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(Article begins on next page)

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Microwave-assisted flash conversion of non-edible polysaccharides and post-harvest tomato plant waste to levulinic acid

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A microwave-assisted protocol for the conversion of non-edible polysaccharides and tomato plant waste to levulinic acid has been developed. Full conversion has been achieved in all cases at 2 min irradiation and clean levulinic acid was obtained without any purification in high yields (63–95%).

Although fossil fuels and their derivatives are still the main feedstock for the chemical industry,1 the demand for renewable sources has steadily increased over the last two decades. Biomass has been recognized as a major worldwide renewable source of fixed carbon and one which can be used for the production of biofuels and biochemicals.[2]

We have recently investigated the catalytic conversion of starch-based industrial waste into reducing sugars under microwave and ultrasound irradiation used alone and in a joint fashion.[3] This efficient non-conventional depolymerization process[4] has paved the way for further studies in the search for more selective end-product isolation. Levulinic acid (LA), a sugar derived keto-acid (4-oxopentanoic acid), is a key intermediate for the production of fine chemicals and biofuels. LA may be converted into numerous value-added chemicals, such as fuels, solvents, anti-freeze agents, herbicides, polymers, resins, pharmaceutical agents and food fragrances (Fig. 1).[5]

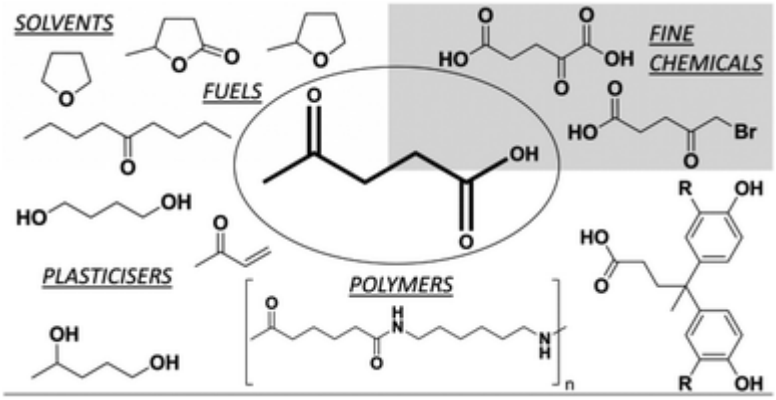
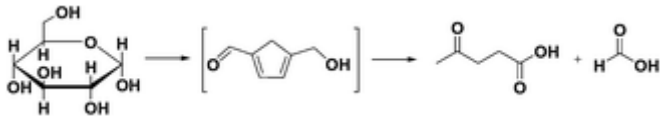


Fig. 1 Levulinic acid: a platform for chemicals and fuels.

Cellulose, starch or C6 sugars can be converted into LA and formic acid via degradation of monosaccharides (MSC) formed by chemical or enzymatic hydrolysis. Sugar dehydration first generates 5-(hydroxymethyl)furfural (HMF) and finally LA (Scheme 1).6 LA can also be produced from hemicellulose in a 3 step process in which furfural and furfuryl alcohol are intermediates.7 Cellulose, hemicellulose and lignin are the main components of several types of lignocellulose waste and non-food feedstock.



Scheme 1 Conversion of sugar to LA and formic acid.

Numerous catalysts, acids and solvents have been described in the LA forming process: trifluoroacetic acid in fluorinated solvents,[8] solid catalysts including amberlites[9] and zeolites,[10,11] acetone, water, supercritical carbon dioxide fluids,[12] and ionic liquids.[13,14]

In general, the most common procedure for the hydrolysis of cellulose and biomass entails the use of mineral acids. Cha and Hanna showed that the main mineral acids' order of reactivity was HBr > HCl > H_2SO_4 corresponding to the strength of their primary dissociation constants.[15] Volatile acids (*e.g.* HCl) are preferred because they make the recovery of LA simpler,[16] although they usually give around 7–10% yield (wt%) in long reaction times. The treatment of typical biomasses like rice hulls and straw, corn stalks and saw dust with HCl at 160–190 °C generates numerous by-products including small molecules, heterogeneous sugar and lignin-like polymeric products.[5,17] Despite the high cost of fractionation and purification,[18] in southern USA the industrial production of LA has already a capacity of 3000 tons of feedstock per year (Biofine Technology LCC),[19] mainly from local tobacco bagasse and paper mill sludge.

Non-conventional energy sources such as microwaves (MW) can dramatically enhance reaction rates in organic synthesis.[20,21] Dielectric heating is a valid response to stubborn, time consuming reactions,[22] and can be applied on a range of scales, from millilitres to kilograms.[23]

In this work, we address all the requirements for the potential industrial production of LA using cost-effective feedstock[17] and a very fast MW process. A suitable lignocellulosic feedstock was found in the form of tomato plant waste at the end of the crop harvest season (Ragusa, Sicily).[24] The inherent chemical complexity of food waste makes it a very attractive source to convert crop residues and agro-industrial byproducts into value-added chemicals. This goal can be achieved by means of sustainable and integrated processes using low environmental impact technologies and efficient energy sources such as microwaves.[25] Although several chemicals are derived from agricultural residues,[26] so far tomato plants as a source of LA have not been investigated.

We propose a flash procedure that maximised conversion and product selectivity. This was carried out using a latest generation MW reactor (SynthWave by Milestone) designed to rapidly reach high temperatures and pressures (up to 300 °C and 200 bar) and then quickly cool down to room temperature. This LA production technology was first applied to various pure polysaccharides such as cellulose, chitin and chitosan. Szabolcs *et al*.[16] have recently reported significantly improved LA yields (wt%) under MW irradiation: 31% from cellulose (with 2 M HCl at 190 °C for 50 min) and 22.7% from chitosan (190 °C, 20 min). On the basis of these promising results, it was decided that optimisation of the reaction conditions for the production of LA from post-harvest tomato plants (PHTP) should be carried out. The chemical composition of the starting biomass was investigated by solid-state ^{13}C-NMR spectroscopy. To determine the cellulose content, the dry matter was fractionated into its constituents using various solvents, as reported in a previous work.[27] This procedure is expected to separate the major biomass proximate on the basis of the components' solubility in benzene and in HCl at different temperatures,*i.e.* lipids and apolar compounds, hemicellulose and proteins, cellulose and lignin fractions. The ^{13}C-NMR data of the starting biomass and the separated fractions (Table 1) demonstrate, however, that the supposed cellulose fractions recovered after solvent evaporation are not pure cellulose. It contained not only the expected anomeric C and OX (X = H, R) functional groups, but also other C types and functional groups which were similar to those found in the lignin fraction, although present at different relative ratios. As the isolation of a pure cellulose fraction was not demonstrated, a reliable value for the concentration of this proximate could not be obtained.

Table 1 Concentration values as mole fraction of total C for functional groups and C types in the starting biomass and the separated fractions, obtained as previously reported[a] [28]

Fraction	Aliphatic	NR + OMe	OR	Anomeric	Ph	PhOH	COX	C=O
PHTP	14.34	7.22	49.60	11.62	6.82	3.44	6.28	0.61
F2	25.61	9.25	47.43	3.09	0.00	0.00	14.61	0.00
F3	13.98	8.23	47.29	10.80	9.25	5.36	4.11	0.98

a **F2: hemicellulose; F3: cellulose; F4: lignin.**

Fraction	Aliphatic	NR + OMe	OR	Anomeric	Ph	PhOH	COX	C=O
F4	20.69	8.20	45.68	9.44	4.75	2.79	7.21	1.25

In this work, biomass conversion and product yields were calculated on the basis of the dry weight of the starting biomass and of its organic content. Firstly, we evaluated the effect of HCl concentration on MW-assisted degradation of biomass to LA. Although it has recently been reported that low acid concentrations favour the formation of 5-hydroxymethyl-2-furaldehyde (5-HMF) rather than LA,29 no 5-HMF was detected under our conditions when the concentration was changed from 12 M to 0.1 M. Neither biomass conversion nor LA yield was affected by acid concentrations ranging from 12 M to 0.5 M, while no LA was produced and biomass conversion was lower at 0.1 M HCl concentration. As shown in Table 2,30 lower temperatures (≤150 °C) favour the selective hydrolysis of carbohydrates to simple MSC, as demonstrated by GC-MS analysis after sample derivatisation (Fig. 2),31 with no LA. PHTP conversions and LA yields were higher at temperatures above 150 °C and at HCl concentration >0.1 M. Under these conditions, LA was the only product detected by 1H-NMR, 13C-NMR and GC-MS, as confirmed by the spectral patterns in Fig. 3–5.

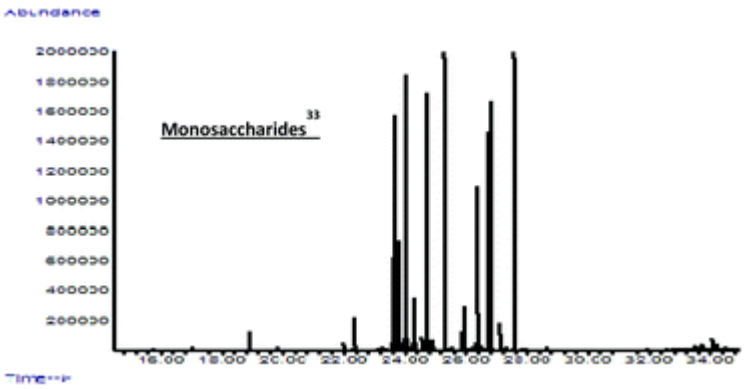


Fig. 2 GC of a derivatized sample containing MSC.

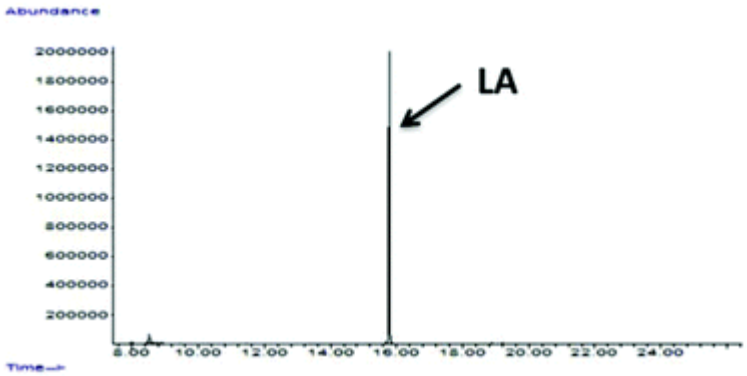


Fig. 3 GC of PHTP (conditions as in Table 3).

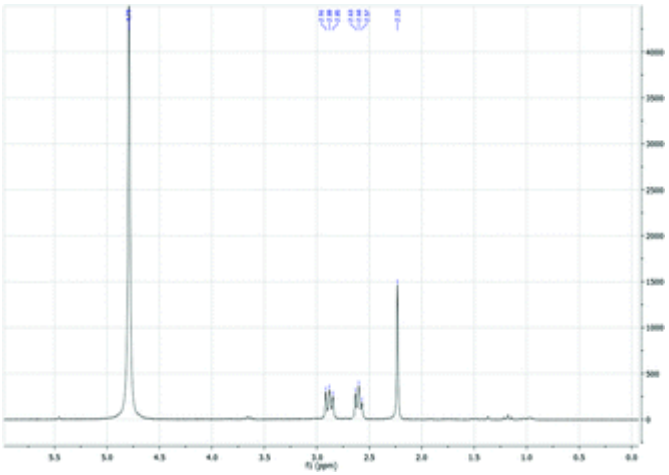


Fig. 4 ^{1}H-NMR (D_2O) of PHTP (conditions as in Table 3).

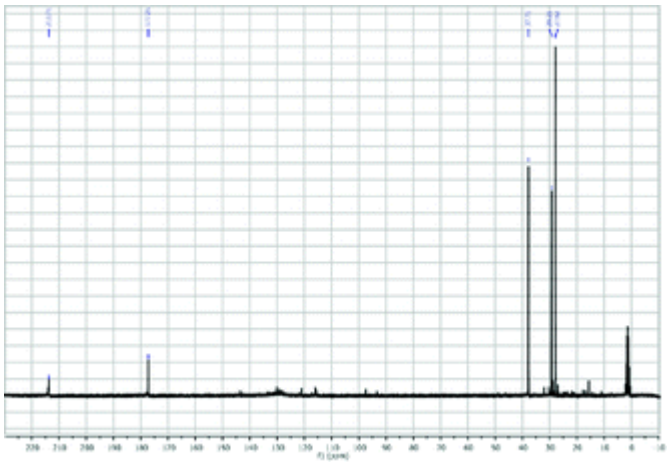


Fig. 5 ^{13}C-NMR (D_2O) of PHTP (conditions as in Table 3).

Table 2 Data for MW-assisted conversion of post-harvest tomato plants (PHTP)[a]

				Yield (%)[32]	
Entry	**HCl (mol L^{-1})**	***T*** **(°C)**	**Conversion (%)**	**LA**	**MSC**
a **Reaction conditions: PHTP/HCl solution = 1/10 (w/v), 2 min MW, N_2 pressure (40 bar).** ***b*** **PHTP/HCl solution = 1/5 (w/v).** ***c*** **Conventional heating: PHTP/HCl solution = 1/10 (w/v), 2 h.**					
1	12	225	80	58	0
2	5	225	79	60	0
3	1	225	78	63	0
4	0.5	225	74	51	0
5	0.1	225	67	0	49
6	1	60	30	0	11
7	1	100	30	0	30
8	1	150	62	0	52
9	1	190	81	61	0
10	1	250	80	56	0
11[b]	1	225	73	59	0
12[c]	12	Reflux	50	5	20

After an easy product recovery via solvent evaporation, entries 3 and 11 showed the best results in both PHTP/HCl ratios 1/10 and 1/5 (w/v). For the sake of comparison, experiments under conventional heating have been performed. As shown inTable 2 (entry 12), both conversion and selectivity were very low even with 12 mol L−1 HCl. We extended our investigation to non-edible polysaccharides such as cellulose and chitosan (Table 3), revealing that full conversion and high LA yields (90 and 95%, respectively) were achieved under the same conditions reported in Table 2.

Table 3 Summary of the results for MW assisted flash conversion of PHTP and non-edible polysaccharides[a]

Sample	**Conversion (%)**	**Yield (%)**
a **Conditions: 2 min MW at 225 °C and N_2 pressure (40 bar), HCl (1 M).**		
Cellulose	100	90
Chitosan	100	95
PHTP[32]	78	63

Conclusions

A highly selective protocol for the direct conversion of post-harvest tomato plants into LA via a MW-assisted flash reaction under mild acidic conditions at high temperature has been developed for the first time. This versatile procedure is applicable to numerous cellulosic biomasses and non-edible polysaccharides and can selectively give either simple sugars or pure LA by varying the reaction temperature. These impressive results come from the outstanding performance of the MW reactor that enables fast heating/cooling and high gas pressure. The use of dielectric heating technology for waste feedstock valorisation offers intriguing future perspectives that go over and beyond the development of a sustainable process for LA production. High-throughput applications of MW-assisted flash hydrolysis would entail the use of flow MW reactors.

Notes and references

1. Y. Yu, X. Lou and H. Wu, *Energy Fuels*, 2008, **22**, 46
2. G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044; D. M. Alonso, S. G. Wettsteinb and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584.
3. A. Hernoux-Villière, U. Lassi, T. Hu, A. Paquet, L. Rinaldi, G. Cravotto, S. Molina-Boisseau, M.-F. Marais and J.-M. Lévêque, *ACS Sustainable Chem. Eng.*, 2013, **1**, 995.
4. G. Cravotto and P. Cintas, *Chem.–Eur. J.*, 2007, **13**, 1902 .
5. D. W. Rackemann and W. O. S. Dohertyand, *Biofuels, Bioprod. Bioref.*, 2011, **5**, 198.
6. B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Green Chem.*, 2006, **8**, 701; J.-P. Lange, E. van der Heide, J. van Buijtenen and R. Price, *ChemSusChem*, 2012, **5**, 150.
7. G. M. Gonzalez Maldonado, R. S. Assary, J. Dumesic and L. A. Curtiss, *Energy Environ. Sci.*, 2012, **5**, 6981; R. Weingarten, J. Cho, R. Xing, W. C. Conner Jr. and G. W. Huber, *ChemSusChem*, 2012, **5**, 1280.
8. H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta and H. J. Heeres, *Green Chem.*, 2009, **11**, 1247; C. Chang, X. Ma and P. Cen, *Chin. J. Chem. Eng.*, 2006, **14**, 708.
9. B. C. Redmon, *US patent*2738367, 1956.
10. J. Jow, G. L. Rorrer, M. C. Hawley and D. T. A. Lamport, *Biomass*, 1987, **14**, 185.
11. A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
12. A. Boisen, T. B. Christensen, W. Fu, Y. Y. Gorbanev, T. S. Hansen, J. S. Jensen, S. K. Klitgaard, S. Pedersena, A. Riisager, T. Stahlberg and J. M. Woodley, *Chem. Eng. Res. Des.*, 2009, **87**, 1318; M. Bicker, D. Kaiser and H. Vogel, *Green Chem.*, 2003, **5**, 280; W. Sangarunlert, P. Piumsomboon and S. Ngamprasertsith, *Korean J. Chem. Eng.*, 2007, **24**, 936.
13. S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, S. Jinliang and X. Ye, *Green Chem.*, 2008, **10**, 1280; C. Moreau, A. Finiels and L. Vanoye, *J. Mol. Catal. A: Chem.*, 2006, **253**, 165.
14. H. Ren, Y. Zhou and L. Liu, *Bioresour. Technol.*, 2013, **129**, 616.

15. J. Y. Cha and M. A. Hanna, *Ind. Crop. Prod.*, 2002, **16**, 109.
16. A. Szabolcs, M. Molnár, G. Dibó and L. Mika, *Green Chem.*, 2013, **15**, 439.
17. A. M. R. Galletti, C. Antonetti, E. Ribechini, M. P. Colombini, N. N. Nassi and E. Bonari, *Appl. Energy*, 2013, **102**, 157; G. A. Sheldon Coulson, *Production of levulinic acid in urban refineries*. Available from Massachusetts Institute of Technology Libraries, Cambridge, MA 02139, USA, 2011, pp. 1–89.
18. L. Yan, N. Yang, H. Pang and B. Liao, *Clean*, 2008, **36**, 158.
19. http://www.biofinetechnology.com/index.php?p=1_7_Biofine-Technology-LLC .
20. *Microwaves in Organic Synthesis*, ed. A. De La Hoz and A. Loupy, 3rd edn, Springer, U.S.A., 2012.
21. C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, **43**, 6250.
22. G. Cravotto, D. Garella, L. Beltramo, D. Carnaroglio, S. Mantegna and C. M. Roggero, *Chemosphere*, 2013, **92**, 299; P. Cintas, D. Carnaroglio, L. Rinaldi and G. Cravotto, *Chem. Today*, 2012, **30**, 58; G. Palmisano, W. Bonrath, L. Boffa, D. Garella, A. Barge and G. Cravotto, *Adv. Synth. Catal.*, 2007, **349**, 2338.
23. R. Morschhäuser, M. Krull, C. Kayser, C. Boberski, R. Bierbaum, P. A. Püschner, T. N. Glasnov and C. O. Kappe, *Green Process Synth.*, 2012, **1**, 281.
24. http://www.unctad.info/en/Infocomm/AACP-Products/COMMODITY-PROFILE-Tomato .
25. C. S. Ki Lin, L. A. Pfaltzgraff, L. Herrero-Davila, E. B. Mubofu, S. Abderrahim, J. H. Clark, A. A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesby and R. Luque, *Energy Environ. Sci.*, 2013,**6**, 426.
26. R. Luque and J. H. Clark, *Sustainable Chem. Process.*, 2013, **1**, 10.
27. P. L. Genevini, F. Adani and C. Villa, *Soil Sci. Plant Nutr.*, 1997, **43**, 135.
28. E. Montoneri, V. Boffa, P. Savarino, D. G. Perrone, M. Ghezzo, C. Montoneri and R. Mendichi, *Waste Manage.*, 2011, **31**, 10.
29. G. R. Akien, L. Qi and I. T. Horváth, *Chem. Commun.*, 2012, **48**, 5850.
30. PHTP was ground in a blade mill; in a typical experiment 2 g of the sample were suspended in HCl (20 or 10 mL). The mixture was irradiated in a MW reactor for 2 min at 225 °C (average power 1000 W) under N_2 (40 bar) under magnetic stirring. After 2 min, the reactor was cooled down. The reaction mixture was passed through laboratory filter paper to remove the insoluble residue. This solid was washed three times with distilled water (3 × 5 mL) and all filtrates were combined. After evaporating the solvent, a brownish viscous solid remained. It was analyzed by ^{1}H-NMR (300 MHz, D_2O), ^{13}C-NMR (75 MHz, D_2O) and GC-MS. NMR spectra were recorded using a Bruker Avance spectrometer.
31. GC-MS analyses were carried out after prior derivatisation. In a typical derivatisation, 10 mg of the sample was solubilized in 1 mL of pyridine. Then, 300 µL of BSTFA (*N*,*O*-bis(trimethylsilyl) trifluoroacetamide) was added to a solution. The mixture was heated for 45 min at 60 °C under magnetic stirring. GC-MS analyses were performed using a GC Agilent 6890 (Agilent Technologies – USA) fitted with a mass detector Agilent Network 5973, using a 30 m long capillary column, i.d. 0.25 mm and film thickness 0.25 µm. Temperature program: from 80 °C (3 min) to 300 °C at 5 °C min^{-1}.

32. Theoretical yield was calculated as soluble organic yield % relative to organic feed recovered after reaction, *i.e.* 100 × (organic content in soluble fraction (g)/organic content in PHTP (g)). The organic content was calculated as the weight loss after calcination of the sample at 650 °C for 5 hours.
33. Monosaccharides identified as ribitol, D-ribose, mannose, α-galactofuranoside, arabinose, β-D-galactofuranose, D-altrose, xylitol, α-D-galactopyranose, glucopyranose, D-glucose, and maltose (library: NIST05).