AGROBIOMASS-DERIVED ACTIVATED CARBONS AS POTENTIAL MATERIALS FOR SUPERCAPACITORS: WHEAT STRAW AND CORN STALK CASE STUDIES

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ABSTRACT: The main goal of AGROinLOG is the demonstration of Integrated Biomass Logistic Centres (IBLC) for food and non-food products, evaluating their technical, environmental and economic feasibility. The project is based on agro-industries, which are willing to deploy new business lines in their facilities, opening new markets in bio-commodities (energy, transport and manufacturing purposes) and intermediate bio-products (transport and biochemicals). More specifically, this work is focused on a fodder industry, whose main activity is related to the dehydration of wheat straw and corn stalk to produce animal bedding and feeding. The object of this study is the evaluation of two biomass-based materials (i.e. wheat straw and corn stalk) to determine the potential of these feedstock as raw materials for the synthesis of activated carbons (ACs) and their further application as supercapacitors.
Keywords: activated carbon, agricultural residues, straw, supercapacitor, wheat

1 INTRODUCTION

Carbon-based materials have attracted remarkable interest in the last years in terms of energetic applications due to their abundance, chemical and thermal stability, processability as well as their suitability to ad-hoc modifications of their textural and morphological properties required to fulfil a wide range of applications. In general, carbon-derived materials are prepared by carbonisation and activated afterwards. This carbonisation stage can be performed by different thermochemical processes, such as slow pyrolysis or hydrothermal treatment of the material, producing the so-called char or hydrochar, respectively. Further activation is required with the objective of developing high porosity and surface area of the material. This is a crucial stage due to its relevance to obtain high specific area and pore volume values, key parameters to provide electrochemical properties suitable for supercapacitors. Great variety of carbonisation and activation stages combinations can be found, both physical and chemical, using a wide range of temperatures and activating agents. These synthesis route conditions (mainly temperature and treatment time), so as the origin of the biomass feedstock, determine the final textural properties of the materials.

One of the most relevant application of activated carbon in terms of energy storage is their use as electrodes in supercapacitors, also called double-layer condensers, where the charge is accumulated in the electrode/electrolyte interface. Despite their lower specific energy, the supercapacitors present higher power in comparison with other energy storage systems. Among the different candidates as supercapacitors, ACs were researched exhaustively due to their possibilities to develop a microstructure, in addition to the good conductivity and excellent stability, high surface area, low cost and availability.

Capacitance values of AC-based supercapacitors are typically proportional to the surface area value. Moreover, these values can be increased due to the pseudo-capacitance effect, by the incorporation of heteroatoms, such oxygen and nitrogen. Nonetheless, an excessive activation might cause an increase of the pore volume, decreasing thus the volumetric energy density and the power. For this reason, it is necessary to develop accurately both the micropore microstructure of the AC and the surface chemistry to obtain high performance materials, without jeopardizing the gravimetric and volumetric capacitances.

Based on these facts, two types of biomass, wheat straw (WS) and corn stover (CS) were studied and evaluated as potential raw materials for the synthesis of activated carbons and their subsequent application as supercapacitors under the AGROinLOG scope.

2 EXPERIMENTAL METHODOLOGY

2.1 Synthesis of ACs

CS and WS were firstly subjected to a milling process in a Retsch blade mill, to reduce the particle size of the original material down to a ca. 100-300 µm, suitable for analysis and further use as AC precursors.
The resulting materials were carbonised by two different thermochemical processes: slow pyrolysis (Spy) and hydrothermal carbonization (HTC). SPy was performed at 550 °C (10 °C/min heating ramp; 30 min isotherm), allowing the total release of the volatile material contained in the biomass and obtaining a solid char. HTC was carried out at 200 °C for 24 h and the solid char was recovered by filtration and further dried in a vacuum stove at 60 °C for 24 h.

In this work, chars produced by either HTC or SPy were subjected to a physical activation process with CO2 at 800 °C in order to increase their porosity and to promote the micropore development. These experimental conditions were selected according to previous works studies in the literature [1, 2].

2.2 ACs characterisation techniques

The textural, structural, crystallographic, and morphological properties of ACs were analysed by several physicochemical characterization techniques:

- X-ray diffraction (Bruker D8 powder Advance Series 2)
- N_2 adsorption at 77 K and CO_2 adsorption at 273 K

(Micromeritics ASAP2020)
- Thermogravimetric analysis. (Thermobalance Libra F1 Netzsch)
- SEM microscopy (EDX Hitachi S-3400 N) with energy dispersive X-ray analysis (Röntec XFlash Si(Li))
- Elemental analysis (Thermo Flash 1112 Analyzer)

2.3 Electrochemical characterization

Electrochemical characterization was carried out in a three-electrode cell, with a 0.5 M H_2SO_4 electrolyte, using a thin film of the carbon material (loading of 1 mg·cm-2) on a glassy carbon electrode (7 mm diameter) and 15 wt% Nafion® as a binder.

Capacitance values were calculated by two different methods: (1) by cyclic voltammetry at 10 mV·s-1 integrating the area between 0.2 and 0.8 V vs. RHE and considering the average value between positive and negative scans; (2) by charge-discharge experiments at 0.1 mA and considering the average value between positive and negative current values from the slope of potential vs. time.

3 RESULTS

3.1 Synthesis of ACs

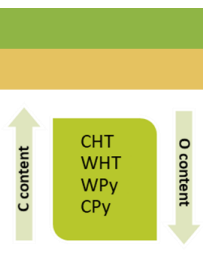
SPy yielded a char production between 27-29 wt.% for both biomasses, whereas HTC yielded between 42-48 wt%. In the meantime, CO_2 activation yielded between 36-40 wt.% for SPy and 61-65 wt.% for HTC. However, the overall yield showed no significant differences between biomasses, nor carbonisation processes, achieving values between 16-18 wt.%.

3.2 ACs characterisation

Previously to ACs characterisation, the raw biomasses were also characterised (results not shown in this work). Proximate analysis and ultimate analysis showed similar values to this kind of agricultural biomass types [3]. They had a high volatile material content and low ash content were observed in both corn and wheat samples. S content was very low and below analysis detection limit of the equipment.

Table I: Elemental analysis of activated carbons

Elemental analysis (wt %) of ACs					
Sample	C	H	N	S	O*
CPy	62.1	1.26	1.08	0.12	35.44
WPy	70.3	1.24	0.93	0.12	27.41
CHT	86.6	1.21	0.9	0.02	11.27
WHT	80.2	0.93	1.09	0.06	17.72
* calculated by difference					



As for the ACs, they were mainly composed by C and O, showing small amounts of N and S. As shown in Table I, C and O contents followed an opposite trend, (i.e. the higher the carbon content, the lower the oxygen content) and were in agreement with overall yields values.

According to X-ray diffraction results, crystalline structures of ACs were similar to this kind of materials, showing amorphous graphitic carbon-based structures [4].

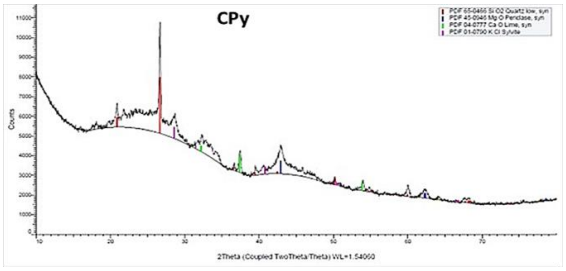


Figure 1: Example of XRD diffractogram (CPy sample)

Crystalline impurities present in the samples were also determined by this technique, such as SiO2, MgO, CaO and KCl and aluminum silicate oxide, associated to the inorganic content of the parent biomasses due to the uptake of minerals during their life cycles. HTC derived biomass had lower content of these inorganic species as compared to the SPy-derived ACs. The presence of water in HTC treatment may help dissolving these salts and hence they were not found in the final AC [5].

SEM microscopy was carried, supported by energy dispersive X-ray spectroscopy analysis (EDX), performed simultaneously in order to determine the presence of other elements, such as Na, Al, Si, or Cl, among others, confirming the presence of inorganic elements already detected by XRD:
- Mg, Al, Si, Ca and K: present in all samples
- Na and P: present in all samples, except for CHT
- Cl: present only in CPy and WPy

SEM micrographs at two different magnifications were provided (x500 and x2500), showing the size and morphology of the AC particles. As a general trend, the SEM micrographs are typical for this kind of materials and consist of irregular shaped particles with different morphologies. It is interesting noticing the presence of rounded particles for the case of the HTC derived AC; typically formed under certain conditions during the hydrothermal treatment.

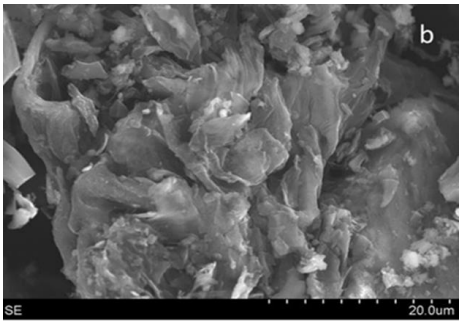


Figure 2: Example of SEM micrograph, 20µm scale (CPy sample)

Textural properties play a key role in the electrochemical properties of ACs. The BJH (Barrett-Joyner-Halenda) method was employed for N_2 isotherms and pore size distribution, whereas Dubinin-Radushkevich equation to CO_2 adsorption data was used for micropore size distribution.

Table II: Textural properties of ACs

Textural properties of the four biomass-derived ACs				
Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_{TOTAL} ($cm^3 \cdot g^{-1}$)	$V_{MESO,N2}$ ($cm^3 \cdot g^{-1}$)	$V_{MICRO,CO2}$ ($cm^3 \cdot g^{-1}$)
CPy	810	0.390	0.111	0.150
WPy	682	0.306	0.063	0.146
CHT	522	0.243	0.052	0.136
WHT	518	0.241	0.061	0.131

S_{BET} values, calculated applying the BET method to the N_2 isotherm, followed this order: CPy> WPy>CHT~WHT, which is the inverse order as that found for the C content (see Table I). The largest SBET values were obtained for the samples carbonized using the SPy method. Samples obtained from HTC method had lower SBET values, revealing that further studies should be conducted in order to fine tuning the CO_2 activation conditions (T and holding time). Total and micropore volumes followed the same trends as the BET surface area.

Finally, thermogravimetric analysis (TGA) was performed to study differences between the thermal resistance and the weight loss of the samples. Tests were carried out under air flow (10 °C/min) from room temperature up to 900 ºC.

Clear differences were observed between the samples carbonized using either HT or slow pyrolysis routes. SPy-derived samples showed lower thermal resistance and the weight loss started at ca. 375 °C, as compared to the HT derived samples (425-450 °C). Besides this, higher residual mass, associated to the inorganic content of the samples, was obtained for the HT derived samples, confirming the observation above mentioned from SEM characterization. In fact, the larger amount of inorganic content may also explain the differences in the starting burn-off temperature, since these inorganic species may catalyse the combustion of carbonaceous materials.

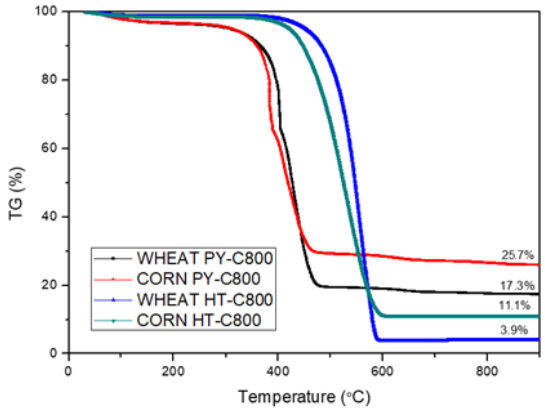


Figure 3: TGA profiles of AC samples

3.3 Electrochemical tests

Electrochemical test results can be found in Figure 1 and Table I. Cyclic voltammograms exhibit an almost rectangular shape with negligible contribution of pseudocapacitance processes, the difference between charge and discharge related capacitance being lower than 1.5 %.

Meanwhile, chrono-potentiometric experiments showed the typical triangular variation of potential with time, with a good linear correlation during the whole interval of measured potentials

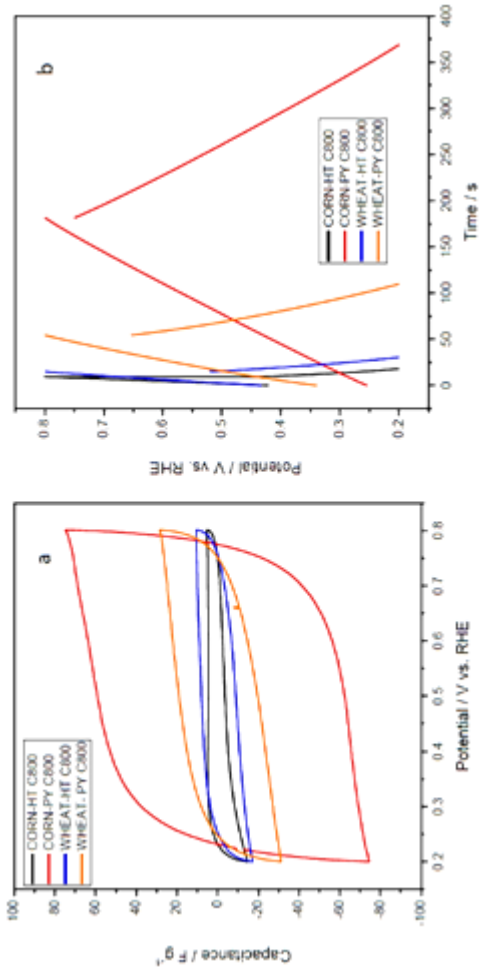


Figure 4: a) Cyclic voltammograms at 10 mV s^{-1}; b) Galvanostatic curves at 0.1 mA (~260 mA g^{-1}).

In both electrochemical tests, samples prepared by SPy showed the largest capacitance, being the corn biomass the one with highest values. Poor capacitance values were obtained through HTC carbonization process, for both biomass types. These differences could be related to the experimental conditions used for the synthesis of the HTC-based ACs. Particularly, an optimization of the conditions for the CO_2 activation stage could improve the textural properties of the ACs and, thus, the electrochemical properties.

The better results obtained for those samples prepared by SPy + CO_2 activation are clearly related to their more developed textural properties, lighting a clear relationship between the S_{BET} surface area and the capacitance value. Also the amount and distribution of meso- and micropores were relevant, although microporosity (ca. 0.52 nm) did not play a relevant role by itself since the amount of these micropores was inversely proportional to the capacitance behaviour. On the other hand, the amount of microporous centred at 0.83 nm and those found between 1 and 2 nm are directly related to the capacitance values.

Table III: Capacitance values of the biomass-derived ACs

Capacitance values of the four biomass-derived ACs		
Sample	Capacitance [F g^{-1}] (a)	Capacitance F g^{-1}] (b)
CPy	56.3	81.7
WPy	18.4	26.1
CHT	4.6	8.9
WHT	8.2	10.5

(a) Measured by cyclic voltammetry at 10 mV s^{-1} integrating the area between 0.2 and 0.8 V vs. RHE and considering the average value between positive and negative scans.
(b) Measured by charge-discharge experiments at 0.1 mA and considering the average value between positive and negative current values from the slope of potential vs. time.

Not only a high specific area is needed to achieve an AC with suitable supercapacitor performance. According to the literature, the pore size and pore geometry of the carbon materials are important factors, as the latter has a direct influence on the electric double layer [4]. Micropores (<2 nm) can increase the specific capacitance, when their size matches the size of electrolyte ions [5]. Mesopores plays also a paramount role in the supercapacitor behaviour since it is known to promote the electron diffusion and faster ion transportation [6]. Consequently, CPy samples showed best capacitance results since they presented an optimum combination of meso- and microporosity as compared to the other AC´s.

4 CONCLUSIONS

The results here presented clearly demonstrated the possibility of obtaining highly microporous materials form agro-waste biomass with very good electrochemical properties as supercapacitors. However, further research would be needed in order to optimize experimental conditions of ACs synthesis, especially for the CO_2 activation stage.

Best results at the conditions evaluated in this work were found for the Corn derived biomass prepared by slow pyrolysis and CO_2 activation at 800 °C, obtaining a maximum capacitance value of 81.7 F g^{-1}.

5 REFERENCES

[1] O. Ioannidou and A. Zabaniotou, "Agricultural residues as precursors for activated carbon production - A review," Renewable and Sustainable Energy Reviews, vol. 11, pp. 1966-2005, 2007.

[2] T. Zhang, W. W. P., L. T. Fan, M. Fan, D. Daugaard and R. C. Brown, "Preparation of activated carbon from forest and agricultural residues through CO2 activation," Chemical Engineering Journal, pp. 53-59, 2004.

[3] S. V. Vassilev, D. Baxter, L. K. Andersen y C. G. Vassileva, «An overview of the chemical composition of biomass» Fuel, vol. 89, nº 89, pp. 913-933, 2010.

[4] J. Han, J. H. Lee and K. C. Roh, "Herbaceous Biomass Waste-Derived Activated Carbons for Supercapacitors2," Journal of Electrochemical Science and Technology, 2(9), vol. 2, no. 9, pp. 157-162, 2018.

[5] M. T. Reza, J. G. Lynam, M. H. Uddin and C. J. Coronella, "Hydrothermal carbonization: Fate of inorganics," Biomass and Bioenergy, vol. 49, pp. 86-94, 2013.

[6] R. Heimböckel, F. Hoffmann and M. d. Fröba, "Insights into the influence of the pore size and surface area of activated carbons on the energy storage of electric double layer capacitors with a new potentially universally applicable capacitor model," Physical chemistry Chemical Physics, vol. 21, pp. 3122-3133, 2019.

[7] Y. Lu, S. Zhang, C. Yin, J. Bai, Y. Zhang, Y. Li and Y. Ma, "Mesoporous activated carbon materials with ultrahigh mesopore volume and effective specific surface area for high performance supercapacitors," Carbon, vol. 124, pp. 64-71, 2017.

6 ACKNOWLEDGEMENTS

This publication is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727961.

The work was performed in the framework of the European project AGROinLOG (Grant Agreement No 727961) "Demonstration of innovative integrated biomass logistics centres for the Agro-industry sector in Europe". in collaboration with Instituto de Carboquímica (Spanish National Research Council). www.agroinlog-h2020.eu.

The experimental results are part of the confidential deliverable (*D3.4 - Report on validation of produced blend pellets in combustion facilities and for production of bio-commodities*) and are subject of Intellectual Property with all rights reserved by AGROinLOG project.

7 LOGO SPACE