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Microwave-assisted conversion of carbohydrates to levulinic acid: an essential step in biomass conversion†

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Degradation of non-edible carbohydrates to levulinic acid (4-oxopentanoic acid) was studied by using dielectric heating with microwave energy. Levulinic acid and its reduced and dehydrated derivative, γ-valerolactone (GVL), can be used for the production of small-molecule, functionalized hydrocarbons, which might be potential platform molecules for the chemical industry. First, simple model compounds (fructose, glucose, saccharose and cellobiose) were hydrolyzed in order to find the optimum reaction conditions (*e.g.* reagent, reaction temperature, acid concentration, time) for the degradation and transformation of polysaccharides (cellulose, chitin, chitosan) by using controlled microwave irradiation. Cellulose, a non-edible biopolymer of plant origin, was successfully converted to levulinic acid under the optimized conditions (2 M H_2SO_4, 170 °C, 50 min) with a yield of 34.2% in a mono-mode Multisynth microwave reactor. The reactions proceeded with hydrochloric acid catalysis as well, and a slightly better yield was achieved, however, using HCl (a chlorine containing catalyst) raises serious environmental concerns. The hydrolysis of glucosamine-based glycans (D-glucosamine, *N*-Ac-D-glucosamine, LMw-chitosan, MMw-chitosan, chitin) was also studied and optimized with sulfuric acid as a catalyst in a mono-mode Multisynth microwave reactor. The highest yield of levulinic acid was obtained with 2 M H_2SO_4 at 190 °C for 30 min. *N*-Ac-D-glucosamine, D-glucosamine, LMw-chitosan and MMw-chitosan resulted in levulinic acid with yields between 20.6% and 32.7%, the larger molecular weight chitin was degraded to levulinic acid with a yield of 37.8%.

Introduction

The global chemical industry is almost exclusively based on non-renewable resources, *i.e.* fossil fuels, which also provide 90% of all our energy needs. While it is very difficult to predict the exact date of depletion of crude oil and natural gas, the development of alternative strategies to supply sustainable fuels and carbon based feedstocks should be accelerated.[1,2] The global efforts to reduce the carbon dioxide emission also demand new and innovative strategies for the green production of fuels,[3] platform molecules and value-added chemicals.[4] Hydrogenation of carbon dioxide could be one of the approaches to produce carbon-based building blocks and intermediates.[5] In addition, nature can help to convert carbon dioxide to biomass, one of the most preferred renewable resources.

Carbohydrates, as the main part of biomass, are present in the form of sugars, starches, cellulose, lignocellulose, and chitin. Based on the biorefinery concept, sugars and starches have already been successfully used.[6] However, the selection and consumption of appropriate resources have become a controversial issue due to the dramatically increased utilization of edible resources. In addition, the selective conversion of non-edible biomass components, such as cellulose, chitin, *etc.*, into platform molecules plays a key role in sustainable development.[7] Consequently, the simple conversion of biomass into carbon based chemicals[6,8,9] and fuels[10] has become the focus of interest. It was established that saccharose can be converted to various C_5-oxygenates *via* levulinic acid (LA),[11] which is one of the most important intermediates of the proposed biomass based carbon cycle.[12] Due to its reactive functional groups, levulinic acid has been identified as a valuable bio-based multipurpose building block of functionalized C_3–C_6 oxygenates (Fig. 1).[13] One of the most important derivatives is γ-valerolactone (GVL),[12] which could be considered as a sustainable liquid and can be produced by catalytic hydrogenation of levulinic acid.[14] GVL has been successfully used for the production of ionic liquids,[15] pentane-1,4-diol,[11,14b] butene isomers,[18a] alkanes,[11] adipic acid,[16] polymers,[17] transportation fuels,[18] *etc.*

The synthesis of levulinic acid from saccharose in the presence of HCl as a catalyst was first reported by Mulder.[19] This

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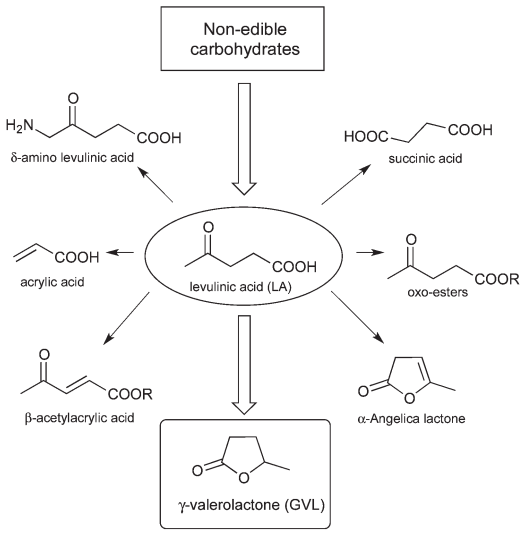
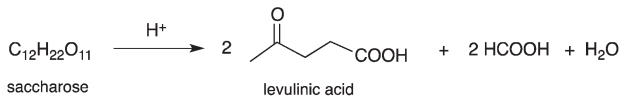


Fig. 1 Levulinic acid based platform molecules.



Scheme 1

transformation involves hydrolysis of the glycosidic bond and two consecutive dehydration steps in the formation of equimolar amounts of levulinic acid and formic acid (Scheme 1). Recently, several papers were published on the conventional acid catalyzed conversion of different carbohydrates to levulinic acid.[9,20]

Beyond cellulose, chitin is the second most abundant biopolymer on the Earth. It is an industrial waste of the food industry, it is obtained from crustaceans such as shrimps, crabs, *etc.* Similarly to cellulose, chitin could be a sustainable green feedstock for production of valuable platform molecules. Recently, a few papers have been published on the microwave-assisted degradation of polysaccharides.[21] However, the majority of these works was performed by using carbohydrates of plant origin.[22,23] A most recent study by Kerton *et al.* reports the degradation of chitosan (a partially deacetylated form of the natural chitin) to levulinic acid by using microwave irradiation under aqueous conditions.[24] Although different Lewis-acids including lanthanide-trifluoromethanesulfonates were found to be active catalysts, $SnCl_4{\cdot}5H_2O$ showed the highest activity for the transformation of chitosan into LA with an average yield of 24 wt%. It is noteworthy that selective formation of levulinic acid and 5-hydroxymethyl-2-furfural (5-HMF) can be influenced by the concentration of the catalyst as well. Kerton *et al*. also reported that the microwave-assisted decomposition of *N*-Ac-D-glucosamine under non-aqueous conditions results in the formation of 3-acetamido-5-acetylfuran, which could be a nitrogen containing platform molecule.[25]

We report here a detailed investigation of the effect of different reaction parameters (*e.g.* reagent, temperature, acid concentration, reaction time) on the degradation of different carbohydrates to levulinic acid using microwave technology.

Results and discussion

The catalytic dehydration of non-edible carbohydrates to levulinic and formic acid is a particularly attractive approach for carbohydrate-based biomass conversion. Since formic acid can be catalytically decomposed to carbon dioxide and hydrogen by using palladium, silver, copper,[26] or even more efficiently in the presence of tris[(2-diphenylphosphino)ethyl]phosphine $[P(CH_2CH_2PPh_2)_3]$ modified iron catalyst,[27] the latter could be used for efficient GVL production.[14a] Alternatively, transfer hydrogenation of levulinic acid with formic acid, as a hydrogen source, in the presence of the Shvo-catalyst results in the formation of 4-hydroxyvaleric acid, which spontaneously turns to GVL *via* ring closure dehydration.[28] Horváth *et al.*[11] found that levulinic acid was obtained by dehydrating saccharose under acidic conditions (1.8 M sulfuric acid) at 140 °C for 8 h with a yield of 35%. Additionally, under the same conditions using a green and highly acidic catalyst (Nafion-NR-50), a similar yield was obtained, however, much longer time (40 h) was necessary.[11] Since the seminal papers of Gedye[29] and Giguere,[30] microwave dielectric heating has become a popular tool in common organic laboratories. It has been shown that controlled microwave heating dramatically decreases reaction time, increases product yield, and enhances product purity by reducing unwanted side reactions.[31]

In this work, we are focusing on the application of this modern technology in order to find milder and more efficient methods for the hydrolysis and transformation of glycans into small organic platform molecules.

We started systematically to optimize the reaction conditions. Firstly, the effect of temperature on the microwave-assisted degradation of saccharose to levulinic acid was examined. By varying the temperature from the initial 100 °C to 140 °C for 10 min, the yield of levulinic acid increased from 2.1% to 34%. To compare the effect of different heating methods on the degradation of carbohydrates, parallel samples were treated as follows: 400 mg (2.22 mmol) of D-fructose was dissolved in 8 mL 2 M H_2SO_4 and heated in the microwave oven at 170 °C. The yield of levulinic acid was found to be 42.7% using microwave irradiation for 30 min. Compared with traditional heating, the same sample was treated in a conventional Schlenk tube in an oil bath at the same temperature for 8 h, with a 31.3% yield. It is worthy of note that a similar yield was obtained with the dehydration of saccharose (35%, 8 h).[11] As expected, if dielectric and conventional heating are compared the reaction time was significantly shorter and the yield was always higher when microwave heating was applied. The monosaccharide, D-glucose (400 mg, 2.22 mmol), was also transformed under identical conditions. In this case, the yield of LA was moderate (15%) under conventional heating and 2.7 times higher (40.5%) when dielectric heating was applied, moreover, the reaction time was much

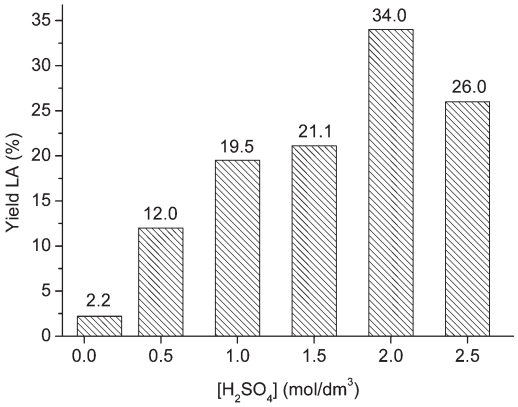


Fig. 2 Influence of sulfuric acid concentration on the yield of interconversion of saccharose (400 mg) to levulinic acid (in 8 mL solution; t = 10 min; T = 140 °C); yield (%) = 100% × $n_{\text{levulinic acid}}/n_{\text{saccharose}}$.

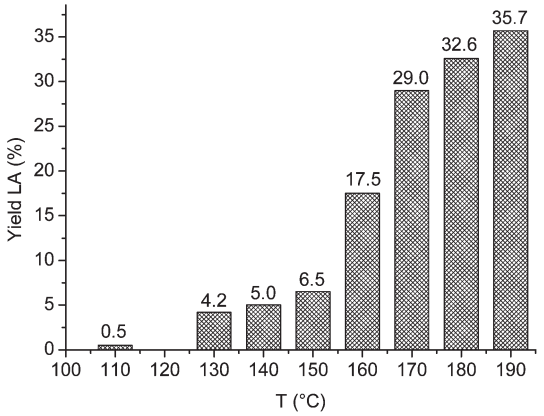


Fig. 3 Influence of reaction temperature on the yield of interconversion of cellobiose (400 mg) to levulinic acid (in 8 mL 2 M sulfuric acid; t = 10 min); yield (%) = 100% × $n_{\text{levulinic acid}}/n_{\text{cellobiose}}$.

shorter (30 min). These results are in accord with the present scientific opinion of the effect of microwave irradiation on the chemical reactions in general.[31b]

Subsequently, the effect of the chemical composition and concentration of the acid catalyst was studied. Although dehydration of carbohydrates was successfully performed by using various acids, mineral acids were the most efficient ones.[6] The conversion of carbohydrates to levulinic acid is highly affected by the acid concentration as well. It was recently reported by Horváth *et al.*[32] that low acid concentration (10^{-5}–10^{-1} M) favors the formation of 5-hydroxymethyl-2-furaldehyde (5-HMF) with a maximum in the case of 0.5 M acid catalyst concentration. It was also established that the acid concentration has a significant effect on the selective formation of both 5-HMF and levulinic acid from chitosan in the presence of a metal based catalyst.[24] Subsequently, the influence of the concentration of sulfuric acid on the formation of levulinic acid was tested in the range of 0.1–2.5 M (Fig. 2). Working below 1 M sulfuric acid concentration, the formation of levulinic acid was slowly increasing (simultaneously, the amount of 5-HMF was decreasing) by increasing acid concentration. Above 1 M sulfuric acid concentration, a higher yield of levulinic acid was observed reaching a maximum at 2 M H_2SO_4. Comparing the results obtained under conventional and microwave conditions, the heating method practically has no influence on the optimum acid concentration. Secondly, cellobiose, which is a disaccharide (and considered as a dimeric building block of cellulose), was used as a model substrate for the optimization of reaction temperature using 2 M H_2SO_4 for 10 min. The amount of levulinic acid gradually became higher by increasing reaction temperature up to 190 °C (the practical upper limit of our instrument) without any maximum, as expected (Fig. 3). Although a higher amount of levulinic acid was obtained at higher temperature, over 170 °C a significantly increasing amount of humin formation was observed. It was found that to obtain a similar yield of levulinic acid, higher temperature was necessary for the hydrolysis of cellobiose than that of saccharose. This observation can be explained by the conclusion of recent studies.[32,33] It is well known that the formation of 5-HMF from glucose proceeds *via* isomerization to fructose. The five fructose isomers (D-fructoketose, D-fructopyranoses, D-fructofuranoses) are present in equilibrium. In an acidic environment, both the furanoses and the pyranoses, through the appropriate oxocarbenium intermediate, lose two water molecules. However, the products are completely different, furanoses form exclusively 5-HMF and pyranoses *via* an unknown mechanism are converted to humins.[32] It was also proposed that by increasing temperature, the equilibria are shifted to the protonated pyranose form, the precursor of humins. Hydrolysis of cellobiose provides two D-glucose molecules, which must be firstly converted to D-fructose, which is transformed into 5-HMF, then into levulinic acid. On the other hand, hydrolysis of saccharose gives one molecule of D-glucose and D-fructose each, the fructose is directly converted to 5-HMF, then to levulinic acid under an acidic environment. It was verified by the ^{13}C-NMR analysis of the neat aqueous dehydration mixture of 400 mg (2.22 mmol) D-fructose (ESI Fig. S1†). While the presence of 5-HMF cannot be detected, the equimolar formation of formic and levulinic acid (^{13}C-NMR, δ, ppm: HCOOH: 166.2; $CH_3(CO)CH_2CH_2COOH$: 27.9, 29.3, 37.8, 177.6, 213.5) was clearly indicated. Furthermore, the amount of possible unreacted substrates or water-soluble by-products was under the detection limit of our instrument. The calculated mass balance was found to be 89.5% (ESI Fig. S4†). It should be noted that the filtered and dried black tar (100.5 mg) cannot be dissolved either in organic solvents or water. Based on the result of elementary microanalysis, this solid material was pure carbon powder (>99%). The pyrolysis analysis of the same sample resulted in <1% solid residue, without the observation of any melting. The NMR analysis of the EtOAc soluble unidentified brown residue (67.8 mg in ESI Fig. S4†) indicated the formation of high carbon containing "humins" (ESI Fig. S5 and S6†). It was proposed that these oligo- and polymers might be formed by the acid catalyzed oligomerization of the reaction intermediates containing C=C double bonds.[34]

Table 1 Acid catalyzed transformation of biomass carbohydrates into levulinic acid

				Yield of LA	
Entry	Substrate	Additive	t [min]	[mol%]	wt%
1	D-Fructose	HCl	30	49.4	31.8
2	D-Fructose	H_2SO_4	30	42.7	27.5
3	D-Glucose	HCl	30	48.6	31.4
4	D-Glucose	H_2SO_4	30	40.5	26.1
5	Cellobiose	HCl	30	44.0	29.9
6	Cellobiose	H_2SO_4	30	41.3	28.0
7	Cellulose	H_2SO_4	30	21.4	15.4
8	Cellulose	HCl	50	46.0	31.0
9	Cellulose	H_2SO_4	50	34.2	23.0
10	D-Glucosamine	HCl	10	36.4	19.6
11	D-Glucosamine	H_2SO_4	10	25.6	13.8
12	*N*-Ac-D-glucosamine	HCl	10	22.4	11.8
13	*N*-Ac-D-glucosamine	H_2SO_4	10	20.6	10.8
14	LMw-chitosan	HCl	20	31.9	22.7
15	LMw-chitosan	H_2SO_4	20	19.3	13.7
16	MMw-chitosan	HCl	20	37.0	26.3
17	MMw-chitosan	H_2SO_4	20	32.1	22.8
18	Chitin	HCl	30	32.7	18.7
19	Chitin	H_2SO_4	30	37.8	21.6

Reaction temperature for carbohydrates of plant origin (entries 1–9): 170 °C, for animal origin carbohydrates (entries 10–19): 190 °C; (LMw: low-molecular-weight, MMw: medium-molecular-weight, both 75–85% deacetylated, Sigma-Aldrich); yield (mol%) = 100% × $n_{\text{levulinic acid}}/n_{\text{substrate}}$; yield (wt%) = 100% × $m_{\text{levulinic acid}}/m_{\text{substrate}}$.

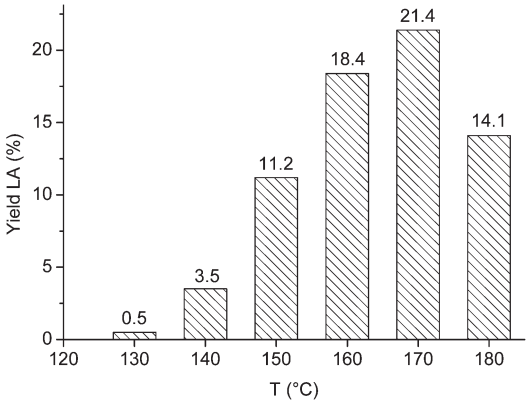


Fig. 4 Influence of reaction temperature on the yield of interconversion of cellulose (400 mg) to levulinic acid (in 8 mL 2 M H_2SO_4; t = 30 min); yield (%) = 100% × $n_{\text{levulinic acid}}/n_{\text{cellulose}}$.

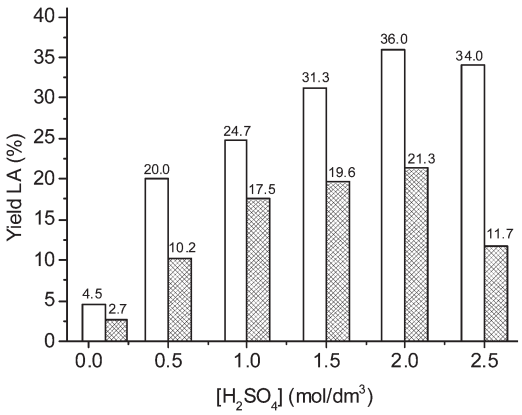


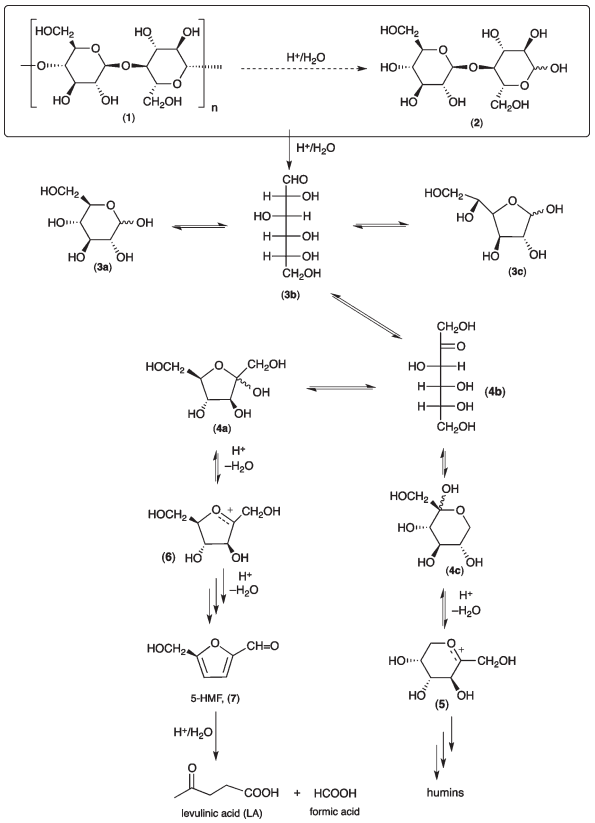
Fig. 5 Influence of sulfuric acid concentration on the yield of interconversion of cellobiose ▯ (400 mg; t = 10 min) and cellulose ▩ (400 mg; t = 30 min) to levulinic acid (T = 170 °C); yield (%) = 100% × $n_{\text{levulinic acid}}/n_{\text{substrate}}$.

Initially, based on the results of our studies with model disaccharides, 2 M sulfuric acid as a reaction medium and 170 °C as the reaction temperature were set for the hydrolysis of cellulose, a high-molecular weight, insoluble polymer. After a 10 min microwave irradiation the yield of levulinic acid was very low (3.7%). To optimise the yield, the reaction time was increased stepwise. Although the yield increased by using longer reaction time (Table 1, entries 8 and 9), the amount of humins as by-products sharply increased. Thus, 30 min is considered as the optimum reaction time which provided levulinic acid with a moderate yield (Table 1, entry 7). Subsequently, the effect of temperature on the formation of levulinic acid was investigated from 130 °C to 180 °C. The optimum temperature was found to be 170 °C (Fig. 4). Above this value, the formation of humins became more significant, which can be explained by the higher equilibrium concentration of the protonated pyranose forms. In order to verify the optimum acid concentration, dehydration of cellulose and cellobiose was performed in a concentration range of 0.1–2.5 M H_2SO_4. The optimum conditions for cellobiose were found to be 2 M H_2SO_4 at 170 °C for 10 min; and for cellulose 2 M H_2SO_4 at 170 °C for 30 min (Fig. 5).

The optimized reaction conditions (*e.g.* acid concentration, time, temperature, yield) for the production of levulinic acid from carbohydrates of plant origin are summarized in Table 1, entries 1–9. For a comparison, the reactions were performed by using 2 M H_2SO_4 and 2 M HCl as well under identical conditions. Although aqueous hydrochloric acid was found to be a slightly more efficient catalyst for the dehydration of carbohydrates, the presence of chlorine is an environmental concern. Generally speaking, the difference between chlorine-free (H_2SO_4) and chlorine-containing (HCl) catalyzed reactions was not significant (except for LMw-chitosan, Table 1, entries 10 and 11). In addition, hydrochloric acid can easily desorb from the reaction mixture to the atmosphere, while sulfuric acid cannot.

The interconversion pathway of carbohydrates of plant origin is depicted in Scheme 2. It was found that dehydration of fructofuranose (**4a**) gave the highest yield of levulinic acid (42.7%, Table 1, entry 2). It is important to note that the transformation of fructose (**4a–c**) into 5-HMF (**7**) starts from protonated furanose intermediate (**6**).[32]

Starting from D-glucopyranose (**3a**), which is in equilibrium with D-fructofuranose (**4a**) under the applied reaction conditions,[33] slightly lower conversion (40.5%, Table 1, entry 4) was observed. Presumably, glucose (**3a–c**) to fructose (**4a–c**) isomerization is fast enough to result in **6**, which is a key intermediate of the whole process. Intermediate **6** either irreversibly dehydrates to 5-HMF (**7**) or reversibly isomerizes



Scheme 2 Decomposition of carbohydrates of plant origin to levulinic acid based on Horváth's proposed mechanism from ref. 32.

via (**4a–c**), at 170 °C to protonated fructopyranose intermediate (**5**), which is responsible for the formation of humin by-products.[32]

Due to the relatively weak β(1 → 4) glycosidic bond between the two D-glucose units, dehydration of cellobiose (**2**) provided a similar amount of levulinic acid (41.3%, Table 1, entry 6).

Expectedly, the high molecular weight cellulose (**1**) resulted in the lowest yield of levulinic acid using 30 min reaction time, however by allowing a longer reaction time (50 min) the yield could be improved (Table 1, entries 7 and 9). Cellulose was insoluble in our hydrolysis cocktail, thus its partial hydrolysis to soluble oligomers should precede its further degradation to D-glucose. Theoretically, D-glucose could be derived from **1** by terminal cleavage of the polymer chain. The relatively low concentration of fructose has an unfavorable effect on the levulinic acid formation. On the other hand, the longer reaction time favors humin and tar formation from the corresponding C_6-isomers (**5**).[13,32] The reproducibility of the catalytic reaction was confirmed by repeating the degradation of cellulose in the presence of H_2SO_4 at 170 °C for 50 min. The yield of levulinic acid was found to be 34.2% (Table 1, entry 9) and 33.9% in the repeated experiment.

In order to evaluate the utilization of polysaccharides of animal origin for the production of levulinic acid, various N-containing carbohydrates (chitin, chitosan, and their monomers: D-glucosamine and *N*-Ac-D-glucosamine) were studied in

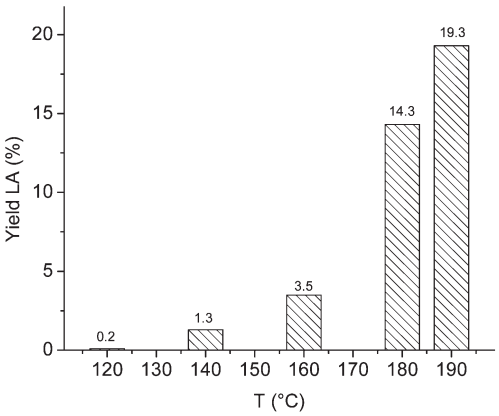


Fig. 6 Influence of temperature on the yield of transformation of chitosan (300 mg) to levulinic acid (in 12 mL 2 M H_2SO_4; t = 20 min); yield (mol%) = 100% × $n_{\text{levulinic acid}}/n_{\text{substrate}}$.

the presence of hydrochloric and sulfuric acid. Based on the results obtained from cellulose and cellobiose (Fig. 5), 2 M sulfuric acid (or hydrochloric acid) was applied. By using LMw-chitosan (low-molecular weight chitosan) as a model compound, the effect of the irradiation time and reaction temperature on the levulinic acid formation was measured in the range of 10–30 min and 120–190 °C (Fig. 6; 190 °C is the temperature limit of our instrumentation). After 10 min, only a trace amount of the product was detected, and over 30 min an increasing amount of tar formation was observed, thus, the reaction time was set to 20 min in further experiments. By increasing the reaction temperature, in parallel the amount of levulinic acid increased as well, however no temperature maximum was observed in the temperature range applied (*cf.* hydrolysis of cellobiose). Consequently, further investigations were performed at 190 °C (Table 1, entries 10–19).

Importantly, applying 20 min irradiation time for the conversion of monomers (D-glucosamine, *N*-Ac-D-glucosamine) resulted in extensive humin formation, thus, in the presence of 2 M sulfuric acid, the reactions were performed only for 10 min. Moreover, the yield of levulinic acid (Table 1, entries 11 and 13) was practically the same for *N*-Ac-D-glucosamine and D-glucosamine, which indicates that *N*-acetylation has negligible influence on the levulinic acid formation. In order to compare the result obtained (59.4%) for D-glucosamine[24] in the presence of a tin based catalyst, the degradation was carried out using H_2SO_4 as a catalyst for 30 min, resulting in a similar yield of levulinic acid of 64.5% (ESI Fig. S7†). It is clearly proven that the catalyst has no influence on the equilibrium of humin and/or tar formation, as expected. The reaction was monitored by NMR spectroscopy, neither 5-HMF nor amide by-products were detected in the reaction mixture. It can be explained that under acidic conditions interconversion of 5-HMF to levulinic acid is faster than its formation. Although the formation of a ketimine intermediate and NH_3 elimination from D-glucosamine were proposed recently, none of them could be detected from chitin and chitosan.[24] Interestingly, the yield of transformation after 20 min microwave

irradiation was 19.3% for LMw-chitosan (Table 1, entry 15), and almost double, 32.1%, for MMw-chitosan (Table 1, entry 17). The two kinds of chitosans are commercial products (Sigma-Aldrich), no data are available on their exact composition. It was recently reported[24] that hydrolysis of the glycosidic bonds of chitosan is a slower reaction than the subsequent dehydration steps of D-glucosamine which go through the open-chain aldohexose form to levulinic acid, furthermore the reaction rate of the hydrolysis of glycosidic bonds can be influenced by the acid concentration. To obtain the same yield of levulinic acid, transformation of chitosan was performed for a much longer time (50 min instead of 30) than that necessary for the degradation of the glucosamines. This can be explained by the slow formation of carbonium ion in the rate-determining step when more concentrated acid is used.[35] During the degradation of chitin (polymer of *N*-acetyl-D-glucosamine) at 190 °C, only a trace amount of levulinic acid was detected after 20 min. However, by increasing the reaction time to 30 min, a significant amount of levulinic acid (37.8%, Table 1, entry 19) was formed.

Conclusions

This study demonstrates that polysaccharides of both plant and animal origin can be successfully converted to levulinic acid in the presence of sulfuric acid by using microwave dielectric heating. Investigating the effect of acid concentration on the formation of levulinic acid showed that the maximum yield of levulinic acid was obtained in the presence of 2 M sulfuric acid for saccharose, cellobiose and cellulose. The reactions were performed in the presence of hydrochloric acid as well. It is proposed that chlorine containing catalysts can be avoided without significant compromise on the yield of transformation. The reaction time was significantly reduced by using microwave irradiation as a more effective heating method compared to conventional heating. However, the heating method had no influence on the product yield, only the rate of hydrolysis was accelerated. It was found that the optimum temperature for the acid catalyzed decomposition of cellulose was 170 °C, and the reaction time was 50 min. The systematic investigation on carbohydrates of animal origin shows that chitosan and chitin can be used as renewable feedstocks for the production of levulinic acid with a yield of 20–39%. This study proves that non-edible biomass can be a possible source and/or raw material of platform molecules such as levulinic acid, *i.e.* it clearly corresponds to the principles of biorefinery.

Experimental

All chemicals were purchased from Sigma-Aldrich Kft., Budapest, Hungary (except ethyl acetate which was obtained from Molar Chemicals Kft., Budapest, Hungary) and used without further purification. Deuterated solvents were purchased from Euriso-top SAS, Saint-Aubin Cedex, France. NMR spectra were recorded in a 5-mm NMR tube using a Bruker Avance-250 spectrometer. Hydrolysis and dehydration reactions were performed in a 10-mL quartz reactor with a Milestone Multisynth AFC-FO 300 microwave instrument (Labsystem Kft., Budapest, Hungary) equipped with an automated safety release system.

The Multisynth microwave reactor was used always in the single-mode option. The reactions were conducted between 110 and 190 °C by using the automatic temperature control system of the instrument. The upper limit of the energy applied was set to 250 W and the reaction time was varied from 10 minutes to 50 minutes. In a typical experiment, the carbohydrate sample solution was mixed or suspended (depending on the solubility of the sample) with 4 mL 2 M sulfuric or hydrochloric acid. After completing the reaction, the reactor was cooled down by applying the air-cooling system at maximum power. Due to the small size of the reaction flask all reactions were repeated three more times to collect enough material for further analysis. The combined reaction mixture (*ca.* 16 mL) was passed through a laboratory filter paper in order to remove the insoluble, brownish impurities, which formed occasionally. This solid by-product was washed first with distilled water (3 × 3 mL) and ethyl acetate (3 × 3 mL), then all filtrates were combined (*ca.* 34 mL). The phases were separated, and levulinic acid was completely extracted from the solution with ethyl acetate (4 × 15 mL). The combined organic phase was dried over $MgSO_4$. After evaporating the solvent a brownish-yellowish, viscous liquid remained. It was identified as levulinic acid by ^{1}H-NMR and ^{13}C-NMR, its yield was calculated from the ^{1}H-NMR spectrum using benzene as an internal standard (ESI Fig. S2 and S3†). Yield was calculated as yield (%) = $n_{\text{levulinic acid}}/n_{\text{substrate}}$.

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