSIONS

1. We evaluated the feasibility of the catalytic conversion of cheap or waste renewables to levulinic acid. The acid catalyzed hydrothermal conversion of raw biomass (wood sawdust, paper sludge, wheat straw, olive tree pruning, tobacco chops) to this platform chemical can be carried out with high yield in the presence of dilute HCl.
2. The optimization of the main reaction parameters (type and amount of acid catalyst, temperature, duration, biomass concentration, electrolytes addition) allowed an increase of yield up to 83 % of the theoretical yield, the highest value so far reported with raw biomass. Microwave irradiation made it possible to increase the catalytic performances, with significant energy and time saving.
3. The hydrothermal conversion of the soluble precursor inulin to levulinic acid was carried out in the presence of niobium phosphate, a heterogeneous acid catalyst which had never been used for this reaction. This heterogeneous system also showed promising results in preliminary experiments involving a water slurry of wheat straw.
4. Given the appreciable yields of LA, starting from negative value feedstock, the process seems worthy of further optimization.

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