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Smart Valorization of Waste Biomass: Exhausted Lemon Peels, Coffee Silverskins and Paper Wastes for the Production of Levulinic Acid

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In recent years, the replacement of fossil resources with renewable ones has focused great interest, expecially as regards the production of new valuable bio-products and bio-fuels, in progressive replacement of the traditional petroleum-based ones.The Waste Management Policy strongly encourages the valorization of waste biomasses into added-value bio-chemicals, instead of their traditional combustion for energy recovery or, even worse, of their landfill disposal. In this context, the acid-catalysed hydrothermal conversion of negative-value bio-wastes into levulinic acid (LA) represents a smart exploitation possibility, already developed and optimized on pilot-scale, and widely adaptable to different kinds of feedstocks. In this work, the LA production was investigated starting from two bio-wastes deriving from industrial Italian food-processing, e.g.exhausted lemon peels and coffee silverskins, together with that of a clean cellulose powder, which derives from the cutting operations occurring during the tissue paper production. The effect of the main reaction parameters on the LA synthesis, in particular the concentration of the acid catalyst, the biomass loading, the reaction temperature/time and, additionally, the effect of an upstream milder acid pretreatment, was investigated and discussed. Moreover, in the case of coffee silverskin, a preliminary extraction step of the water-soluble phenolics has further improved the fractionation and exploitation of this waste biomass. These compounds have been proposed as natural antioxidants, which represent very valuable niche products for nutraceutical uses. The described examples confirm the feasibility of an integrated valorization of the waste biomass, well in agreement with the Biorefinery concept.

1. Introduction

In recent years, the interest of the Industrial Chemistry has moved towards the exploitation of any kind of waste biomass for the synthesis of new valuable bio-fuels and bio-products, in place of the dwindling traditional fossil ones. Moreover, this approach is strongly encouraged by the Waste Management Policy, which favors the waste re-use, rather than its immediate landfill disposal, by this way achieving significant environmental, social and economic benefits. In this context, the acid-catalysed hydrothermal route for the synthesis of levulinic acid (LA) represents a smart solution, fully meeting all of the above-mentioned advantages (Licursi et al., 2016). This platform chemical has been classified by the United States Department of Energy as one of the top-12 promising building blocks, being a valuable intermediate for the synthesis of new fuel additives, fragrances, solvents, pharmaceuticals, and plasticizers (Antonetti et al., 2016). The fundamental requirement for the economic improvement in LA production regards the use of negative-value wastes, otherwise sent to disposal, with good cellulose content (Puccini et al., 2016). This choice reduces the LA production price, allowing significant economic benefits. In this context, wastes deriving from i) the "Limoncello" liqueur production, ii) coffee roasting thermal treatment, and iii) converting operations to produce tissue paper products, fully meet this specification. These industrial productions are strategic for the Italian territory and generate these waste streams in high amounts. In more detail, "Limoncello" is a typical liquor of Campania Region, which is obtained from the steeping of the lemon peels in ethanol for a variable time. About 15 lemons are necessary for a liter of pure alcohol, thus the exhausted lemon peel (ELP) is an abundant

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waste of the Italian food industry. Due to the steeping step, this solid waste results more enriched in cellulose and simple sugars than the untreated lemon peels, thus representing a very suitable feedstock for LA production. Coffee is the most important agricultural commodity in the world and is second only to petroleum in global trade activity and value. Regarding coffee silverskins (CS), it is the residual thin tegument wrapping the green coffee beans, and it is the only by-product of the roasting process (Niglio et al., 2017). Murthy and Madhava Naidu (2012) reviewed the options for recycling the by-products and wastes from coffee production. Also CS represents a good feedstock for LA production because of its high cellulose content, declared up to about 60 wt% (Narita and Inouye, 2014). Moreover, this waste is a very valuable source of natural antioxidants, in particular phenolic acids (Iwai et al., 2012), exploitable for the preparation of food supplements and nutraceutical formulations (Licursi et al., 2018). These compounds can be strategically extracted upstream of the hydrothermal conversion of the entire feedstock to LA. The last noteworthy example of valuable exhausted biomass is the cellulose powder (CP) derived from the converting process for the production of tissue paper products. In this process, clean virgin cellulose is used as starting feedstock for the production of the final product, and a significant waste stream (~400-500 tons per year, in the Lucchese area) is recovered as CP in the converting section, where the paper coil is unrolled and the sheet is subjected to mechanical operations (stripping, embossing, cutting, etc.) to give the final commercial product (toilet paper and handkerchiefs). The recovered CP is gathered by aspiration and sent to the landfill because it is too fine to be used again within the same papermaking process. However, it is mainly composed of pure short-fibers of cellulose and, because it has been already mechanically reprocessed, it should be more easily hydrolysable to LA, and therefore it certainly represents an ideal feedstock for this purpose.

In this research, the hydrothermal conversion of these bio-wastes into LA was carried out adopting water as the reaction solvent and dilute hydrochloric acid as the homogeneous catalyst for the conversion of the cellulose fraction into LA. For this purpose, the discussed hydrolysis reactions have been carried out both in microwave (MW) and autoclave system. MW irradiation certainly represents a very appropriate tool to make the hydrothermal process efficient, allowing a rapid heating of the reaction environment, thus significantly shortening the reaction times to give LA, if compared with the traditional heating systems (Antonetti et al., 2015). Therefore, MW system is proposed in this work as a smart alternative to the autoclave one, allowing a faster screening of the appropriate reaction conditions, with remarkable energy and time savings, at the same time ensuring good reproducibility between all experiments, but on a smaller laboratory scale.

The hydrothermal treatment occurs by depolymerisation (hydrolysis) of both cellulose and hemicellulose fractions, which ideally leads to C6 and C5 monosaccharides, respectively. These undergo dehydration to give reactive furanic intermediates, e.g. 5-hydroxymethylfurfural (5-HMF) and furfural (Sampath and Srinivasan, 2017). Regarding 5-HMF, it rehydrates by ring opening, leading to the formation of LA and formic acid, in equimolar amount (Garcés et al., 2017). In both cases (C5 and C6 paths), insoluble humins are the main solid by-products obtained within this process, deriving from condensation reactions of the furanic intermediates and C5/C6 sugars (van Zandvoort et al., 2013). Their production must be minimized by optimizing the reaction conditions to give selectively LA. A scheme of the investigated route is reported in Figure 1:

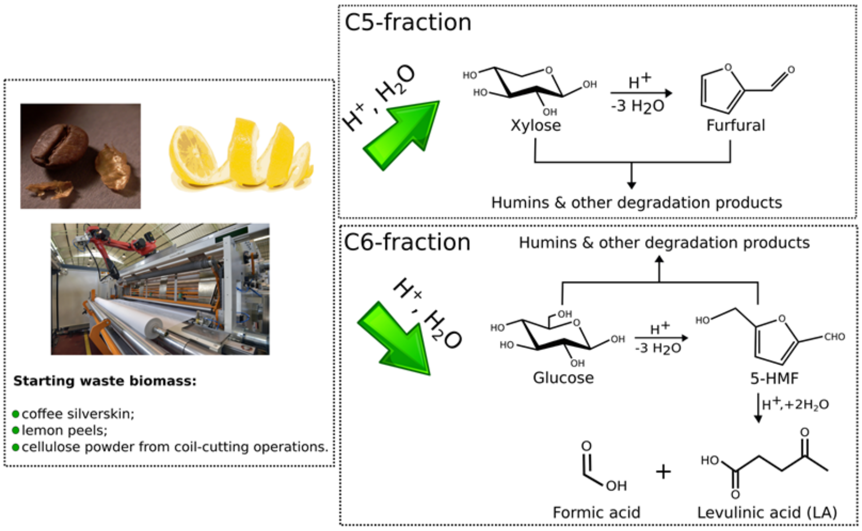

Figure 1: Scheme of the hydrolysis of the investigated wastes to LA.

The described examples highlight the importance of an integrated valorisation of a waste biomass, in agreement with the Biorefinery concept and the environmental sustainability, nowadays oriented towards the "*Zero Waste*" policy.

2. Materials and Method

2.1 Materials

ELP are recovered downstream of the production of the "Limoncello" liqueur, and this feedstock was provided by a producer from the Campania Region, Italy. CS were produced from the bean rosting process and provided by a local coffee roasting company. Lastly, CP was produced as a waste of the coil cutting operations for the production of the finished tissue paper products. It was collected from different local paper Companies (Sofidel®, ICT® and Eurovast®, all in Lucca, Italy) and provided by the Center of Paper Quality "Lucense"® (Lucca, Italy). All the starting feedstocks were dried up to constant weight before their use. LA (98% purity) and furfural (99% purity) were purchased by Sigma-Aldrich and used as analytical standards.

2.2 Experimental procedure

The hydrolysis of ELP was carried out in a stainless steel autoclave. This reaction was carried out in the presence of dilute hydrochloric acid as the homogeneous catalyst and sodium chloride 0.25 M. The reactor was pressurized with 30 bar of nitrogen and immersed in an oil bath up, previously heated to the set-point temperature (200 °C). At the end of the hydrolysis reaction, the autoclave was cooled at room temperature, depressurized, and the recovered solid-liquid slurry was filtered. The hydrolysis of CS and CP was carried out by a single-mode microwave reactor (CEM Discover S-class System), also in this case employing dilute hydrochloric acid (1.68 wt%), a solid/liquid ratio equal to 7 %, at different reaction temperatures and at fixed reaction time (20 minutes). At the end of each hydrolysis reaction, the reactor was rapidly cooled at room temperature by blown air, and the solid-liquid slurry was recovered and filtered. The extraction procedure of the water-soluble antioxidants from the CS was carried out by means of the above mentioned MW system (CEM Discover S-class System). For this purpose, CS were mixed with water, adopting a solid/liquid ratio of 14 %, adopting different reaction temperatures and times.

2.3 Analytical equipment

The fractionation of the water-soluble phenolics from the starting CS was monitored by UV-Vis spectroscopy, adopting a Cary 60 UV-Vis Agilent Spectrophotometer. The amount of polyphenols in the isolated extract was determined by the Folin-Ciocalteu assay, according to the procedure reported by Singleton (Singleton et al., 1999). The antioxidant activity of the extract was estimated by DPPH radical scavenging assay (Narita and Inouye, 2012). Regarding the hydrolysate solutions, these were analyzed by HPLC Perkin Elmer Flexer Isocratic Platform, which was equipped with a Benson 2000-0 BP-OA (300 mm x 7.8 mm) column, which was kept at 60 °C, and with a WATERS 2410 Refractive Index detector. A 0.005 M H_2SO_4 solution was employed as mobile phase, with a flow-rate of 0.6 mL/min. Calibration curves of LA and furfural were acquired by analyzing solutions of the commercial standards, at different concentrations. LA and furfural mass yield (Y) was expressed as ratio between the amount of the compound in the reaction mixture (in grams, M) and that of the starting dried feedstock (in grams, m), according to the Eq(1):

$$\mathrm{Y(wt\%)} = \frac{\mathrm{M}}{\mathrm{m}}\,\mathrm{x}\,100 \qquad (1)$$

3. Results

The best results obtained for the conversion of the ELP into LA are reported in Table 1. In all the hydrolysis tests, a small amount of sodium chloride was employed, thus advantageously exploiting the benefit of an electrolyte on LA production, mainly given by the interruption the hydrogen bonding of the cellulose network (Raspolli Galletti et al., 2012). Furthermore, the catalytic performances in the autoclave system have been improved by adding a preliminary hydrolysis pre-treatment at lower temperature, which makes the undissolved cellulose more easily accessible to the subsequent real hydrolysis reaction, the latter occurring at higher temperature (Raspolli Galletti et al., 2012). In comparison with MW irradiation, the adoption of this pre-hydrolysis step represents an immediate approach for the improvement of LA yield from raw biomass, in a preliminary autoclave screening.

Table 1: Hydrolysis of ELP to LA. Formulation and autoclave reaction conditions: ELP = 1.75 g; [NaCl] = 0.25M; reaction temperature = 200 °C; reaction time = 30 min.

Run	Biomass/liquid (%)	HCl (wt%)	Temperature of pretreatment (°C)	Time of pretreatment (h)	Y_{LA} (wt%)
1	7	1.68	-	-	4.5
2	7	1.68	80	2	8
3	7	1.68	120	2	12
4	5	1.68	120	2	17
5	5	3.36	120	2	22

These results highlight the effectiveness of the pretreatment step at lower temperature, making the cellulose more swellable, e.g. accessible, to the next acid-catalysed hydrolysis step at higher temperature (run 1 and run 2, Table 1). By increasing the temperature of the pretreatment up to 120 °C, it has been possible to further improve the LA yield up to 12 wt% (run 3, Table 1). A further improvement of the LA yield was achieved by decreasing the solid/liquid ratio from 7 to 5 % (run 3 and run 4, Table 1), indicating that at higher biomass loading the amount of the adopted catalyst was insufficient for the optimal conversion to LA, or the humin formation was favoured (Peng at al., 2010). By doubling the HCl concentration (run 5, Table 1), LA yield was further improved up to 22 wt%, thus confirming the first hypothesis.

In this work, the preliminary recovery of the water-soluble phenolics of CS source and the subsequent conversion of the solid residue into LA was investigated, in both cases adopting microwave (MW) as the only heating system. In this regard, MW heating represents a very efficient tool for a fast screening of the appropriate reaction conditions for the hydrothermal treatment (Antonetti et al., 2015). In fact, MW significantly reduces the ramping time to reach the set-point temperature and to cool the reaction mixture, thus minimizing degradation of the reaction intermediates, and at the same time leading to significant energy and time savings (Galia et al., 2015). Different extraction tests were carried out, monitoring by UV-Vis spectroscopy the intensity increase of the specific absorption bands due to the phenolic compounds. The best water-extraction pretreatment was achievedby heating the aqueous slurry at 100 °C for 5 minutes, in this case approaching an extraction yield of about 10 wt%. The UV-Vis analysis of the extracts has revealed the presence of an absorption band centered at 272 nm, which is ascribed to $\pi \rightarrow \pi *$ transitions of the caffeine (Belay et al., 2008), together with a shoulder at about 320 nm, due to $n \rightarrow \pi^*$ transitions of phenolic acids, mainly caffeic and ferulic acid (Navarra et al., 2017). After having optimized the extraction procedure, both the content of polyphenols and the relative antioxidant activity of the aqueous extract were determined. The highest content of polyphenols, quantified by the Folin-Ciocalteau assay and expressed as milligrams of gallic acid equivalent (GAE) per grams of biomass, resulted 12.6, in agreement with the data reported in the literature for this biomass (Maimulyanti and Prihadi, 2017), always adopting water as the only extraction solvent. However, our optimization has been realized adopting milder reaction conditions, e.g. at lower temperatures and shorter reaction times, advantageously exploiting the higher efficiency of the MW heating (Narita and Inouye, 2012). Regarding the antioxidant activity, it was determined by the DPPH assay and expressed as EC_{50}, which represents the dilution factor of the antioxidant to reduce the DPPH concentration to 50% of its starting value (Narita and Inouye, 2012), and it amounted to 296 times.

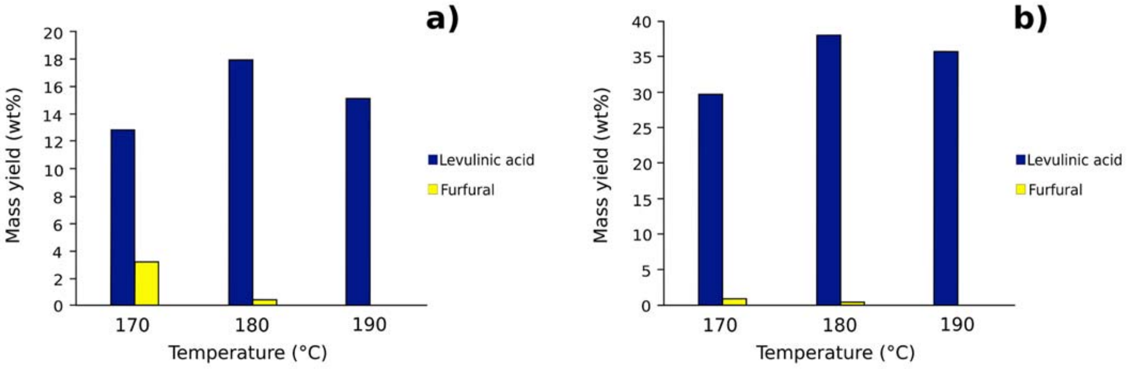

Figure 2: a) Results of the hydrolysis of CS to LA; b) Results of the hydrolysis of CP to LA. Formulation and MW reaction conditions: CS = 0.35 g; CP = 1.20 g; HCl = 1.68 wt%; biomass/water ratio = 7 %; reaction time = 20 minutes).

After having optimized the extraction of polyphenols from CS, the solid residue from the water extraction, which was still rich in cellulose, was subsequently hydrolysed to LA, by the one-pot acid-catalysed treatment. Our research group has previously investigated the conversion of cellulose-rich biomasses, including mainly the lignocellulosic and waste ones and achieving, in many cases, very promising results. In particular, some of the best ones were obtained adopting lignocellulosics such as giant reed (*Arundo Donax L.)* (Antonetti et al., 2015) and *Pinus Pinaster* (Rivas et al., 2015), with corresponding LA yields equal to 23 wt% and 17 wt%, respectively. In these cases, it was found that the optimal LA production with dilute hydrochloric acid required analogous reaction conditions, in particular dilute acid (1-2 wt%) and hydrolysis temperatures in the range 170-190 °C, with reaction times in MW within half an hour. On this basis, these reaction conditions have been reproposed and optimized for the conversion of the CS water-extraction residue into LA. The obtained results are reported in Figure 2a.

The above data confirm that the adopted reaction conditions are appropriate for the CS conversion into LA, achieving a maximum yield of about 18 wt%, at 180 °C. This result is in agreement with those obtained for traditional lignocellulosic biomasses, such as giant reed (Antonetti et al., 2015), indicating their similar recalcitrance to the hydrolysis treatment, as confirmed by the high lignin content of the starting CS, amounting at about 30 wt% (Narita and Inouye, 2014). Furthermore, it has been possible to identify the presence of low amounts of furfural, which derives from the corresponding hydrolysis of C5 sugars (Figure 1). The furfural yield decreases by increasing the reaction temperature, and its presence becomes negligible at 190 °C, due to its complete degradation into solid huminic by-products (Antonetti et al., 2015).

Lastly, the conversion of the CP into LA was investigated. Also in this case, a close temperature screening was carried out (170-190 °C), adopting the same acid concentration already used for the conversion of the other feedstocks, e.g. 1.68 wt%. The obtained results under MW irradiation are reported in Figure 2b. Also in this case, the highest LA mass yield was obtained at 180 °C, corresponding to about 40 wt%. This very high LA yield is due to its high cellulose content of the starting CP (74.6 wt%, as glucans), mainly composed of fragmented short-fibers deriving from cutting operations, and to the low lignin amount, both these aspects making easier its acid-catalysed conversion to LA.

4. Conclusions

Three cases of study of suitable waste feedstocks for LA production have been reported: two wastes deriving from the Italian food industry (ELP and CS), and a short-fiber CP originating from coil-cutting operations for the production of tissue paper products. Different reaction parameters have been optimized, including reaction temperature, hydrochloric acid concentration, biomass loading, and the further addition of a milder thermal pretreatment, which helps the next hydrolysis to LA. Upstream of the process, the high cellulose content of the starting feedstock is the main requisite for achieving good LA yields. In this regard, the highest obtained LA mass yield was got starting from the CP, followed by ELP and, lastly, CS. An additional exploitation of the CS was achieved introducing a preliminary extraction step of the water-soluble phenolics, which can be used as bioactive antioxidants in nutraceutical applications. All the investigated examples highlight the importance of a complete and integrated valorisation of a waste biomass, fully in agreement with the Biorefinery concept.

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