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Levulinic Acid from Orange Peel Waste by Hydrothermal Carbonization (HTC)

Monica Puccini*[a], Domenico Licursi[b], Eleonora Stefanelli[a] Sandra Vitolo[a], Anna Maria Raspolli Galletti[b], Hero Jan Heeres[c]

[a] Dipartimento di Ingegneria Civile e Industriale, University of Pisa, Largo Lucio Lazzarino 1, 56122 Pisa, Italy
[b] Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Giuseppe Moruzzi 3, 56124 Pisa, Italy
[c] Department of Chemical Engineering, University of Groningen, Nijenborgh 4, Groningen 9747 AG, Netherlands
monica.puccini@unipi.it

With the awareness of the need for optimal and sustainable use of natural resources, hydrothermal treatment of biomass and biomass waste for energy and resource recovery has received increasing attention. The hydrothermal carbonization (HTC) of a biomass is achieved using water as the reaction medium and applying mild temperatures (180–250 ° C) under saturated pressure (autogenous or provided by a gas) for several hours. The thermochemical process applied to biomass includes simultaneous reactions of hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization of the original precursor. The main resulting products are a carbon-rich solid, known as hydrochar, and a water phase containing soluble organic compounds. In this work, an experimental study on HTC process of orange peels to assess the yield of levulinic acid in water phase during the acid-catalyzed hydrolysis is reported. The results are promising, and comparable with other lignocellulosic biomass sources.

1. Introduction

In the last decade, there has been an increasing interest in the conversion of non-food, cheap and renewable biomass into new green biofuels and bioproducts, to be used for industrial applications in place of those of traditional fossil source (Seggiani et al., 2012). In this context, the exploitation of lignocellulosic biomass has become extremely attractive, thanks to its high availability and to the high content of cellulose, hemicellulose and lignin (Frigo et al., 2014). The biorefinery concept provides that all these fractions should be individually exploited (Fig. 1). Biomass hydrothermal treatment (HTC) is a mild and versatile process for the solubilization and/or conversion of its cellulose/hemicellulose fraction into interesting building blocks (Choi et al., 2015). An example is levulinic acid, a versatile intermediate for the synthesis of various organic compounds. The advantage of HTC is that it can convert wet input material into carbonaceous solids at relatively high yields without the need for an energy-intensive drying before or during the process. This opens up the field of potential feedstocks to a variety of nontraditional sources: wet animal manures, human waste, sewage sludges, municipal solid waste (MSW), as well as agricultural and algal residues.

The citrus-processing industry generates in the Mediterranean area huge amounts of orange peels as a byproduct from the industrial extraction of citrus juices. According to the global citrus fruit production (over 88 Tg per year 55% of which being orange fruits), the annual world supply of orange peel wastes should be around 21 Tg (Marin et al., 2007). The applications of agro-industrial waste includes the extraction of pectin, the recovery of essential oils, the production of clouding or thickening agents, and the removal and purification of carotenoids to obtain natural pigments suitable for food or juice coloring (Seggiani et al., 2009).

The conversion of orange peels into solid biofuel (De Morais et al., 2015) and bioethanol (Santi et al., 2014) is currently extensively investigated, in order to overcome the main bottlenecks (process heat duty, high viscosity of the medium to be fermented and distilled, price of cellulolytic and pectolytic enzymes, availability of genetically modified microorganisms to ferment both hexoses and pentoses and thus maximise the ethanol produced, high energy demand of the distillation step).

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Hydrothermal carbonization (HTC) may represent an alternative thermochemical conversion of orange peels to solid char and valuable building blocks that may be recovered from the process water phase. HTC had fallen into relative obscurity after the initial discovery and the research activity in the early 20th Century to understand natural coal formation, until recent studies on HTC of waste biomass has gained renewed interest due to great opportunities to produce valuable carbon materials with specific properties and applications (Libra et al., 2011). HTC comprises, in general, the mildest reaction conditions compared to all other hydrothermal conversions (Pavlovič et al, 2013). Most frequently, temperatures in the range 180-250 °C and autogenous pressures up to approximately 2 MPa are applied, with residence times from one to several hours (Fiori et al., 2014). This process simulates a long-time carbonization process at lower temperatures for coal production, producing a carbonaceous material known as hydrochar. Besides production of a solid fuel with a brown coal-like high heating value (the so-called hydrochar), this carbonaceous material may find many other potential applications in agriculture, environmental engineering, catalysis, energy storage, sensor industry, medicine, etc. During the treatment, the organic substrate undergoes changes in its structure by numerous reactions (such as hydrolysis, dehydration, decarboxylation, aromatization, recondensation, depolymerization) and even 80 wt % of initial biomass can be converted to hydrochar, the rest represented by gas (mainly CO_2) and aqueous extractive compounds (sugars, acetic acid and other organic acids).

HTC treatment of orange peel wastes has been recently investigated by Titirici et al. (2007) and Fernandez et al. (2015) with attention focused on the solid hydrochar product and the feasibility of its upgrading as adsorbent. The aim of this study was to assess the orange peel hydrothermal conversion into levulinic acid in water phase during the HTC process.

2. Materials and methods

2.1 Materials

Oranges from southern Italy, were purchased from a local market, washed and peeled. The orange peels were chopped and oven-dried at 100 °C. The dried samples were then crushed, milled and sieved to obtain particles with size below 100 μm.

Analytical grade sulphuric acid (95-97 wt%) was purchased from Merck GmbH (Darmstadt, Germany); deionised water was applied to prepare the solutions.

2.2 Experimental procedure

The HTC treatment was carried out in glass ampoules with a length of 150 mm, an internal diameter of 3 mm and a wall thickness of 1.5 mm. The ampoules were filled with a predetermined amount dried orange peel. Subsequently, an aqueous solution (0.5 cm^3) of the sulphuric acid catalyst at the desired concentration was added. The ampoules were sealed with a torch. The sealed ampoules were placed in a constant temperature oven (±1 °C). At various reaction times, ampoules were taken from the oven and quenched in an ice–water bath (4 °C) to stop the reaction. The ampoule was opened, and the liquid was separated from the solids (humins, insoluble lignin/lignin decomposition products and ash) using a micro-centrifuge (Omnilabo International B.V.) for approximately 15-20 min at 1200 rpm. A certain amount of the clear solution was taken (100–200 μL) and diluted with water (2 cm^3). The composition of the solution was determined using HPLC equipped with a BioRad Organic Acid column Aminex HPX-87H.

2.3 Analytical equipment

The elemental analysis of raw orange peel was carried out using GmbH Elementar. The sample was heated in the oven from 25 ◦C up to 1000 ◦C at a heating rate of 10 ◦C/min. The gases generated from heating were analyzed by an electrical conductivity detector.

The FT-IR analysis was used to study the main functional groups present in orange peel. The samples were mixed with KBr in a ratio of 1:100 (w/w) to produce tablets. The spectral range was from 4000 to 400 cm^{-1}, and 28 scans were taken at a resolution of 4 cm^{-1}.

The composition of the liquid phase after the reaction was determined by using an HPLC system consisting of a Hewlett Packard 1050 pump and a Waters 410 refractive index detector. An aqueous solution of sulphuric acid (5 mm) at a flow rate of 0.55 cm^3 min^{-1} was used as the mobile phase for the Aminex HPX-87H Organic Acid column, which was operated at 60 °C. The concentration of compound in the liquid phase was determined using calibration curves obtained by analyzing standard solutions with known concentrations.

The yield of levulinic acid (LA) is defined as the ratio of the mass of LA (M_{LA}) and the total mass of the dried raw material fed to the reactor:

$$Y_{LA}(wt\%) = \frac{M_{LA}}{m_{OP}} \times 100 \tag{1}$$

where m_{OP} represent the mass of the dried orange peels.

3. Results and discussion

Orange peel contains soluble sugars (glucose, fructose, galactose, arabinose, and galacturonic acid), and insoluble polysaccharides, basically cellulose and hemicellulose as the most important components. The elemental composition of orange peel resulted to be the following (wt%): C, 42.89; H, 6,14; N, 1.17; O, 49,80. It can observe that these valuea are very close to those reported in specialty literature (Li et al., 2008).

The FT-IR spectrum of dried orange peel, reported in Fig. 1, showed the main functional groups present in the material, with peaks characteristic of lignocellulosic materials. The broad band centered at 3400 cm^{-1} is associated with stretching of the O-H and N-H groups present in proteins, fatty acid, carbohydrates. The band at 1742 cm^{-1} is related to carbonylic group of esters. The peaks at 1098 cm^{-1} and 1023 cm^{-1} are due to the C-O stretching, and are characteristic bands of cellulose and hemicellulose from lignocellulosic materials.

Experiments on the acid-catalysed hydrolysis of the dried orange peels were carried out to gain insights into the type and amount of reaction products. The reactions were conducted at different temperatures, from 150 to 180 °C.

In all experiments, dark-brown insoluble products were formed. These are likely mixtures of humin type of by-products from the acid-catalyzed decomposition of glucose and HMF, the products of condensation reactions of C5-sugars and furfural, residual insoluble lignin and ash (Girisuta et al.,2006a,b).

The yield profile when hydrolysing the orange peels in a strong acid medium (1.0 M sulphuric acid) at different temperatures is given in Fig. 2. The yield profiles show that the temperature had a small effect on the LA yield At the end of reaction (after 120 min), the yield of LA reached a level of about 21.3 % at 160 °C. The yield was reduced when performing the reaction at higher temperatures. These findings are in line with the experimental and modelling studies on the acid-catalysed hydrolysis of cellulose to LA (Girisuta et al., 2007).

To gain insights into the effects of the acid catalyst concentration on the LA yield, a series of experiments was carried out varying the sulphuric acid concentration from 0.1 M to 1 M. The results are shown in the Figs. 3 and 4.

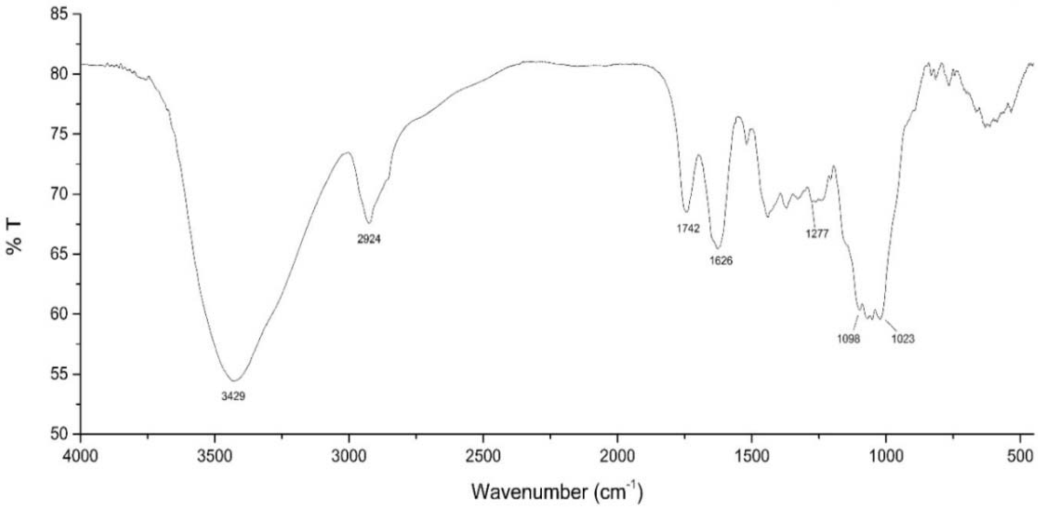

Figure 1: FT-IR spectrum of orange peel.

The amounts of LA at the end of the reaction when using 0.1 M sulphuric acid were considerably lower than found for 1 M acid, at 150 °C and 180 °C. The acid concentration had a significant effect on the LA yield, with higher concentrations leading to higher yields.

On the basis of the experimental data at different acid concentrations, it may be concluded that the product composition at the end of the reaction are a strong function of the acidity of the reaction medium: in strong acidic medium, the formation of levulinic acid was favoured.

Table 1 shows a comparison between the LA yields from earlier studies on a variety of lignocellulosic biomass sources with the results provided here for orange peels. Clearly, the yields of LA are depending on the biomass source and reaction conditions. High LA yields were usually obtained by hydrolysing biomass feedstock with a high content of C6-sugars, such as pulp slurry and starch, at high temperatures. The LA yield from the orange peels was comparable with sugarcane and bagasse. This is the consequence of the relatively lower amounts of C6-sugars in the orange peels compared to other lignocellulosic biomass sources (>40%).

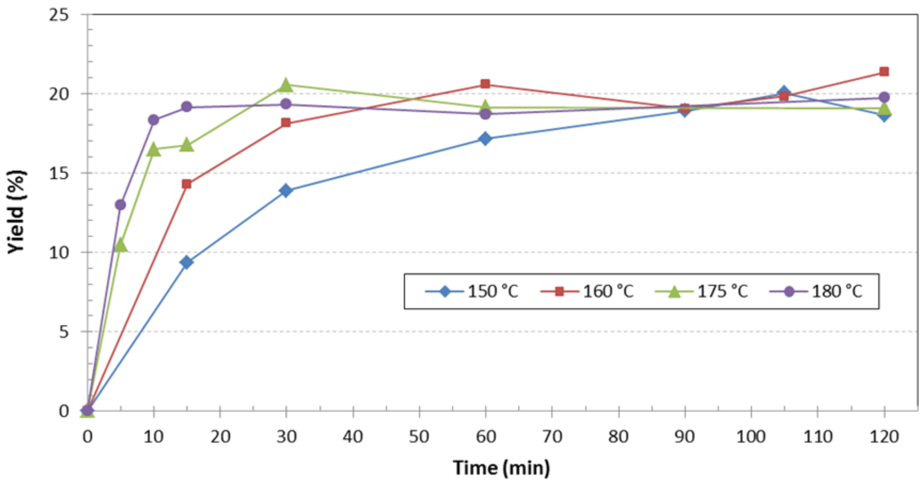

Figure 2: Yield profile of levulinic acid during reaction at different temperatures (1 M acid concentration)

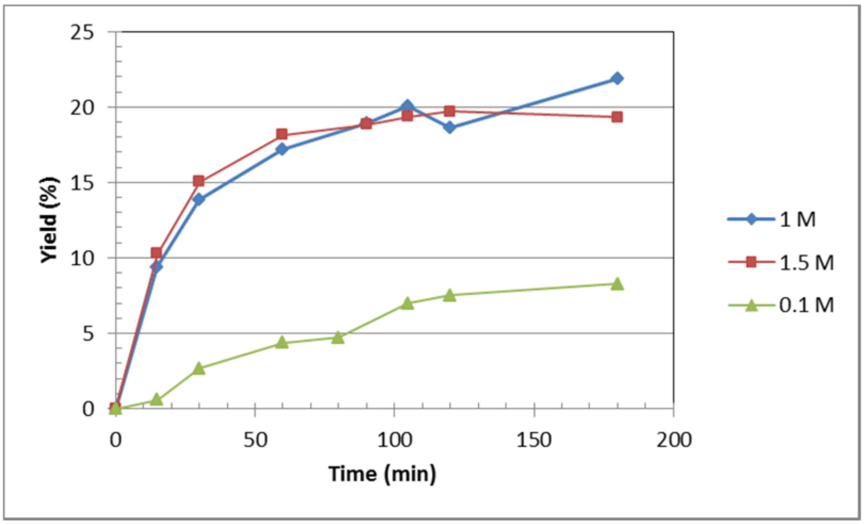

Figure 3: Yield profile of levulinic acid during reaction at different acid concentration at 150 °C

Table 1: LA yields from a variety of lignocellulosic biomass sources

Feedstocks	Temperature (°C)	Acid	Time (h)	Y_{LA} (wt%)
Wood sawdust	190	HCl	0.5	9
Cane sugar	100	HCl	24	15
Bagasse	25-195	H_2SO_4	2	18
Starch	200	HCl	0.5	35
Corn starch	162	HCl	1	26
Pulp slurry	160	HCl	1	41

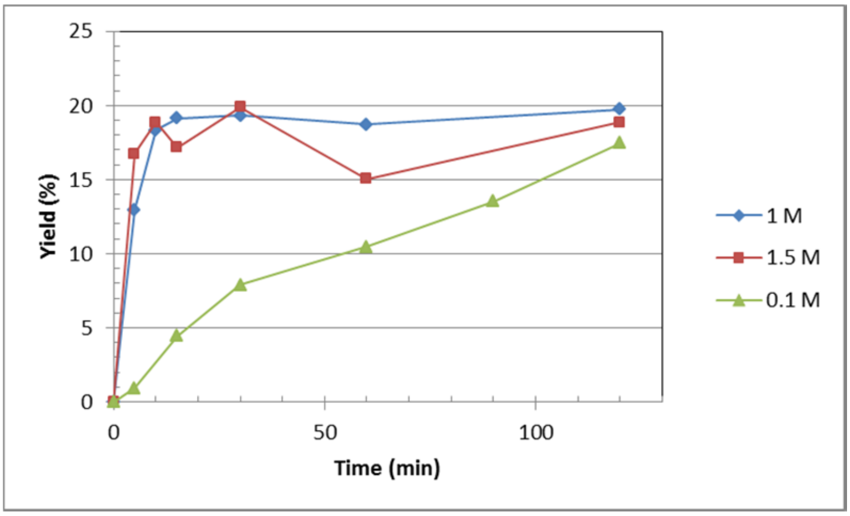

Figure 4: Yield profile of levulinic acid during reaction at different acid concentration at 180 °C

4. Conclusions

The acid-catalysed hydrolysis of the orange peels to levulinic acid was carried out in different reaction conditions, including variations in temperature (from 150 to 180 ° C) and sulphuric acid concentrations (between 0.1 and 1.0 M). The experimental results showed that he yield of levulinic acid depends strongly on the applied reaction conditions. The temperature had a small effect on the LA yield. Instead, The acid concentration had a significant effect on the LA yield, with higher concentrations leading to higher yields. In strong acidic medium (1 M), the formation of levulinic acid was favoured reaching an LA yield of about 21.3 % at 160 °C. This value is comparable to other lignocellulosic biomass sources.

Reference

De Morais C.L., Monteiro Santos C., Rosa A.H., 2015, Thermodynamic parameters of a solid biofuel from orange peel, Chemical Engineering Transactions, 43, 583-588

Choi S., Song C.W., Shin J.H., Lee S.Y., 2015, Biorefineries for the production of top building block chemicals and their derivatives, Metabolic Engineering, 28, 223-239

Fernandez M.E., Ledesma B., Roman S., Bonelli P.R.,. Cukierman A.L., 2015, Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants, Bioresource Technology, 183, 221-228

Fiori L., Basso D., Castello D., Baratieri M., 2014, Hydrothermal carbonization of biomass: design of a batch reactor and preliminary experimental results, Chemical Engineering Transactions, 37, 55-60

Frigo S., Gabbrielli R., Seggiani M., Vitolo S., Puccini M., 2014, Small-scale wood-fuelled CHP plants: A comparative evaluation of the available technologiesChemical Engineering Transactions, 37, 847-852

Girisuta B., Janssen L.P.B.M., Heeres H.J., 2006a, A kinetic study on the conversion of glucose to levulinic acid, Chem. Eng. Res. Des. 84, 339–349

Girisuta B., Janssen L.P.B.M., Heeres H.J., 2006b, A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid. Green Chem. 8, 701–709

Girisuta B., Janssen L.P.B.M., Heeres H.J., 2007. Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic Acid. Ind. Eng. Chem. Res. 46, 1696–1708

Li X., Tang Y., Caoa X., Lua D., Luoa F., Shao W., 2008, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, Colloids and Surfaces A: Physicochem. Eng. Aspects 317, 512–521

Libra J.A., Ro K.S., Kammann C., Funke A., Berge N.D., Neubauer Y., Titirici M., Führer C., Bens O., Kern J., Emmerich K., 2011, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, Biofuels, 2(1), 89-124

Marin F.R., Soler-Rivas C., Benavente-Garcia O., Castillo J., Perez-Alvarez J.A., 2007, By-products from different citrus processes as a source of customized functional fibres, Food Chemistry, 100(2), 736-41

Pavlovič I., Knez Z., Škerget M., 2013, Hydrothermal reactions of agricultural and food processing wastes in sub- and supercritical water: a review of fundamentals, mechanisms, and state of research, Journal of Agricultural and Food Chemistry, 61, 8003-8025

Santi G., Crognale S., D'Annibale A., Petruccioli M., Ruzzi M., Valentini R., Moresi M., 2014, Orange peel pretreatment in a novel lab-scale direct steam-injection apparatus for ethanol production, Biomass and Bioenergy, 61, 146-156

Seggiani M., Puccini M., Pierini M., Giovando S., Forneris C., 2009, Effect of different extraction and precipitation methods on yield and quality of pectin, International Journal of Food Science and Technology, 44, 574-580

Seggiani M., Prati M.V., Costagliola M.A., Puccini M., Vitolo S., 2012, Bioethanol-gasoline fuel blends: Exhaust emissions and morphological characterization of particulate from a moped engine, Journal of the Air and Waste Management Association, 62(8), 888-897

Titirici M.M., Thomas A., Yu S.H., Muller J.O., Antonietti M., 2007. A direct synthesis of mesoporous carbons with bicontinuous pore morphology from crude plant material by hydrothermal carbonization, Chemistry of Materials, 19, 4205-4212.