This is an author version of the contribution published on:

[ChemSusChem, 2015, 8 (8), 1342-1349. DOI 10.1002/cssc.201403183]

The definitive version is available at:
From lignocellulosic Biomass to Lactic - Glycolic Acid Oligomers: a gram-scale Microwave-assisted Protocol


To Professor Bernd Ondruschka, a pioneer and a master of applied microwave chemistry.

Abstract: The conversion of lignocellulosic biomass into platform chemicals is the key step in the valorisation of agricultural waste. Of the biomass derived platform chemicals currently produced, lactic acid plays a particularly pivotal role in modern bio-refineries as it is a versatile commodity chemical and building block for the synthesis of biodegradable polymers. Microwave-assisted processes which furnish lactic acid avoid harsh depolymerisation conditions while cutting down reaction time and energy consumption. We herein report a flash catalytic conversion (2 min) of lignocellulosic biomass into lactic and glycolic acids under microwave irradiation. The batch procedure was successfully adapted to a microwave-assisted flow process (35 mL/min), with the aim of designing a scalable process with higher productivity. The C2 and C4 units recovered from the depolymerisation were directly used as the starting material for a solvent and catalyst-free microwave-assisted polycondensation that afforded oligomers in good yields.

Introduction

A combination of environmental concerns and the diminishing availability of fossil sources has prompted the scientific community to search for alternative energy and chemical sources. Lignocellulosic biomass is the most abundant renewable source of biofuels and biochemicals that is suitable for the biorefinery concept.[1] Lignocellulosic biomass (cellulose, hemicellulose and lignin mixtures), in the form of plant and agricultural waste, is an ideal and freely available source of raw sugars for industrial processes as it does not affect food supplies nor entail ethical issues. It is well known that plant biomass can be converted into useful materials via hydrothermal treatment under harsh conditions.[2,3] Indeed, product mixtures of varying compounds, such as monosaccharides,[5] 5-hydroxymethylfurfural,[6] and organic acids are obtained. For these reasons, catalytic systems for the selective transformation of cellulose into high value-added chemicals are becoming more and more attractive. Lactic acid (LA) plays an important role in bio-refinery management as it is a versatile commodity chemical widely used in food processing as well as the pharma and cosmetic industries.[7] LA is used to prepare ethyl lactate (a green solvent),[8] 1,2-propanediol[9] and biodegradable plastics.[10] In particular, LA and glycolic acid (GA) copolymers such as PLGA have been synthesized, via direct poly-condensation and ring opening polymerization, to improve the properties of polyactic acid (PLA).[11] Their biocompatibility, biodegradability and efficient bioabsorption mean that PLGA and PLA have found a number of applications in medical fields.[12,13] LA is normally produced via monosaccharide fermentation,[7] however this biological approach is not able to directly convert lignocellulose to monosaccharides without pre-treatment. The development of fast, sustainable and cost effective chemical processes,[14,15] for LA production has therefore become one of the hottest research topics in the last few years.[16] Some authors have recently reported the use of alkaline hydrothermal processes in the conversion of glucose or cellulose to LA and other short chain carboxylic acids.[17,18] Other catalytic systems involve the application of divalent and trivalent metal cations.[19] However, all these processes require high temperatures and long reaction times.

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The last three decades have seen the development of environmentally friendly procedures which involve the generation of high energy micro-environments by means of non-conventional energy sources, such as microwaves (MW)\textsuperscript{[20]} and ultrasound (US).\textsuperscript{[21]} The peculiar properties of MW as a source of volumetric and selective dielectric heating can be efficiently exploited in the extraction of natural matrices\textsuperscript{[22]} and the hydrolysis of biopolymers and their further conversion into platform chemicals.\textsuperscript{[23]} In particular, as reported by Fan et al. the hydrolysis step is particularly driven by MW irradiation’s weakening of the cellulose hydrogen bond network, which is in turn due to selective action on polar -CH$_2$OH groups.\textsuperscript{[24]} MW-assisted protocols for the acid-catalysed flash conversion of cellulose, chitosan and post-harvest tomato plants (PHTP) to levulinic acid have recently been reported and have yielded high conversions and selectivity.\textsuperscript{[25,26]} Several catalytic systems such as ionic liquids,\textsuperscript{[27]} zirconia,\textsuperscript{[28]} TiO$_2$,\textsuperscript{[29]} large-pore mesoporous tin phosphate,\textsuperscript{[30]} have been used in the MW-assisted conversion of polysaccharides into 5-hydroxymethylfurfural (HMF) and other platform chemicals. Besides the efficient conversion process, MW irradiation also played a pivotal role in the preparation of supported nanocatalysts.\textsuperscript{[31]}

Moreover, in the last few years the innovative peculiar features of most recent dedicated MW reactors for gram-scale synthesis (from low vacuum to high pressure, fast heating and cooling etc.) enable high efficiency and versatility.

This work investigates new MW-assisted processes for lignocellulosic biowaste valorisation. This goal has been achieved over two steps: firstly, the conversion of cellulose and PHTP into high value-added chemicals (LA and GA) and the use of these platforms for the synthesis of bio-based co-polymers. A continuous flow MW process for the conversion of cellulose into levulinic acid using a dedicated tubular reactor has also been developed. This method makes the valorisation of agricultural residues feasible and overcomes waste disposal issues. MW technology dramatically enhances reaction rates while also reducing energy consumption.

Results and Discussion

Catalyst effect on MW-assisted conversion

It is well known that cellulose can be converted into glucose and other chemicals via alkaline hydrolysis\textsuperscript{[32]} and then, in the same conditions, to LA or HMF. Although industrial interest mainly lies in the direct conversion of lignocellulosic biomass into platform chemicals, several investigations described the simple conversion of monosaccharides. Scaling up is strictly related to process efficiency: conversion, selectivity and energy consumption are the key points for industrialization. Esposito et al.\textsuperscript{[18]} have tested various alkaline systems (calcium, strontium and barium hydroxide) for the conversion of glucose to LA. Barium hydroxide was the most promising of these and afforded LA in yields of up to 57%. The authors proposed a mechanism for LA formation based on a retro-aldol reaction following the isomerisation of glucose to fructose. This reaction pathway highlights the key role of divalent cations in the stabilization of dicarbonyl intermediate. This feature has been extensively investigated by Wang et al.,\textsuperscript{[19]} who evaluated the effect of several divalent and trivalent ions and showed that Pb(II) gave the highest LA selectivity. The authors used computational studies to show that the presence of divalent ions significantly decreased the activation barrier for the retro-aldol fragmentation of fructose thus changing the main reaction pathway from the formation of HMF to the formation of LA.

Using one of our previous works on the MW-assisted flash conversion of cellulose and PHTP waste to levulinic acid\textsuperscript{[25]} as a foundation, we applied a similar protocol to divalent and trivalent metal ion catalyzed syntheses of LA in a high-pressure stainless steel MW reactor (power 1.5 kW, pressure up to 200 bar). The catalytic activity of several salts, including Pb(OAc)$_2$, Pb(NO$_3$)$_2$, Zn(OAc)$_2$, ZnCl$_2$, AlCl$_3$, Al(NO$_3$)$_3$ and SnCl$_2$, was tested. As shown in Figure 1, the ball-milling pre-treatment of cellulose strongly influenced subsequent conversions. This is a clear example of how a combination of different “enabling technologies” can improve process efficiency in biomass conversion. The milled cellulose was then used to evaluate which catalytic system provided the best results under MW irradiation in batch and flow reactors.
LA and GA were obtained, after the flash process, in a mixture with other minor products such as levulinic acid, HMF and monosaccharides (Table 1). Conversion (Figure 1) and selectivity (Table 1) were strongly influenced by the anion used, probably because of different salt hydrolysis constants.

Table 1. MW-assisted conversion of milled cellulose.

| Entry | Catalyst     | Yield (%) | LA | GA | Others
<table>
<thead>
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<tbody>
<tr>
<td>1</td>
<td>Pb(OAc)$_2$</td>
<td>6</td>
<td>4</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pb(NO$_3$)$_2$</td>
<td>15</td>
<td>13</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Zn(OAc)$_2$</td>
<td>3</td>
<td>0</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ZnCl$_2$</td>
<td>28</td>
<td>6</td>
<td>28</td>
<td></td>
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<tr>
<td>5</td>
<td>AlCl$_3$</td>
<td>10</td>
<td>0</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Al(NO$_3$)$_3$</td>
<td>27</td>
<td>25</td>
<td>30</td>
<td>$^{[d]}$</td>
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<tr>
<td>7</td>
<td>SnCl$_2$</td>
<td>18</td>
<td>3</td>
<td>9</td>
<td></td>
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</tbody>
</table>

$^{[a]}$ Reaction conditions: milled cellulose (500 mg), catalyst (35 mM), 190 °C, 2 min, N$_2$ (2 MPa). $^{[b]}$ Quantified by GC-MS. $^{[c]}$ Mainly levulinic acid. $^{[d]}$ Mainly monosaccharides.

$^{[a]}$ Confirmed by theoretical computations.$^{[19]}$
The best selectivity (table 1; entries 2,6) in terms of LA and GA were achieved with Pb(NO₃)₂ and Al(NO₃)₃. Using Al(NO₃)₃, high amounts of monosaccharides were detected in a mixture with LA and GA. This means that the conversion from monosaccharides to acids with Al³⁺ is slower than the conversion with Pb²⁺ in these experimental conditions. Both acids can be obtained via retro-aldol reactions, as shown in Figure 2. The isomerisation of glucose to fructose, followed by a C₃-C₄ retro-aldol reaction, leads to LA after several dehydration/hydration steps and a 1,2 hydride shift. In contrast, a C₂-C₃ retro-aldol reaction affords C4 and C2 intermediates when starting from glucose. Indeed, the C2 fragment undergoes a hydration step followed by isomerisation through a 1,2 hydride shift before giving GA.

It is well known that Pb(II) generates Pb(II)-OH in water and promotes the isomerisation of glucose.[33,34] The equilibrium between glucose and fructose is a crucial step in LA and GA selectivity (figure 2). Method optimization was performed, on the basis of these results, using Pb(NO₃)₂ and Al(NO₃)₃ catalysts. The reaction was followed by purification via simple stirring in the presence of a strong acidic cation-exchange resin.

Method optimization

Figure 3 compares the effect of ball milling pre-treatment conditions (speed and time) on the conversion of cellulose. Almost complete conversion was achieved after 60 min at 550 rpm milling.

![Figure 3. Effect of ball milling treatment on the conversion of cellulose.](image)

Higher temperature (from 190 to 220 °C) dramatically affected conversion yield and selectivity. Conversion rose from 12 to 95% and LA and GA yields increased as well (table 2 entry 1; and table 2 entry 4). In spite of respectable selectivity in the 170 - 190 °C range, conversions were too low (table 2, entries 1,2) even at longer reaction times (table 2, entry 3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>T (min)</th>
<th>Conversion (%)</th>
<th>Yield (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>LA</td>
<td>GA</td>
</tr>
<tr>
<td>1</td>
<td>170</td>
<td>2</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>2</td>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>30</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>2</td>
<td>97</td>
<td>43</td>
</tr>
<tr>
<td>5[^e]</td>
<td>220</td>
<td>2</td>
<td>95</td>
<td>8</td>
</tr>
</tbody>
</table>

[^d] Reaction conditions: 220 °C, 2 min, catalyst (35 mM), cellulose (500 mg), N₂ (3 MPa); Blank: microcrystalline cellulose (without ball milling treatment).
The same reaction protocol was carried out using Al(NO₃)₃ and gave a good conversion. However, monosaccharides, formed at 190 °C (Table 1, entry 6), were not converted to LA and GA even when the temperature was increased to 220 °C (Table 2, entry 5). Our experimental results, according to the two competitive mechanisms described by Wang et al., prove that Pb²⁺ favours the retro-aldol reaction while Al³⁺ promoted dehydration into levulinic acid (Table 2, entry 5).[19]

The optimization study also analysed the best catalyst concentration (5, 15, 35, 75 mM) under the same temperature and pressure conditions. The final MW-assisted protocol was as follows: 220 °C, 3 MPa (N₂) using 20 mL water solution of Pb(NO₃)₂ (35 mM) for 2 min irradiation, affording 97% conversion with 43 and 18% yield for LA and GA, respectively (Figure 4a).

The same method used on milled PHTP biomass gave 50% conversion and 34 and 21% yields for LA and GA, respectively (Figure 4b). Biomass conversion and product yields were calculated on the basis of the dry weight of starting biomass and its organic content (the weight loss after sample calcination at 650 °C for 5 hours). These results prove the versatility of the method; it is efficient not only on purified cellulose but also when applied to a more complex matrix, such as lignocellulosic biomass. The MW-assisted protocol dramatically improves conversions and yields over conventional heating while also cutting down reaction time from 4h to 2 min.[19]
A flow mode procedure was investigated with the aim of scaling-up the optimized batch protocol and the professional pressurized reactor FlowSYNTH – Milestone/MLS was used (see the figure S2 in supporting info). This multimode MW reactor (70 mL, 1.6 kW) can operate at high temperature (up to 260 °C) and pressures (up to 3 MPa). The feeding pump can work at flow rates of between 10 and 200 mL/min, i.e. up to more than two column volumes per min. or 12 L/h. 300 L/day can be processed, assuming 24 h operation. Preliminary cellulose sonication in water (immersion horn 21.1 kHz, 150 W, 30 min) afforded a stable colloidal suspension which was well suited for the flow reactor, according to instrument specifications. (see figure S3 in supporting info).

Various different catalyst concentrations (35 and 75 mM) and flow rates were tested, namely 35 mL/min (2 min residence time) and 18 mL/min (4 min residence time). As shown in Figure 5, a steady state (constant yields and variables) was reached after 3 column volumes in all experiments. There were contrasts with the batch experiments; a catalyst concentration of 35 mM ensured good conversion (>80%) but low yields in LA (<20%) even at longer residence times (Figure 5a, c). The optimal catalyst concentration in flow experiments was 75 mM (Figure 5b, d), however longer reaction times increased the amount of other chemicals produced (mainly levulinic acid), reducing the yields of LA and GA. Similar results to batch experiments (table 2, entry 4) were obtained at a 75 mM catalyst concentration and a 35 mL/min flow (Figure 5b). Under these conditions, a productivity of 2.1 L/h (50.4 L/day) was obtained which corresponds to 0.55 kWh energy consumption. This is a promising result considering the further applications on negative cost feedstocks.

![Figure 5. Continuous MW-assisted flow conversion of milled cellulose](image)

**Bio-based polymers and oligomers**

The selectivity achieved in this flash-MW-assisted protocol is a good starting point for the synthesis of bio-based polymers and oligomers. As already pointed out, co-polymers of LA and GA (PLGA), are endowed with
properties which make them suitable for medical applications.[35-38] For example, high molecular weight PLGA co-polymers have been used in prolonged drug delivery systems because they slow degradation to nontoxic monomers (LA and GA). In contrast, low-molecular weight co-polymers are suitable for short-term drug release applications and, furthermore, their drug matrices do not need to be retrieved from the body. High molecular weight PLGA has been synthesised via the ring-opening polymerization of the cyclic LA and/or GA diester. However, the direct poly-condensation of LA and GA afforded PLGA oligomers.[39] Even if the intermediate step for making the cyclic diester was avoided, yields were affected by removal of water in the condensation of carboxylic and hydroxyl groups. Several procedures involve the use of Sn, Zn and Sb salts based catalytic systems[40] to synthesize co-polymers with different LA/GA ratios. A process based on direct poly-condensation without catalysts, solvents and initiators has been reported for the production of PLA.[41] Water was removed under vacuum, but the process required high temperatures (>160 °C) and very long reaction times (up to 95 h).

This work’s MW-assisted poly-condensation dramatically reduced temperature and reaction times using a catalyst- and solvent-free protocol to obtain PLGA oligomers. Indeed, the oligomers were synthesized in our MW-assisted process in only 3 h at 130 °C, in vacuum conditions (70 mbar), which allowed for efficient water elimination via a dedicated MW-reactor. The increasing power intensity (see figure S12 in supporting info) throughout the reaction was a good indicator of oligomer formation. The decreasing polarity of the system during reaction progress required an increase in MW emissions to keep the reaction temperature stable. Three oligomers with different LA/GA ratios were prepared. These reflect the ratios obtained from biomass conversion in the first part of the work (table 3).

TGA analyses show that all samples degraded completely into volatile species at approximately 360 °C (table 3). Considering the LA/GA ratio obtained from the best PHTP MW-assisted-conversion protocol (Figure 4b), the oligomer synthesised at a 70/30 (LA/GA) feed (table 3, entry 3) shows a number average molecular weight which is comparable to the PLGA used for short term drug delivery.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed (mol %) LA/GA</th>
<th>Yield (%)</th>
<th>Polymer composition LA/GA</th>
<th>Mn[gd]</th>
<th>Mw/Mn[gd]</th>
<th>Td (°C)[d]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>100/0</td>
<td>80</td>
<td>100/0</td>
<td>2229</td>
<td>1.53</td>
<td>362</td>
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<tr>
<td>2</td>
<td>50/50</td>
<td>75</td>
<td>53/47</td>
<td>2923</td>
<td>1.47</td>
<td>365</td>
</tr>
<tr>
<td>3</td>
<td>70/30</td>
<td>77</td>
<td>69/31</td>
<td>2510</td>
<td>2.00</td>
<td>359</td>
</tr>
</tbody>
</table>

[a] 130 °C, 3h, 70 mbar. [b] Estimated from the integral height of hydrogen in 1H-NMR spectra. [c] Determined by GPC analysis. [d] Determined by TGA.

Figure 6. TGA spectrum of PLGA 69/31 oligomer (heating rate of 10°C min⁻¹).
The FTIR spectrum of PLGA 69/31 (Figure 8) shows a sharp, well-defined absorption at about 1752 cm\(^{-1}\) for the characteristic ester carbonyl group of the oligomer. This feature, together with the clearly diminished presence of the acidic hydroxyl stretch, confirms that LA and GA have been polymerized. All other co-oligomer sample IR spectra were of similar informative value (See supporting info).

PLA and PLGA 69/31 SEM images (Figure 9) show different morphologic surfaces. The PLA surface is homogeneous, whereas the PLGA surface is not. The globular zones on the PLGA surface could be ascribed to the insertion of GA into the oligomer chain.
Conclusions

This work describes the first instance of a fast protocol for the preparation of bio-based oligomers/polymers from lignocellulosic biomass that is fully driven by MW irradiation. In addition, the batch procedure has been redesigned, with an eye on process scale-up, to create flow-through conditions in a commercial MW flow reactor. Impressive results come from the poly-condensation step, where fast polymerization (compared to conventional methods) occurs in solvent- and catalyst free conditions. Working in a batch pressurized MW system, we have developed a selective flash protocol which gives LA and GA at high conversion values, from both cellulose (97%) and PHTP (50%), using a dilute catalyst solution (35 mM). This method is able to produce LA and GA along two different proposed reaction pathways; C3-C4 or C2-C3 retro-aldol reactions. The batch protocol was converted into a flow process in which yields and conversions were maintained, productivity increased and energy consumption low (0.55 kWh). The LA and GA mixture was a good starting material for the synthesis of bio-based oligomers (PLA and PLGA) via direct poly-condensation. A rotovap-like MW reactor working in vacuum was used to develop a solvent and catalyst free protocol under mild conditions (130 °C, 3 h). MW-assisted procedures certainly play a fundamental role in the design of sustainable methods which address the biorefinery concept.

Experimental Section

Reagents and equipments

All chemicals and solvents were purchased from Sigma–Aldrich and used without further purification. Cellulose and PHTP were ball milled in a planetary ball mill (PM100 Retsch GmbH), which was equipped with a single milling beaker (stainless steel, 125 mL) which used 25 stainless steel milling balls (Ø = 10 mm). In the flow experiments, ball milled cellulose was suspended in water using a dedicated ultrasonic device: a titanium immersion horn (Danacamerini - Italy) working at 21.1 kHz under temperature control. Batch MW-assisted reactions were carried out in a SynthWAVE (MLS GmbH, Milestone Srl) reactor, which houses a closed MW-cavity. RotoSYNTH (MLS GmbH, Milestone Srl) was used for polycondensation reactions. Flow experiments were carried out in a FlowSYNTH (MLS GmbH, Milestone Srl) reactor using a high pressure dosing pump, DMH 28x (Allodos pump, Grundfos). Energy consumption was measured on a Gossen-Metrawatt SECUTEST SIII instrument. NMR spectra were recorded on a Bruker Avance 300 (300 MHz and 75 MHz for 1H and 13C, respectively) at 25°C; chemical shifts were calibrated to the residual solvent proton and carbon resonances. GC-MS analyses were performed in a GC Agilent 6890 (Agilent Technologies - USA) which was fitted with a mass detector Agilent Network 5973, using a HP-5 column (30 m long capillary column, i.d of 0.25 mm and film thickness 0.25 μm). The molecular weights of the polymers were estimated on a gel permeation chromatograph (GPC) in THF (0.8 mL/min,) stabilised using BHT using Shimadzu UFLC chromatograph equipment with a CTO-10AS vp Column Oven and refractive index detector RID-10 A. The calibration curve was obtained using polystyrene standards. Thermogravimetric analyses (TGA) were performed on a TGA 4000 (Perkin Elmer), using a heating ramp of 10 °C min⁻¹, operating under N₂ with alumina crucibles. Infrared spectra (FTIR) were recorded as a KBr pad using the Spectrum BX FT-IR System (Perkin Elmer). Sample morphology was investigated by means of a Zeiss Evo50 SEM equipped with an energy dispersive detector and a LaB6 source.

Methods

Biomass conversions

In a typical batch experiment, samples (500 mg) were suspended in a water solution of Pb(NO₃)₃ (35 mM) and the mixture was heated for 2 min at 220 °C under MW irradiation (average power 960 W) in a N₂ (3 MPa) atmosphere and magnetic stirrer (450 rpm). The reactor was cooled after 2 minutes. In the flow experiments, a preliminary calibration of the flow rate was required. The flow was adjusted using the pump settings which adjusted both pump speed and stroke volume to achieve the desired flow rate. The backpressure valve regulator was set at 3 MPa to largely counterbalance the vapour pressure generated by the reaction mixture at the operation temperature (220 °C). The stirrer was set to 80% of its maximum speed and chiller temperature was set at 70 °C. The reactor was first filled with water and the inlet tube was then transferred to the reaction mixture to begin processing at the desired temperature and flow rate. The first column volume from any given run
should be ignored because inevitable priming solvent back-mixing caused by imperfect plug-flow will have occurred.

Ball milled cellulose (22.5 g) and water (900 mL) were sonicated together (21.1 kHz, 150 W, 30 min) at a controlled temperature (30 °C) before the flow experiments. Pb(NO₃)₃ (10.43 or 22.36 g) was then added to the colloidal suspension and the reaction mixture was pumped into the MW-flow-reactor and samples were collected after each column cycle, for a total of six cycles. Total energy consumption (kWh) was measured for the MW reactor, stirrer functions and pump.

Reaction mixtures were passed through laboratory filter paper to remove insoluble residues. This solid was washed three times with distilled water (3 x 5 mL) and all filtrates were combined. The solution was stirred together with a strongly acidic cation-exchange resin (Amberlite IR 120 resin; Rohm and Haas, exchange capacity = 5.05 mequiv/g) for 15 min at room temperature to remove the catalyst. A cloudy oil was obtained after freeze drying (-80 °C, 0.2 mbar). ¹H-NMR analyses were performed in D₂O. GC-MS chromatograms were recorded after preliminary product derivatization (10 mg) in pyridine (1 mL) using BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) (300 μL). The mixture was heated for 45 min. at 60°C under magnetic stirring and the product was directly analysed by GC-MS. GC conditions were: injection split 1:20, injector temperature 250°C, detector temperature 280°C. Gas carrier: helium (1.2 mL/min), temperature program: from 70°C (2 min) to 300°C at 5°C/min.

**MW-assisted polycondensation**

The required amounts of lactic and/or glycolic acids were added to a dedicated 50 mL RotoSYNTH flask and the reaction mixture was kept in rotation. The MW program was as follows: 10 min from 25 °C to 130 °C, then 3 h at 130 °C. Pressure was gradually decreased from 1000 to 70 mbar during the ramp time. The resulting oligomers were dissolved in CH₂Cl₂ after cooling to room temperature and precipitated in an excess of methanol. Purified products were dried under vacuum.

**Acknowledgements**

This work was funded by the University of Turin (fondi ricerca locale 2013). Part of this work was carried out by Giorgio Grillo during his master thesis in Chemistry.

**Keywords:** lignocellulosic biomass; waste valorization; lactic and glycolic acids; microwaves; PLGA


