Apple waste: A sustainable source of carbon materials and valuable compounds

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ABSTRACT. The implementation of sustainable strategies based on the integral valorisation of residues is the most efficient way to achieve a profitable circular economy. This comprehensive study highlights the potential of apple waste from juice and cider production as precursor of porous carbons and provides guidelines to achieve a wide spectrum of physico-chemical properties. Hydrothermal carbonization (HTC) of apple bagasse is proposed as a feasible integrated process with zero waste that allows stabilizing this highly pollutant residue in the form of a carbon-enriched solid while extracting valuable compounds in aqueous phase. The liquid fraction resulting from HTC at 200 °C contains high total phenolic contents and antioxidant activity, the major products being catechol (1,2-dihydroxybenzene) and HMF (5-hydroxymethyl-

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2-furfural). The successful upgrading of the solid by-product into porous carbons provides additional advantage for a more cost-effective waste management. It is reported that a simple one-step activation leads to apple derived-carbons with specific surface areas up to $2000 \text{ m}^2 \text{ g}^{-1}$ and electrochemical capacitances as high as $260\text{-}290 \text{ F g}^{-1}$. Their excellent performance as supercapacitor electrodes make them very promising for the storage of electrical energy from renewable sources.

KEYWORDS. *Apple waste, Biocarbon, Porous carbon, Hydrothermal carbonization, Bioactive compounds, Supercapacitor.*

INTRODUCTION

Apple processing industries contribute around 20 million tons/year of waste worldwide.¹ The apple pomace, consisting of peel, pulp, stems and seeds, contains a high content of insoluble (lignin, cellulose, hemicelluloses) and soluble (pectins, β -glucans, galactomannan gums, nondigestible oligosaccharides) fibers.² Its degradation involves uncontrolled fermentation and high chemical oxygen demand ($300 \text{ g COD/kg pomace}$) and, therefore, its use as fertilizer without any pre-treatment impacts the environment. On the other hand, the low protein content and the seasonally availability of apple bagasse limit its application as feedstuff.³

Some investigations reported on its potential for bakery goods⁴ and spirits production⁵ as well as bio-adsorbent for wastewater treatment.⁶ Nevertheless, obtaining vinegar is the most widespread process for recycling apple pomace but this activity involves only a small proportion of the huge amount of residue generated industrially. In this context, around 80% of the highly

biodegradable apple paste is landfilled, incinerated or composted.¹ Such a waste processing generates an additional cost for the beverage industry and an environmental impact which cannot be overlooked. Undoubtedly, the recycling of these residues as source of high-added value products would make their management much more profitable and environmental friendly.⁷

As far as the major fraction of bioactive compounds is retained in the residue from the standard processes of extraction of apple juice,^{3,8} apple wastes could potentially be a good feedstock for recovering multifunctional healthy products.^{9,10} Actually, biorefinery processes are attracting much interest for obtaining polyphenols with antioxidant, antimicrobial, anti-inflammatory, anticarcinogenic and cardiovascular-protective properties for food, pharmaceutical and cosmetic applications.^{1,8,10,11} Apple residues can be also transformed into various natural active compounds such as pectins,¹² organic acids,¹³ aroma and flavours,¹⁴ dietary fibres^{3,12} and enzymes.¹⁵ On the other hand, they are also suitable for producing biofuels (ethanol and butanol).¹⁶ All these approaches are promising but the complex processes of recovery and extraction, the low yields and the practical suitability and marketability of the products block their large-scale development.^{9,10}

In the framework of nearly zero net CO₂ impact, thermochemical treatments such as pyrolysis and gasification are an option for energy generation. They essentially consist in heating at temperatures above 400 °C to produce a solid that contains around 50% of the carbon in the feedstock, the rest being released as volatile products (H₂, syngas, etc.).¹⁷ Whereas the efficiency of the apple waste for energy valorisation is too low compared to other biomass residues,¹⁸ apple derived-carbons appear promising for removal of pollutants from aqueous streams¹⁹ and electrical energy storage.²⁰

With the help of novel data and others quoted in the literature, this comprehensive study highlights the residual biomass of the industries producing apple juice and cider as an easily exploitable resource for the production of low-cost porous carbons. A number of different end-products with diverse textural and chemical features are reached by selecting the synthesis method. As an example of their suitability for advanced applications, their excellent performance as electrodes in supercapacitors is illustrated.

It also proposes the hydrothermal carbonization (HTC) as a non-polluting technological route, driving towards an integral valorisation with zero waste. HTC allows stabilizing the highly degradable apple bagasse in the form of a carbonaceous material (hydrochar) while extracts rich in bioactive compounds are eco-friendly obtained. Further upgrading of the hydrochar into sustainable activated carbons provides a bonus for a more cost-effective waste management.

EXPERIMENTAL SECTION

Raw material. This study is based on the solid waste of a mixture of apples hydraulically pressed for manufacturing natural cider by a local cellar (Llagar Fanjul, Siero, Asturias (Spain)). The as-received apple bagasse was divided into two lots. One of them (A1) was immediately subjected to thermal treatments whereas the second one (A2) was kept under aerobic conditions for 8 days at room temperature before being used as feedstock.

Synthesis of hydrochars. 10 g of apple bagasse A1 and 10 g of water were loaded into a stainless steel autoclave and heated up to 200 °C under autogenous pressure for 12 h. Similar run was also accomplished on A2. The aqueous phase and the solid were separated by filtration. The resulting hydrochars, A1H and A2H, were washed with 100 ml of water and dried at 100 °C for 24 h.

Preparation of activated carbons. Samples of apple pomace A1, dried and ground below 1 mm, were physically or chemically activated following one-pot process. The former was carried out in a quartz reactor under a CO₂ stream (370 cm³ min⁻¹), using heating rate, temperature and holding time of 5 °C min⁻¹, 800 °C and 30 min, respectively. The chemical activation was carried out by thoroughly ground the apple bagasse and KOH (1:2, weight ratio) and subsequent heating (5 °C min⁻¹) up to 800 °C for 1 h under a N₂ (72 cm³ min⁻¹). The resulting sample was washed with HCl (10%) and boiling distilled water to remove any inorganic salts. Finally, it was dried in an air oven at 100 °C for 24 h. The samples were named respectively A1C and A1K for physical and chemical activation.

Both activation processes were also applied to the hydrochar A1H, the carbons A1HC and A1HK being obtained respectively.

To evaluate the incidence of the fermentation of the feedstock, the bagasse A2 and the hydrochar A2H were subjected to physical activation. It resulted in the synthesis of A2C and A2HC.

Characterization of materials and compounds. The assessment of the bio-composition of the apple pomace, in terms of crude protein, total fat, acid detergent fiber, neutral detergent fiber, crude fiber, total phenolic content and radical-scavenging activity was accomplished as detailed in the Supplementary Information. The results are summarized in Table S1.

Elemental analysis of C, H and N was carried out in a LECO TruSpec Micro microanalyser whilst oxygen was determined with a LECO TruSpec Micro-O. The humidity, volatile matter and ash content were determined by a Setaram TGA24 thermogravimetric analyzer. Surface [O]-functionalities desorbing as CO₂ and CO were evaluated by temperature programmed desorption (TPD) runs.²¹

The calorific power (expressed by the higher heating value, HHV) was determined by using an automatic bomb calorimeter IKAWEEME C4000.

The characterization of the porous structure was based on physical adsorption of N₂ at −196 °C (Micromeritics ASAP 2010) and CO₂ at 0 °C (Micromeritics TriStar 3000). The analysis of N₂ isotherms was accomplished within the Dubinin's theory and by the comparison plot and QSDFT model (Quantachrome software package). The standard assessment by the BET equation has not been taken into account in view of its shortcomings to characterize microporous materials with pore sizes outside the range 0.9-1.1nm.²² CO₂ isotherm was analyzed by the NLDFIT approach and the Dubinin-Raduskevich equation.

The electrochemical performance was evaluated in a sandwich-type capacitor set up with two carbon pellets (90 wt.% of carbon, 5 wt.% of PTFE and 5 wt.% of carbon black (Super P)) separated by glassy fibrous paper and placed in a Swagelok cell with aqueous 2M H₂SO₄ electrolyte. The system was subjected to cyclic voltammetry (10 mV s^{−1}) and galvanostatic charging-discharging at 0-1 V under current densities of 1-200 mA cm^{−2}. These tests were complemented with electrochemical impedance spectroscopy measurements by sinusoidal signal of ±15 mV from 2·10^{−4} Hz to 60 kHz (Autolab-Ecochimie PGSTAT30 - FRA32 M module).²³

Low molecular weight polyphenols were quantified by HPLC/DAD analysis according to a validated method ²⁴ and using an external calibration. Phloretin-2'-xyloglucoside was estimated as phoridzine, flavonol glycosides as quercitrin and furanic compounds as 5-hydroxymethyl-2-furfural. The total phenolic content (TPC) and the radical-scavenging activity (AA) were analysed by the Folin-Ciocalteu and DPPH colorimetric methods, respectively.²⁵

RESULTS AND DISCUSSION

Carbons from apple wastes. Within the standard values reported for lignocellulosic materials, apple waste mostly consists of carbon and oxygen with contents around 47 and 46 wt.% (Table 1). After being kept in air for 8 days at ambient temperature, these percentages slightly change to 50 and 44 wt.%, respectively (Table S2). In agreement with previous results for fermented apple pomace with selected yeasts,^{26,27} a relevant increase in the concentration of crude protein, total fat, acid detergent fiber, neutral detergent fiber, crude fiber and total phenolic content are detected in the aerated pomace A2 whereas the radical-scavenging activity slightly decreases.

Table 1. Chemical and textural features of the as-received apple waste and the corresponding hydrocarbon and activated carbons obtained by one-pot activation with CO₂ or KOH.

Sample	Elemental analysis				Ash	TPD		Specific surface area	
	(wt.%, dry ash free)				(wt.%,	(μmol g ⁻¹)		(m ² g ⁻¹)	
	C	H	N	O	dry basis)	CO ₂	CO	S _{CO2}	S _{N2}
A1	47.1	6.4	0.5	46.0	2.3	3750	4277	-	-
A1H	65.6	5.8	0.8	27.9	2.4	3484	6478	-	68
A1C	90.0	0.9	1.4	7.7	8.4	949	2359	1070	923
A1HC	92.8	0.9	1.3	5.0	5.5	661	1708	967	844
A1K	93.0	0.3	0.4	6.3	5.8	1980	3846	2023	1524
A1HK	93.9	0.3	0.3	5.5	6.5	2433	4475	1898	1175

The thermal treatment of apple bagasse in N₂ provokes a variety of reactions such as dehydration, depolymerisation, carbonylation, carboxylation and transglycosylation. As illustrated by the TGA profile displayed in Fig. S1, they lead to a significant weight loss at 200-350 °C which corresponds to the decomposition of free sugars and the degradation of hemicellulose (197-327 °C), cellulose (277-427 °C) and, to a lesser extent, lignin (277-527 °C). Remaining cellulose and most lignin generate a second weight loss peak between 450 and 550 °C.²⁸ Depending on the experimental conditions (heating rate, temperature, soaking time, gas flow rate, particle size, etc.), the weight evolution may vary slightly but the main profile is maintained²⁸ and the carbon yield oscillates around 25-30%.²⁹⁻³¹ As far as preliminary tests revealed no significant differences between the carbon materials resulting from A1 and A2 (Table S2 and Fig. S2), the study was mainly focused on the fresh feedstock.

The remarkable reduction in the H/C and O/C ratios (Fig. 1) indicates that the pyrolysis of the apple bagasse at 400 and 750 °C under N₂ increases notably the aromaticity degree. This process ultimately enhances the calorific power from 18.7 MJ kg⁻¹ of the feedstock (standard value for biomass³²) up to 29.2 MJ kg⁻¹ for C-400 and 29.9 MJ kg⁻¹ for C-750. As found for similar materials from biomass,³³ the HHV of the apple-biochars compares with that of lignite and high-volatile bituminous coals.³⁴

Figure 1: Van Krevelen diagram of apple wastes and a diversity of carbons obtained by different processes^{30,31,35}

Fernandez et al.³⁰ reported that the carbonization of apple residue at 400 °C leads to an ultramicroporous material with a specific surface area as high as 400 m² g⁻¹, approximately. The average size of the pores is around 0.67 nm although the presence of constrictions greatly hinders the access of molecules larger than 0.4 nm. On the other hand, the porosity of the biochar prepared at 750 °C is close to 0.1 cm³ g⁻¹ but it resulted to be virtually inaccessible even to a molecule as small as CH₂Cl₂ (0.33 nm).

Compared to the pyrolysis, the activation is found to be a very interesting process to obtain a great diversity of porous carbons from apple wastes. The overall picture provided by the van Krevelen-type diagram (Fig. 1) reveals the impact of the production method and the activated carbons fall into well-differentiated families, attending to their chemical features. As opposed to the highly O-functionalized carbons (15-30 wt.% total oxygen) obtained by carbonization and subsequent activation with steam,³¹ those produced by one-pot activation with

CO₂ or KOH are mostly made of carbon, the total quantity of O being limited to around 7 wt.% (Table 1). Between both sets, H₃PO₄ as activating agent leads to materials with an intermediate content of oxygen (10-14 wt.%).^{36,37} It is remarkable the highly condensed structure obtained by one-pot activation of apple pomace by CO₂ or KOH, similar to that of grape bagasse-carbons produced by the same procedure.²¹ The similarity also extends to the surface nature (Fig. S3), most functionalities corresponding to weak acidic carboxylic-, lactone- and carbonyl/quinone-groups (Table S3).²¹

A comprehensive analysis of the porous features of a variety of apple-activated carbons indicates little influence of the standard synthesis parameters. In the case of using the typical two-steps procedure, the heating rate and the temperature used in prior carbonization do not have a significant effect on the porosity of the final activated carbons.^{30,31} Additionally, the temperature of the subsequent activation step also has small impact and the porous development depends basically on the loss of mass (burn-off degree) experienced by the biochar.³¹

On the contrary, the apple bagasse is very sensitive to the activating reagent and a proper selection allows modulating the porosity within a wide range. The heating of biochars produced at 400 and 750 °C under water vapour at 600-750 °C generates essentially microporous carbons with specific surface areas from 600 to 900 m² g⁻¹ and average micropore size of 0.9-1.1 nm. The total pores volume increases linearly with the activation degree but some mesoporosity is only observed for burn-off of around 75%.³¹ A narrower microporosity (0.75-0.83 nm in average size) and specific surface areas between 550 and 750 m² g⁻¹ are obtained under the same carbonization conditions and subsequent gasification at 750 °C with CO₂. Further treatment up to 70% b.o. notably increases the micropore volume and the pores size (1.3-1.5 nm) but the surface of the resulting highly activated carbons remains around 800 m² g⁻¹.³⁰ As opposed, the direct activation

of apple residues by CO₂ generates an ultramicroporous carbon (Fig. S4) which achieves 1070 m² g⁻¹ (Table 1), mostly in pores below 0.6 nm (Fig. 2). It is interesting to note that the same process on winery wastes generates comparable materials.²¹

Fig. 2 Pore size distribution of activated carbons derived from one-pot activation with CO₂ (a) and KOH (b) with and without prior hydrothermal treatment.

Fig. 3 summarizes what can be expected from apple bagasse when subjected to physical activation. Regardless of the agent (steam, CO₂) or if the process takes place in one or two steps, one observes a regular increase in the micropore volume (W_o) and the average micropore size (L_o) with a gradient of $\sim 2 \text{ nm cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$. This general pattern (based on N₂ as molecular probe) indicates that the combination of a high micropore volume and relatively narrow pores is difficult to be obtained. Consequently, the chances of reaching a specific surface area above 1000 m² g⁻¹ by physical activation of apple waste are rather limited. The comparison of the isotherms of A1C and A2C in Fig. S2 indicates no relevant effect of the feedstock fermentation degree on the subsequent porosity development.

Fig. 3. Variation of the average micropore width L_0 with the micropore volume W_0 for carbons obtained by the activation of different precursors under diverse conditions: Physical activation of apple bagasse by one-pot (■) and two-steps (■)³⁰ with CO₂ and steam (■)³¹, cider leeds (■), grape bagasse and seeds (■ ■)²¹ by one-step-CO₂. Chemical activation of apple pomace (●), cider leeds (●), grape bagasse, seeds and stems (● ● ■)²¹ by one-pot with KOH, cherry pits (●)³⁸ by two-steps-KOH and wood (●)³⁹ by two-step-NaOH

Regarding chemical activation, previous studies on apple bagasse suggested a tendency to generate mesoporous carbons whose surface does not exceed 1000 m² g⁻¹. Suárez-García et al.^{35,36} reported that the use of phosphoric acid promotes the creation of a well-developed mesoporosity up to 30 nm and Hesas et al.³⁷ showed that pores of 7-8 nm are enhanced when H₃PO₄-activation is combined with microwave radiation. On the other hand, the use of ZnCl₂-activation on apple residues resulted in supermicropores and small mesopores centred at around 2.5 nm.¹⁹

It is noteworthy that this general trend is challenged by using KOH as activating reagent. Fig. S4 shows that this process engenders an essentially microporous carbon, A1K, exhibiting a wide pore size distribution below 2 nm with a noticeable presence of ultramicropores smaller than 0.6 nm (Fig. 2). Its accessibility to the N₂ molecule at −196 °C is somewhat restricted but, as proven by CO₂ adsorption, its total surface reaches the outstanding value of 2023 m² g^{−1} (Table 1).

Fig. 3 displays that the microporosity evolution by KOH-activation of apple residues closely follows the general behaviour observed for other precursors of lignocellulosic origin (wood, cherry stones, winery wastes, etc.) treated with alkali reagents.^{21,38,39} Compared to physical activation, the lower gradient $\Delta W_o/\Delta L_o$ suggests that the creation of micropores prevails over the enlargement of their size.

Indeed, the possibility of having a great variety of physico-chemical characteristics opens up a wide spectrum of applications for biocarbons derived from apple waste. The heat treatment of the bagasse with ZnCl₂ produced an activated carbon which successfully adsorbed Pb (II) and Zn (II)¹⁹ from aqueous streams whereas those obtained in presence of H₃PO₄ resulted useful for the adsorption of Cr (VI)⁴⁰ and methylene blue.³⁷

Beside their suitability for eliminating pollutants, apple based-carbons have also a niche in more advanced fields such as electrical energy storage. Thus, hard carbons synthesized by H₃PO₄ activation and subsequent heating at 1100 °C operated successfully in negative electrode materials of Na-ion batteries,²⁰ a KOH-activated carbon was an excellent support of hybrid nickel–cobalt hydroxide nanowires for asymmetric supercapacitors⁴¹ and steam-activated carbons displayed promising properties for supercapacitor electrodes.³¹

Supercapacitors store electrical energy through ions accumulation at the electrode/electrolyte interface and currently have wide applications from portable devices to electric vehicles. In recent years, many efforts are being devoted to reduce the cost of electrodes⁴². As reported by Fernández-López et al.,³¹ apple based-carbons produced by steam activation are able to reach specific capacitances of around 170 F g⁻¹ in aqueous H₂SO₄, which compete with the value of 157 F g⁻¹ of the carbon Super DLC-30 commercialized by Norit for supercapacitors. However, the capacitance is markedly reduced with increasing current density and the power supplied by the corresponding device is poor (Fig. S5 a-b).

Our work shows that this limitation is overcome by a simpler one-step CO₂-activation. The nearly rectangular shape of the cyclic voltammograms of A1C (Fig. 4a) provides a first indication of the successful formation of an electrochemical double-layer associated to fast charge and ions propagation throughout the porous network. The higher aromaticity degree of this material (Fig. 1) provides lower electrical resistance (Fig. S5 c), which facilitates that 70% of the capacitance reached at 1 mA cm⁻² is retained at 200 mA cm⁻² (Fig. 4b). As a consequence of the enhanced response rate, the cell with electrodes A1C compares with the device assembled with Super DLC-30 (Fig. 4b).

On the other hand, Figs. 4 a and b show the superior electrochemical performance of the material obtained by one-pot KOH-activation. The capacitance of A1K reaches 264 F g⁻¹, close to the maximum value found for a large variety of carbons (under the same testing conditions),⁴³ which translates into excellent energy storage and power delivery (Fig. 4c).

Fig. 4. Electrochemical performance of the carbons obtained from apple waste by one-pot activation with CO₂ or KOH

In the absence of a standard protocol for textural characterization and electrochemical measurements, the comparison with data reported for other biomass based-carbons is not straightforward but Table 2 illustrates the great potential of the materials from apple waste for electrochemical energy storage.

Table 2. Specific surface area (S_{BET}) and gravimetric capacitance of different biomass derived-carbons

Precursor	S_{BET} (m ² g ⁻¹)	C (F g ⁻¹)/Electrolyte	Ref.
A1C	564	170 / H ₂ SO ₄	This paper
A1HC	609	125 / H ₂ SO ₄	This paper
A1K	2454	264 / H ₂ SO ₄	This paper
A1HK	1536	284 / H ₂ SO ₄	This paper
Fibres oil palm	1704	149 / H ₂ SO ₄	44
Coffee endocarp	1050	176 / H ₂ SO ₄	45
Cherry stone	1171	232 / H ₂ SO ₄	38
Rubber wood sawdust	913	138 / H ₂ SO ₄	46
Cellulose carbamate	3700	289 / KOH	47
Cottonseed hull	2573	304 / KOH	48
Absorbent cotton	1022	270 / KOH	49
Waste paper	416	160 / KOH	50

Hydrothermal carbonization

Hydrochar and activated hydrochars. At glance, the hydrothermal carbonization of the wet apple bagasse appears an effective way to reduce significantly the volume occupied by this polluting residue (Fig. 5) while enhancing the sequestration of carbon. The stable solid by-product obtained after autogenous pressure heating at 200 °C retains 75% of the carbon present in the feedstock and the rest is in organic compounds dispersed in the aqueous phase.

Fig. 5. Products obtained from apple waste by hydrothermal carbonization at 200 °C and extraction with water at 60 °C

The position of the hydrochars A1H and A2H in Fig. 1 evidences the lower carbonization degree achieved by HTC compared to the standard pyrolysis (C-400, C-750). However, in line with other lignocellulosic precursors,^{21,33,51} the bio-polymers degradation⁵² of apple waste at 200 °C is sufficient to obtain a material with 65.6 wt.% of carbon and 27.9 wt.% of oxygen (Table 1). The higher carbon content of A1H conforms to the 30% increase in the calorific power

compared to the feedstock A1 and its HHV of 24.8 MJ kg^{-1} fits into the values of peat and lignite³⁴ and other biomass derived-hydrochars.⁵³ Taking into account the mass yield and the energy densification ratio (HHV carbon material/HHV feedstock), the energy yield for HTC is as high as 71%. As comparison, apple-chars C-400 and C-750 provide $29\text{-}30 \text{ MJ kg}^{-1}$ but the energy yield is only around 45% and significant amounts of harmful gases are released during production. Moreover, standard carbonization requires pre-drying and much higher temperature and the final materials are enriched in inorganic impurities. On the contrary, the similar ash content in A1 and A1H indicates that a significant fraction ($\sim 50\%$) of the mineral matter is dissolved during the hydrothermal treatment.

The predominantly microporous structure of apple-chars is not detected in the apple-hydrochars. The N_2 and CO_2 adsorption on A1H and A2H reports no relevant narrow porosity and the specific surface areas of only 68 and $50 \text{ m}^2 \text{ g}^{-1}$, respectively, corresponds to wide mesopores, macropores and external surface (Fig. S2).

The successful use of the apple-hydrochars as precursors of activated carbons brings added profitability. Fig. 3 shows that both physical and chemical activation of the apple-hydrochar follow the general patterns found for the original feedstock, although some peculiarities are observed. The higher aromaticity degree of A1H (Fig. 1) leads to a slightly lower microporous development in the subsequent CO_2 -activation but it is compensated by narrower micropores and a small additional contribution from the wide porosity of A1H (Fig. 2 and S4). As a result, the total surface area of A1HC reaches nearly $1000 \text{ m}^2 \text{ g}^{-1}$, comparable to that obtained by direct activation of apple bagasse (Table 1). The fact that A1HC has 20% less electrochemical capacitance (Figs. 4 a and b) is explained by the decrease in the density of

surface functionalities (Table 1) which provides lower pseudocapacitance from redox-type reactions.

A prior HTC also affects the porosity development along activation with KOH. As summarized in Fig. 2, it diminishes the ultramicroporosity and makes the porosity less accessible (significant decrease in S_{N_2}). Nevertheless, it is still possible to get an activated carbon with a total area close to $2000 \text{ m}^2 \text{ g}^{-1}$ (Table 1) and a surface enriched in oxygenated groups. Both features facilitate that A1HK surpasses the high electrochemical capacitance of A1K, reaching a superior value close to 300 F g^{-1} (Fig. 4b). As illustrated by Table S4, it competes favourably with other biomass derived-carbons.

Liquid extracts rich in compounds. The extraction of bioactive compounds from biomass wastes is mostly carried out with toxic organic solvents that are hardly removed from the final products and also require a proper process for final recycling. In this context, non-polluting techniques with “green solvents” like hot water are preferred.⁵⁴

Using a simple approach as reference, the treatment of the as-received waste with water at 60°C extracts typical phenolic compounds of apple pomace such as: hydroxycinnamic acids, dihydrochalcones and flavonols (not shown). The 60°C -extract from the bagasse kept in air for 8 days at ambient temperature displays a similar antioxidant capacity (AA/TPC ratio) and it also contains tyrosol. The biochemical pathways by which the aromatic higher alcohols such as tryptophol, tyrosol and phenylethanol are formed is related by yeast metabolism. This fact indicates the spontaneous fermentation of the apple pomace in aerobic conditions.²⁷

In spite of the usefulness of the extraction by solvents, it should not be overlooked that a highly degradable solid residue still remains (Fig. 5). As opposed, the hydrothermal carbonization provides a valuable liquid stream from the hydrolysis of water-soluble-compounds

and the disintegration of biomass polymers into their monomeric chains,^{55,56} besides a stable carbon material as solid by-product (Fig. 5).

The phenolic profiles, furfural derivatives, total phenolic content and antiradical activity of the liquid fraction resulting from HTC at 200 °C reveals the possibilities of this alternative technology to obtain polyphenols-rich aqueous solutions from apple wastes (Table 3). It is observed that the treatment of the apple bagasse with subcritical water generates much higher amount of polyphenols than that performed at 60 °C.^{57,58} The degradation products of phenolic compounds can also have an antioxidant activity sometimes higher than the initial phenolic compounds.⁵⁹ As previously reported,¹¹ the highest phenolic contents, the highest in vitro antiradical activities.

As summarized in Table 3, the major products from processing both apple wastes by HTC at 200 °C correspond to catechol (1,2-dihydroxybenzene) and HMF (5-hydroxymethyl-2-furfural) produced from thermal degradation of sugars (Fig. 6). The former has a high potential as precursor of fine chemicals (i.e. perfumes) and pharmaceutical products. The latter is highly suitable for the synthesis of non-petroleum-derived polymeric materials such as dimethylfuran, used in the production of biofuels, and other valuable compounds for plastics manufacturing. Other three unknown compounds exhibiting spectral characteristics similar to furfural ($\lambda_{\text{max}}=282$ nm) are also detected.

Table 3. Composition of the liquid fraction obtained by treatment of apple bagasse at 60 °C and by HTC at 200 °C.

		A1		A2	
		60 °C	200 °C	60 °C	200 °C
TPC (mg tannic acid L ⁻¹)		72 ± 4	999 ± 40	732 ± 82	1174 ± 27
AA (mg ascorbic acid L ⁻¹)		26 ± 2	791 ± 21	275 ± 13	930 ± 5
AA/TPC		0.36	0.79	0.38	0.79
Phenolic compounds (mg L ⁻¹)	Catechol	-	5.49	-	4.16
	Protocatechuic acid	-	-	0.75	-
	Tyrosol	-	-	0.76	-
	Chlorogenic acid	0.84	-	0.89	-
	Cafeic acid	-	-	0.11	-
	Phloretin-2'xiloglucoside	0.66	-	0.56	-
	Phoridzin	0.52	-	1.16	-
	Hyperin	0.12	-	0.17	-
	Rutin+isoquercitrin	0.10	-	-	-
	Quercitrin	0.13	-	0.15	-
Furfural compounds (mg L ⁻¹)	HMF	-	3.17	-	2.06
	Unknown 1	-	0.53	0.49	1.20
	Unknown 2	-	0.47	-	1.06
	Unknown 3	-	1.10	-	3.26

Fig. 6. Chromatogram at 280 nm of main compounds in the liquid by product of HTC at 200°C

CONCLUSIONS

Contributing to a sustainable production in line with the concept of circular economy, apple bagasse is a reliable and easily exploitable resource of valuable materials and compounds.

A number of low-cost carbons, with physico-chemical features tailored for efficient performance in a variety of applications, can be reached by selecting the synthesis procedure. It is found that the activated carbons derived from apple waste can be grouped in different sets, attending to the activating reagent. Thus, those materials produced by simple one-pot activation with CO₂ or KOH display highly functionalized surface and specific surface area of 1000-2000 m² g⁻¹. which result in specific capacitances of 170-290 F g⁻¹ and superior electrical energy storage and power delivery.

Going one step further, integral valorisation of apple bagasse with zero waste appears an achievable goal with the help of the hydrothermal carbonization. This technology shows prospects for sustainable waste management while obtaining high added value-products. On the one hand, HTC of apple residues at 200 °C provides an aqueous extract with high polyphenolic content and antioxidant capacity, the major products being catechol (1,2-dihydroxybenzene) and HMF (5-hydroxymethyl-2-furfural). On the other hand, hydrothermal treatment offers a promising option for sequestration of carbon in the partially carbonized material obtained as solid by-product. The high energy efficiency of the HTC process and the successful use of the hydrochar as precursor of porous carbons constitutes additional advantages for a more profitable disposal of apple residues.

ASSOCIATED CONTENT

Supporting information

Composition of apple wastes used as raw materials. Comparison of the elemental composition of the materials from the as-received apple waste and from the residue kept in air for 8 days. TGA and DTA curves for the pyrolysis of apple pomace under N₂ at 20 °C min⁻¹. Isotherms of N₂ and CO₂ adsorption for carbon materials obtained from the fresh and fermented apple wastes. Profiles of the CO₂ and CO released in TPD experiments for the feedstock, hydrochar and the corresponding activated carbons. Relative presence of oxygen-surface functionalities in the activated carbons. Isotherms of N₂ and CO₂ adsorption for hydrochar and activated carbons derived from apple waste. Evolution of the specific capacitance with current density, Ragone type- plot and Nyquist plot for the carbons obtained by direct activation of apple waste with CO₂ and carbonization and subsequent steam activation at 750 °C.

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