# RECYCLING OF RESIDUES AS PRECURSORS OF CARBONS FOR SUPERCAPACITORS

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## Abstract

It is shown that industrial wastes such as apple pulp (generated in the cider production), cherry stones (from the industrial manufacture of Kirsh and jam) and PET (plastic vessels) can be recycled as activated carbons for electrode material in supercapacitors.
These precursors allow obtaining carbons with large specific surface areas (up to 1200 $m^2g^{-1}$) and average pore sizes around 0.9-1.3 nm, which makes them accessible to electrolyte ions. These features lead to electrical capacitances at low current density as high as 230 F $g^{-1}$ in 2M $H_2SO_4$ aqueous electrolyte and 120 F $g^{-1}$ in the aprotic medium 1M $(C_2H_5)_4NBF_4$ / acetonitrile. Furthermore, high performance is also achieved at high current densities, which means that the activated carbons derived from residues compete well with commercial carbons used at present in supercapacitors.

*Keywords: Apple Pulp Waste, Cherry Stones Residues, PET Waste, Activated Carbon, Supercapacitor*

## INTRODUCTION

The increasing demand for electrical systems that provide high power in short term pulses and display long cycle life has focused the efforts to the development of supercapacitors (SC) [1].

One type of SC corresponds to those referred to as electrochemical double layer capacitors (EDLC). Their performance is based on the charging and discharging of the electrical double-layer formed by electrostatic interactions at the interface between the charged surface of an electrode and the ions of a conducting electrolyte [1, 2].

From an industrial point of view, activated carbons are the best candidates for EDLC electrodes. They are relatively cheap and, depending on the origin and the treatment of the raw material, they allow a great flexibility for their structural and chemical properties.

The priority is actually focused on the development of low-cost carbons which do not represent an economic cornerstone for the large-scale implementation of SC systems [1, 2]. In this context, the utilization of waste materials for the manufacture of highly porous carbons is an interesting strategy.

This work presents the potentiality of residues such as apple pulp, cherry stones and PET as low-cost precursors of microporous carbons with promising properties for electrodes in both aqueous and organic supercapacitors.

## EXPERIMENTAL

A large variety of activated carbons have been produced from apple pulp, cherry stones and PET wastes. Their synthesis has been reported elsewhere. Basically, it was performed by steam activation of apple pulp [3], KOH activation of cherry stones [4] and basic solvolysis and subsequent carbonization of PET [5].

The porous structure of the carbons was analysed by $N_2$ adsorption at 77 K (*Micromeritics ASAP 2010*) and immersion calorimetry at 293 K (*Calvet-type calorimeter*).

The electrochemical performance of carbons was evaluated in two-electrode capacitors by galvanostatic charging-discharging cycles at current densities ranging from 1 to 100 mA $cm^{-2}$ and cyclic voltammetry experiments at scan rates between 2 and 50 mV $s^{-1}$ (potentiostat-galvanostat *Autolab-Ecochimie PGSTAT 30*). The electrolytes were aqueous solution 2M $H_2SO_4$ and 1M tetraethyl ammonium tetrafluoroborate in acetonitrile, $(C_2H_5)_4NBF_4/CH_3CN$. The cell voltage ranged from 0 to 0.8 V for aqueous medium and between 0 and 2 V for the organic electrolyte.

## RESULTS AND DISCUSSION

Table 1 shows that the activation of apple pulp, cherry stones and PET-wastes by different methods leads to materials which fit the textural characteristics for typical activated carbons [6]. It appears that the porosity of these materials consists mainly of micropores (width < 2 nm) with volumes $W_o$ in the range 0.30-0.67 $cm^3g^{-1}$ and average micropore widths $L_o$ between 0.66 and 1.39 nm. These features lead to microporous surface areas $S_{mi}$ from 553 to 1244 $m^2g^{-1}$. These carbons also contain a significant proportion of larger pores which lead to external (non-microporous) surfaces areas $S_e$ up to 107 $m^2g^{-1}$.

For comparison purposes, the table also includes two typical carbons of standard quality, SC-10 (*©ARKEMA-CECA*) and Super DLC-30 (©*NORIT*), used industrially for SC systems.

Table 1. Porosity characteristics of activated carbons derived from waste materials

| Precursor | $W_o$ ($cm^3/g$) | $L_o$ (nm) | $S_{mi}$ ($m^2/g$) | $S_e$ ($m^2/g$) | $S_{total}$ ($m^2/g$) |
|---|---|---|---|---|---|
| Apple pulp | 0.31-0.59 | 0.86-1.39 | 553-1068 | 2-107 | 589-1093 |
| Cherry stones | 0.47-0.67 | 0.90-1.29 | 949-1244 | 5-91 | 954-1292 |
| PET | 0.30-0.53 | 0.66-1.23 | 703-976 | 6-104 | 805-996 |
| Commercial carbons for SC | | | | | |
| SC-10 | 0.65 | 1.31 | 992 | 21 | 1013 |
| Super-DLC | 0.60 | 1.24 | 968 | 11 | 979 |

Regarding to the electrochemical performance, the comparison with data for carbons produced from different precursors and manufacture conditions indicates that the activated carbons derived from wastes follow the general trends observed for the specific capacitance in both aqueous ($H_2SO_4$) and aprotic ($(C_2H_5)_4NBF_4/CH_3CN$) electrolytes [7, 8].

As illustrated by Fig. 1, cherry stones based-carbons are capable of high limiting gravimetric capacitances (expressed per carbon mass of one electrode at 1 mA $cm^{-2}$), which range between 174 and 232 $Fg^{-1}$ in the acidic electrolyte. On the other hand, the specific capacitance of the materials produced from apple pulp varies from 109 to 187 F $g^{-1}$ whereas PET derived-carbons achieve 106-170 F $g^{-1}$.

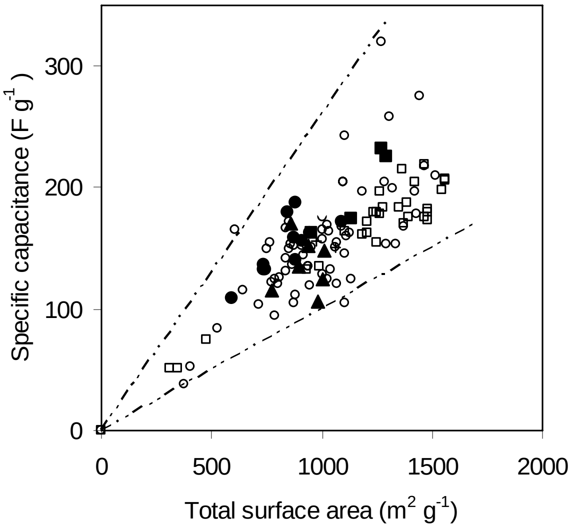


Figure 1. Variation of the specific capacitance at 1 mA $cm^{-2}$ in $H_2SO_4$ with the total surface area of activated carbons derived from apple pulp (●), cherry stones (■) and PET(▲ ) wastes. Other microporous (○) and mesoporous carbons (□) are included for comparison [7-10].

As pointed out earlier [9], these values depend on the specific surface extension of carbons (purely double layer capacitance) and on the certain functional surface complexes (containing mainly oxygen and nitrogen) which contribute in the form of quick redox-type reactions (pseudo-capacitance).

Since the contribution in the non-aqueous electrolyte does practically not depend on the carbon surface chemistry [10], the carbons achieve significantly lower limiting capacitances. In $(C_2H_5)_4NBF_4$/ $CH_3CN$, the limiting specific capacitance of the wastes derived-carbons ranges from 69 to 120 $Fg^{-1}$ (Fig. 2) and it compares favourably with typical activated carbons [7, 8, 10].

An analysis based on the so called Ragone plots relating power-density to achievable energy-density of capacitors (Fig. 3) allowed further evaluation to confirm the relevant potentiality of residues based-carbons in aqueous and organic media (The data corresponds to unit mass of carbon in the capacitor). It is suggested that capacitors built with carbons obtained by chemical activation of cherry stones are more advantageous for the release of the stored electric energy, compared with the two standards SC-10 and Super DLC-30. Carbon prepared at 800ºC provides about 4 Wh $kg^{-1}$ at 5500 W $kg^{-1}$ for 2 V-$(C_2H_5)4NBF_4/CH_3CN$ device, whereas it achieves power density around 1500 W $kg^{-1}$ at 1 Wh $kg^{-1}$ in the 0.8 V-$H_2SO_4$ system.

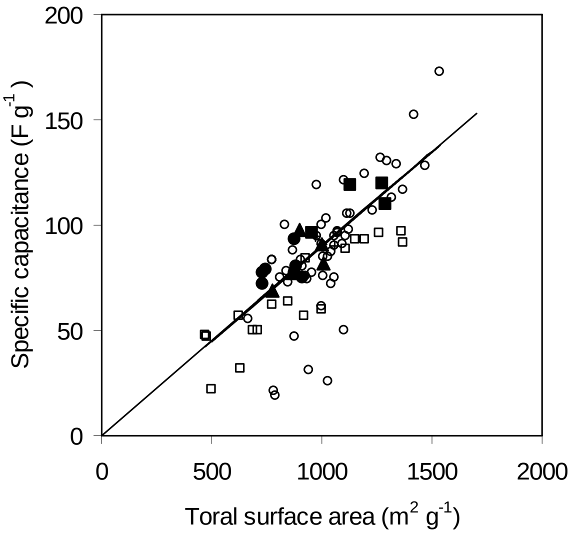


Figure 2. Variation of the specific capacitance at 1 mA cm-2 in $(C_2H_5)_4NBF_4/CH_3CN$ with the total surface area of activated carbons derived from apple pulp (●), cherry stones (■) and PET (▲) wastes. Other microporous (○) and mesoporous carbons (□) are included for comparison [7-10].

Fig. 3 also shows the excellent performance in both electrolytes of carbons prepared by basic solvolysis of PET wastes and subsequent carbonisation of the products. One observes a quite different behaviour for carbons prepared from apple pulp. Due to their relatively high surface area, the energy stored at low discharge rate compares with that of the commercial carbons but these materials are not a good option for high power applications in the aprotic electrolyte since the energy density drops with increasing power output (Fig. 3).

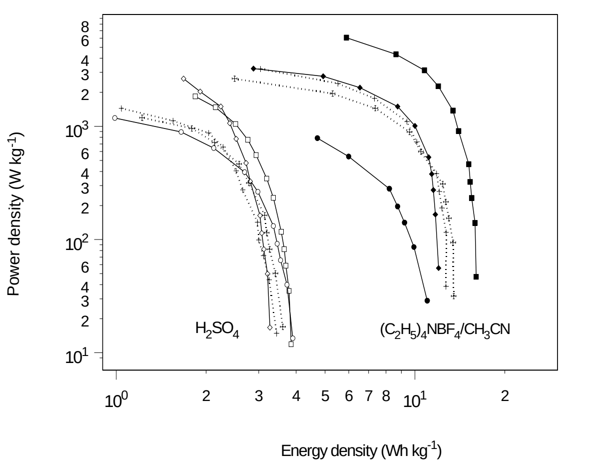


Figure 3. Power density *vs.* Energy density for carbons derived from apple pulp (○,●), cherry stones (□,■) and PET (Δ, ▲). Commercial activated carbons SC-10 (X) and Super DLC-30 (+) are included for comparison.
Open symbols for 2M $H_2SO_4$ aqueous solution.
Closed symbols for 1M $(C_2H_5)_4NBF_4/CH_3CN$ solution.

## CONCLUSIONS

The use of waste materials as precursors of porous carbons for electrode material in supercapacitors offers significant potentials for reducing the cost and the environmental damage resulting from uncontrolled disposal of these residues. This approach is interesting as far as it deals simultaneously with the problems of electrical energy storage and recycling.
The present study shows that the physico-chemical properties of activated carbons produced from industrial wastes such as apple pulp, cherry stones and PET compare with those observed for standard activated carbons. The systematic analysis of the performance of other porous carbons, investigated by the same experimental protocols, illustrates the potential of such residues as precursors of carbons for supercapacitors in both aqueous (2M $H_2SO_4$) and organic electrolytes (1M $(C_2H_5)_4NBF_4/CH_3CN$).

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