**Sustainable coffee based CO₂ adsorbents: towards a greener
production via hydrothermal carbonization**

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Abstract

Activated carbons for adsorption of CO₂ under flue gas conditions were prepared by means of hydrothermal carbonization (HTC) and subsequent CO₂ activation of spent coffee grounds. The HTC of the samples consisted of their heating at moderate temperature with a high water content in autoclave. A preliminary screening concluded that 1:2 biomass/water ratio (spent coffee grounds as received) and no chemicals addition during HTC with further activation in CO₂ at 800 °C for 1 h are suitable conditions for the production of the CO₂ adsorbents. In addition, the Response Surface Methodology (RSM) successfully evaluated the combined effect of HTC temperature and dwell time, in order to maximize the CO₂ capture capacity within the experimental region. Both the lowest temperature and dwell time (120 °C,

3 h) resulted in the maximum CO₂ capture capacity (2.95 wt.%). Two activated carbons (ACs) were then produced: one via hydrothermal carbonization optimized by means of RSM followed by CO₂ activation (HC-Co) and the other one by single step CO₂ activation as described in the Group's patent ES2526259 (AC-Co). Analysis of the features and performances of the two ACs revealed superior chemical and textural characteristics on HC-Co for CO₂ adsorption under post-combustion capture conditions; HTC process is the sole responsible of this enhancement. Moreover, the proposed methodology for the production of CO₂ adsorbents from spent coffee grounds represents a more energy-efficient approach.

Keywords: coffee grounds, hydrothermal carbonization, activated carbon, Response Surface Methodology, post-combustion CO₂ capture.

1 Introduction

Adsorption is one of the separation technologies that are being considered for CO₂ capture applications [1]. Carbon adsorbents with a low carbon footprint can be produced at a low cost from renewable and globally available sources (e.g., biomass from agricultural residues or food industry by-products) through relatively simple heat treatment processes [2]. The primary difference between the terms biochar and hydrochar lies in the application. Biochar is typically produced as a solid by-product in a dry carbonization process like pyrolysis and used for soil amendment and, more recently, carbon sequestration [3]; hydrochar is produced as slurry (a two-phase mixture of solid and liquid) via hydrothermal carbonization (HTC) for further thermochemical conversion (e.g., to a biofuel) [4-9].

Hydrothermal Carbonization (HTC) has been appointed as an attractive process due to its simplicity, low-cost and CO₂ efficiency; it can also be classified as ``green`` since it does not involve organic solvents, catalysts or surfactants [7]. By combining moderate temperature and pressure, HTC is generally performed with water acting as solvent, reactant and even catalyst or catalyst precursor and hence does not require active drying of feedstock [10]. Biomass can be hydrothermally treated in a range of conditions: sub and supercritical conditions according to

the critical temperature (374 °C) and pressure (22 MPa) of water [11]. Usually pressure is not controlled and the autogenic process is built up with the saturation vapor pressure of water (subcritical-water) at the reaction temperature [12]. During HTC, the carbohydrate components from biomass are broken up and dissolved in water, following a complex cascade of aldol-reactions, cycloadditions and condensations, to obtain a carbon rich solid product. This process is energetically favorable when compared to traditional pyrolysis, because it uses milder conditions, does not need previous drying of the precursors and is exothermic; in fact, the heat released by HTC reactions contributes to 1/3 of the energy needs to complete the process [13].

In addition, the high conversion efficiency, elimination of pre-drying requirement, and relatively low operating temperature make HTC a particularly suitable conversion technique for the production of hydrochar from wet biomass feedstock [14-17].

For a given feedstock, the main variables influencing the process, the product distribution and the properties of the hydrochar produced are temperature, pressure, dwell time and ratio biomass/water, as well as the eventual addition of chemicals to the reaction media [18]. It has been found that the temperature has the strongest influence on the process

[18-23] whereas the dwell time has been identified as less important on HTC, especially if long dwell times are used. However, it is worth mentioning that the effect of the dwell time on HTC is subjected to significant variation depending on the raw material and on the values set for the other variables (such as temperature). In this way, different authors report an upward or downward evolution of the HTC solid yield, or even an absence of effect, depending on the experimental conditions [18].

HTC has recently been proposed as a versatile way to produce carbon precursors of activated carbons with tunable surface chemistry and porosity [24-28]. Other studies [13,29] have also reported that hydrochars have good self-binding properties, which is very interesting for their subsequent conformation. Since the application of an adsorbent for a given adsorption process is so highly dependent not only on its porosity but also on its surface chemistry [30,31], the possibility of controlling the process to tailor the final product would be of particular interest [13].

In our group, the development of microporous carbon adsorbents with potential use as CO₂ adsorbents has been a main research topic for many years. The use of spent coffee grounds (lignocellulosic residue with a high moisture content) as raw biomass precursor to produce suitable

adsorbents, either through chemical or physical activation was one of our challenging projects [1,32] since coffee grounds constitute a very abundant residue from the food industry. These studies finally resulted in the issue of a patent (patent number ES2526259). Patent ES2526259 discloses an environmentally benign and low cost methodology to produce CO₂ adsorbents from spent coffee grounds.

The characteristics of the spent coffee grounds and the potential shown by the coffee derived carbons to adsorb CO₂ pave the way to explore alternative routes to produce coffee based carbon adsorbents. Therefore, the present study focuses on assessing the effectiveness of HTC of spent coffee grounds to develop promising activated carbons (ACs) for CO₂ adsorption operating under flue gas conditions.

Firstly, HTC process variables were optimized following the Design of Experiments/Response Surface Methodology (DoE/RSM) approach: the effect of main variables of HTC (temperature, dwell time) on the CO₂ adsorption capacity of the produced activated carbons, under flue gas conditions, was evaluated. To produce a carbon adsorbent, hydrochars were activated using CO₂ as reactive gas. RSM is a particularly useful strategy for investigating interactions between variables, which would be hard to verify by a classical 'one variable at a time' approach. This methodology involves the design of experiments and multiple regression

analysis as tools to assess the effects of two or more independent variables on dependent variables [33]. Recently, a number of works have been published on the application of RSM to matters related with the CO₂ adsorption process performance [34,35], but only a small number of works are devoted to the production of CO₂ adsorbents [36].

Recent studies dealing with spent coffee grounds [37-41] use HTC for the extraction of different compounds such as polysaccharides, proteins, phenolic compounds and minerals, among others, that can be of value for application in food, cosmetic, and pharmaceutical areas [42]. Nevertheless, to the best of authors' knowledge, HTC of spent coffee grounds has not been previously investigated for the production of precursors of activated carbons. To assess the potential of the hydrothermal carbonization and subsequent CO₂ activation for the production of spent coffee based CO₂ adsorbents, the performance of a carbon produced under optimized HTC conditions is compared to a carbon produced by means of the patent's procedure mentioned above (patent ES2526259).

2 Materials and methods

2.1 Precursor material

The biomass used as starting material were solid coffee residues recovered from spent Nespresso® capsules. It is

important to note that the raw material is employed as received, with its intrinsic humidity (67 wt.%).

2.2 Preliminary testing

Before applying the Response Surface Methodology (RSM), screening tests were performed in order to adjust the number of independent variables involved in the process and thus simplify the design of the experiments. In this way, maintaining the HTC temperature and the HTC dwell time constant (180 °C, 12 h), two variables were preliminary evaluated in the hydrothermal carbonization process: biomass/water ratio (b/w) and the addition of chemicals to the reaction media (See Fig. 1). Moreover, in order to tailor the development of microporosity in the hydrochars during subsequent CO₂ activation, the preliminary experiments also involved the testing of both activation temperature (700 and 800 °C) and activation holding time (1 and 4 h), as can be seen in Fig. 1.

184 2.2.1 Biomass/water ratio

185 The influence of biomass/water mass ratio (b/w) was
186 assessed considering two scenarios: with and without water
187 addition, 1:2 and 1:5 ratios, respectively.

188 HTC was performed in a stainless steel autoclave (Parr,
189 United States). A known amount of spent coffee grounds
190 (10.0 ± 0.1 g) was introduced in a 45 cm³ teflon vessel
191 (unstirred) and, depending on the targeted biomass/water
192 ratio, no water was added in the case of 1:2 b/w ratio and
193 10 cm³ of distilled water were mixed with raw biomass for
194 the 1:5 b/w ratio case. Then, the teflon vessel was sealed,
195 placed into the autoclave and heated up inside an air oven
196 to the selected temperature (180 °C), during the chosen
197 processing time (12 h). Carbonization takes place under
198 self-generated pressure with the vapor pressure of water at
199 the corresponding reaction temperature. Once the reaction
200 time was reached the autoclave was cooled down to room
201 temperature inside the air oven. The hydrochars produced were
202 then rinsed by adding 100 cm³ of distilled water (to remove
203 as much of the aqueous products as possible), recovered by
204 filtration (in order to remove residual moisture), and
205 finally dried at 100 °C overnight. The hydrochars were
206 denoted HC12 and HC15, where HC stands for hydrothermal
207 carbonization, whereas 12 and 15 correspond to the

biomass/water ratio; for instance, HC12 represents an HC made from spent coffee grounds with 1:2 biomass/water ratio.

2.2.2 Addition of chemicals to the reaction media

It can be expected that oxidative surface modification of raw lignocellulosic biomass with an oxidizing agent may result in enhanced formation of oxygen functional groups (OFGs), thereby leading to improved activation [43]. In our case, $(10.0 \pm 0.1 \text{ g})$ of hydrogen peroxide (H_2O_2 , 30 wt.%) were added to $(10.0 \pm 0.1 \text{ g})$ of spent coffee grounds and subjected to hydrothermal treatment in the same equipment and conditions described in Section 0. The hydrochar produced was denoted HCP where HC represents hydrothermal carbonization, and P indicates the addition of hydrogen peroxide.

2.2.3 Activation procedure

The hydrochars produced, which present a fine particle size, were conformed into pellets with a diameter of 4 mm and a height of 3 mm using a single stamping tablet machine. No binder was added during the pelletization process [1]. The pellet shaped coffee hydrochars were physically activated in a single stage [44,32], with a stream of $50 \text{ cm}^3 \text{ min}^{-1}$ of CO_2 at different temperatures (700 and 800 °C) and different holding times (1 and 4 h), using a Setaram TGA 92 thermogravimetric analyzer. The heating rate used to reach

the temperature set point was 5 °C min⁻¹. This methodology has been previously validated in our group [36].

2.3 CO₂ capture capacity: gravimetric tests

CO₂ capture capacities of the pellet shaped coffee based activated carbons were estimated in conditions representative of post-combustion capture (50 °C and low partial pressure of CO₂) by means of a thermogravimetric analyzer TGA/DSC1 STARe System from Mettler Toledo following the procedure described elsewhere [45]. The CO₂ capture capacity experiments were performed as shown in Fig. 2: after an initial conditioning step at 100 °C and subsequent cooling down to 50 °C in N₂ flow, the sample is exposed to a mixture of 10% CO₂, balance N₂.

We have confirmed that the total mass uptake, here represented by q_{CO_2} (see in Fig. 2), corresponds to the CO₂ adsorption capacity as determined from the adsorption isotherm of CO₂ at 50 °C and 10 kPa.

2.4 Study of hydrothermal carbonization treatment using the Response Surface Methodology

Once the variables to be included in the design of experiments were defined by the preliminary screening tests, the Response Surface Methodology (RSM) was applied to evaluate the combined effect of the temperature (T) and dwell time (t) during the HTC treatment on the CO₂ capture capacity

of the activated carbons. The objective of the study was to determine the optimum values of HTC temperature and dwell time that would maximize the CO₂ capture capacity of the resultant activated carbons under flue gas conditions (50 °C, 10 kPa). The levels of the independent variables, T and t, determine the operating conditions at which the experiments must be carried out.

In this work, a three-level full factorial design was chosen that involved 13 experiments, which are shown in Table 1, including nine factorial points and four additional replicas at the center of the design by means of which it was possible to estimate the experimental error associated. All the experiments were performed in random order.

The levels of the independent variables, HTC temperature and dwell time, were coded so that variables with different units or of different orders of magnitude could be compared independently of their units. Codification of the levels of the variables consisted in transforming each studied real value into coordinates inside a scale with dimensionless values, which are proportional to their location in the experimental space. In Table 1 the coded values of the independent variables are shown in the first two columns. It has to be born in mind that hydrochars were submitted to subsequent CO₂ activation at 800 °C-1 h prior

to CO₂ adsorption measurements. The experimental values obtained for the response variable, CO₂ capture capacity at 50 °C and 10 kPa, are presented in Table 2.

The mathematical-statistical treatment of the experimental data by fitting a polynomial function and the evaluation of the fitness of the model by analysis of variance (ANOVA) were carried out by following the procedures explained elsewhere [36].

Response surface and contour plots were generated using the software SigmaPlot 13.0. In this way, it was possible to obtain the optimum values for each studied independent variable that would maximize the response in the experimental region studied.

2.5 Preparation of spent coffee grounds ACs

In order to accomplish the second part of the study, two activated carbons from spent coffee grounds were prepared according to our patent's procedure (AC-Co) and to the optimized HTC conditions as defined by the RSM study (HC-Co).

Sample denoted AC-Co was produced by means of CO₂ activation in a single stage. An amount of 40.0 ± 0.1 g of spent coffee grounds conformed in pellets were loaded in a quartz reactor (I.D. 3.8 cm) and activated in a CO₂ flow rate of 370 cm³ min⁻¹. The heating rate used was 5 °C min⁻¹ and the

temperature of activation and holding time were set at 700 °C-
8 h. Prior to activation the residue was air-dried at 100 °C
for 4 h to remove excess water.

Sample denoted HC-Co was prepared in two stages.
Firstly, a known amount of spent coffee grounds
(10.0 ± 0.1 g) was subjected to HTC treatment under the
optimized conditions defined by the RSM study. Then, 2.4 g
of hydrochar conformed into pellets was loaded in a quartz
reactor (I.D. 2.1 cm) and subjected to activation in CO₂ with
a flow rate of 100 cm³ min⁻¹. The heating rate used was
5 °C·min⁻¹ and the temperature of activation and holding time
were set at 800 °C-1 h.

2.5.1 Characterization of the ACs

2.5.1.1 Chemical analysis

The prepared activated carbons were subjected to
proximate and ultimate analyses in order to determine the
chemical composition. Proximate analysis was conducted in a
Setaram TAG24 thermogravimetric analyzer [46] according to
the UNE 32-004-84 standard. The carbon, hydrogen, and
nitrogen contents were determined in a LECO CHNS-932 analyzer
and the oxygen content in a LECO VTF-900 analyzer.

2.5.1.2 Pore structure characteristics

The porosity of the activated carbons was fully
characterized by means of physical adsorption of N₂ at

-196 °C, in a Micromeritics ASAP 2010, and adsorption of CO₂ at 0 °C, in a Micromeritics TriStar 3000. The samples were outgassed at 100 °C under vacuum overnight prior to adsorption measurements. The use of both adsorbates, N₂ and CO₂, provides complementary information about the porous texture of the samples: the adsorption of CO₂ at 0 °C and up to 1 bar is restricted to pores narrower than 1 nm, whereas N₂ adsorption at -196 °C covers wider pore sizes but presents diffusion limitations in the narrower pores. A summary of the employed methodology for textural characterization is included in Table 3.

3 Results and discussion

3.1 Preliminary testing

The CO₂ capture capacity (50 °C, 10 kPa) of the activated carbons prepared in the thermobalance was determined in a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer, as described previously in Section 0.

Firstly, a series of activated carbons were prepared by activation of hydrochar HC15 following the procedure described in Section 2.2.3, at two different temperatures (700 and 800 °C) with a holding time of 1 h. As can be seen in Fig. 3a, the CO₂ capture capacity experiments an increase of 23.89 % only due to the raise in the temperature of activation from 700 to 800 °C; this suggests a greater

development of microporosity at 800 °C that leads to enhanced adsorption capacities. In view of these results, a second series of activated carbons were prepared by activation of hydrochar HC12 at the optimum temperature (800 °C) but selecting two different holding times, 1 and 4 hours. Fig. 3b shows the comparison of the HTC activated carbons derived from HC12 and HC15 after CO₂ activation at 800 °C-1h. It can be observed that the HC12 derived carbon adsorbs 12 % more CO₂ than the HC15 derived sample.

Nevertheless, the holding time raise from 1 to 4 hours barely affects the CO₂ capture capacity of the prepared HTC carbons as can be observed in Fig. 4. Thus, it is concluded that water addition to the process and hence the increase in biomass/water ratio, hinders the development of microporosity and diminishes the CO₂ capture capacity of the derived carbons; on the other hand, activation time barely contributes to the proposed target being the temperature the key parameter of the activation of HTC carbons.

Jain et al. reported the use of hydrogen peroxide in the hydrothermal treatment of coconut shells [43] as a good reactant to increase the number of oxygen functional groups and hence enhance its subsequent activation. Thus, a final activation at 800 °C and 1 h was performed departing from HCP to assess the effect of chemicals addition during HTC on

the CO₂ adsorption performance. Notwithstanding the addition of an oxidant agent to the HTC treatment of spent coffee grounds, it resulted in an important decrease on the CO₂ capture capacity (64.71 %) with respect to sample HC12 activated at 800 °C and 1 h which showed the better adsorption behavior (Fig. a).

During the hydrothermal carbonization process, solubilization of the organics occurs in addition to the formation of tarry substances that could hinder the pores [47]. Consequently, we can observe in Fig. b that HCP derived carbon shows significantly slower kinetics of CO₂ adsorption.

In summary, this preliminary screening of multiple variables associated to HTC and CO₂ activation concludes that the following conditions are suitable for the production of CO₂ adsorbents from spent coffee grounds: 1:2 biomass/water ratio (spent coffee grounds as received) and no chemicals addition for HTC and further activation in CO₂ at 800 °C-1 h.

3.2 Optimization of Hydrothermal Carbonization by means of the Response Surface Methodology

3.2.1 Preparation of hydrochars

In order to accomplish the 13 experiments involved in the three-level full factorial design, the spent coffee grounds (10.0 ± 0.1 g) were subjected to hydrothermal

treatments in the set-up described in Section 0., under the temperature and dwell time conditions as specified in Table 1 of Section 2.4. The produced hydrochars were subsequently activated in CO₂ at 800 °C for 1 h. After filtration and oven drying, the hydrochars appearance varied from a brown wood like lignocellulosic sample to a black coal like material, this effect being more pronounced with increasing dwell time and/or temperature [22,48].

Moreover, it was observed that as dwell time or temperature increased, the separation between the hydrochar and the liquid phase became better defined. Benavente et al. [14] explained that, under more severe conditions, the solid becomes more hydrophobic. The breakdown of the hydroxyl groups on the cell walls of the biomass jointly with the hydrolysis of the hemicellulose and cellulose to monosaccharides increase with both temperature and dwell time. Consequently, the reduction in hydrophilic character of the solid allows physical dewatering to occur easier and, as a result, the moisture content of the hydrochars decreases.

The severity of the HTC treatment can be evaluated by means of the severity factor, which expresses the combined effect of the temperature and dwell time into a single reaction ordinate. This factor is also called index R_0 [9,37]. Long dwell times and high temperatures increase the

severity factor of the HTC process and thereby contribute to the decomposition of the extracts and formation of undesired byproducts [37]. The severity index is calculated as follows (Eq. 1):

$$R_0 = t \times \exp\left(\frac{T - 100}{14.75}\right) \quad (1)$$

where t is the dwell time in hours and T is the temperature in °C. The values of R_0 are usually reported in logarithmic scale.

Table 4 summarizes the logarithmic values of R_0 calculated for all the conditions evaluated for the HTC experiments. As expected, the combined effect of increased temperature and dwell time results in the highest severity. It is however important to note that the severity index at a set temperature barely changes when dwell time is raised from 3 to 12 h. On the other hand, for the same dwell time an increase in temperature from 120 to 240 °C can involve an increase of this index up to 331%. In view of these results, a preliminary conclusion could be drawn about the little influence of dwell time in the HTC process.

It is expected that the more severe the conditions of reaction the lower the solid yield values. In this sense, hydrochar yields (HY) were determined according to the expression:

$$HY = \frac{w_{hydrochar}}{w_{bio}} \times 100 \quad (2)$$

where w_{bio} and $w_{hydrochar}$ denote, respectively, the initial weight of moist biomass and the mass of hydrochar after filtering and oven drying.

Fig. shows the hydrochar yields for each experiment carried out. As expected, it is observed that for a given dwell time, hydrochar yield decreases with increasing temperature. However, solid yield variation with dwell time for a set temperature is less pronounced. This is particularly relevant at 240 °C where the hydrochar yields are nearly coincident for all dwell times studied. At higher temperatures or dwell times the sugars from the degradation of hemicellulose and cellulose into water soluble monomers are further degraded, resulting in lower recovery of mass of solid product [14,48].

Hence, it can be concluded that in the range of operating conditions investigated, the effect of the process temperature seems predominant [18–23] whereas the influence of dwell time on HTC process is less important especially if long dwell times are considered [18]. Nevertheless, both variables will be further assessed by means of the RSM study to evaluate their effect on the CO₂ capture capacity.

3.2.2 Response Surface Methodology

469

470 shows the results of fitting the experimental data by
471 multiple regression analysis. The ANOVA test showed that the
472 model for CO₂ capture capacity under post-combustion capture
473 conditions was statistically significant at a 95% confidence
474 level (p-value<0.05), whereas its lack-of-fit was found to
475 be statistically non-significant at a 95% confidence level
476 (p-value>0.05).

477 also shows which of the terms in the model were
478 statistically significant at a 95% confidence level (p-
479 value<0.05), i.e. T and T², and those that were not
480 statistically significant (p-value>0.05) were eliminated
481 from the model. The Adj-R² and the AAD values were found to
482 be acceptable, 0.684 and 4.49%, respectively.

483 Once the non-significant terms were eliminated, the
484 coded coefficient values were decoded in order to obtain the
485 polynomial model for the response variable as a function of
486 the significant independent variables. The model obtained is
487 shown in Eq. 3 as follows:

$$CO_2 \text{ uptake from flue gas (wt.\%)} = 5.6626 - 0.3136T + 0.0007T^2 \quad (3)$$

488 Fig. presents the response surface plot and the contour
489 plot for the CO₂ capture capacity under flue gas conditions
490 (50 °C and 10 kPa CO₂) as a function of the independent

variables studied, hydrothermal carbonization temperature and dwell time, for all the hydrochar derived activated carbons.

For the HC12 activated materials (Fig.) the dwell time had no effect on CO₂ uptake, whereas a maximum response was obtained in relation to the temperature of the HTC. The CO₂ uptakes within the experimental region under study only changed within a very narrow range causing the non-significant effect of the dwell time. In Fig. b it can be observed that the CO₂ capture capacity under flue gas conditions practically remains constant in the 180-240 °C range whilst it increases as the temperature decreases down to 120 °C (2.95 wt.%). Therefore, in the experimental region studied, the dwell time does not influence the CO₂ capture capacity of the produced hydrochar activated samples, while the temperature is the dominant parameter. Furthermore, RSM analysis corroborates previous observations during the preliminary testing and confirms that there is not a combined effect dwell time-HTC temperature on the CO₂ uptake of the hydrochar derived activated samples. Given that the dwell time did not show a significant effect on the response, the optimum HTC conditions that produce the greatest CO₂ uptake under flue gas conditions are 120 °C-3 h, reaching a maximum value of 2.95 wt.%.

Additional experiments were carried out *a posteriori* as result of the analysis of the response surface plot in Fig. a. From the plot one might think that optimum conditions of HTC correspond to a local maximum constrained by the range of experimental conditions evaluated and that CO₂ adsorption could be enhanced at lower temperatures. Funke et al. [5] explained that preliminary reactions can be initiated at 100 °C although substantial hydrolysis starts at temperature of about 180 °C. With the purpose of verifying the suitability of the temperature range evaluated, two additional experiments were carried out at 80 and 100 °C and the lowest dwell time (3h).

Table 6 reports similar CO₂ uptakes for both experiments (approximately 2.75 wt.%), lower than that for the optimum conditions (2.95 wt.%). Thus, these results confirm the suitability of the temperature range selected on the basis of extensive literature review [5,38-40,42,49] and point out that the optimum conditions obtained from the analysis by RSM correspond to a global maximum.

3.3 Production and characterization of ACs from spent coffee grounds

The AC produced by hydrothermal carbonization under the optimum conditions determined by the RSM, HC-Co, and the sample produced following the patent's procedure, AC-Co,

were fully characterized in order to assess and compare their performances for CO₂ adsorption under flue gas conditions.

3.3.1 Solid yield values

Despite that hydrochar derived activated carbon HC-Co is produced in two stages whilst activated carbon AC-Co is the result of an activation in a single stage, the solid yield values determined for both ACs and reported in Table 7 indicate that the production of HC-Co is more advantageous in terms of adsorbent production per unit of raw biomass.

Activation in a single stage results in a higher mass loss and so a lower solid yield value for carbon AC-Co.

3.3.2 *Proximate and ultimate analyses*

Analysis results of carbons HC-Co and AC-Co are summarized in Table 8. As expected, sample HC-Co shows higher moisture content. Likewise, HTC derived carbon experiments an enrichment in the carbon content of 7.3% with respect to AC-Co.

Nevertheless, the oxygen and hydrogen contents of HC-Co are approximately half those of AC-Co due to the exothermic nature of HTC that lowers both the oxygen and hydrogen content of the feed by mainly dehydration and decarboxylation [5].

3.3.3 *Pore structure characteristics*

The N₂ adsorption isotherms at -196 °C of the carbons are shown in Fig. a. Both activated carbons presented type I adsorption isotherms, characteristic of microporous materials. It is important to note that HC-Co shows the largest N₂ uptake, arising from a higher microporosity development that in the case of AC-Co (see apparent BET surface area and pore volumes obtained from N₂ adsorption data for these samples in

Table 9) .

Both isotherms show a pronounced elbow at very low relative pressures characteristic of narrow microporosity that limit the volume of N₂ adsorbed. It is worth noting that sample AC-Co shows an isotherm with a much sharper elbow than HC-Co suggesting that its pore size distribution (PSD) is much narrower. Therefore, HTC treatment tends to promote the development of larger pores during subsequent activation than single step CO₂ activation. This conclusion is in good agreement with the QSDFT-PSD (Fig. b), where it is clearly seen that the sample with the narrowest PSD is AC-Co, whilst sample HC-Co presents larger contribution of wider pores.

As a result, the incorporation of HTC treatment prior to activation leads to higher BET apparent surface area and higher total pore volume (see

586 Table 9) .

587 The CO₂ adsorption isotherms of the samples at 0 °C are
588 represented in Fig. a. Comparison of the volumes adsorbed of
589 both adsorbates, N₂ and CO₂, gives an indication of the
590 micropore ratio on each sample: CO₂ adsorption at 0 °C
591 evaluates the microporosity of less than 1 nm whereas micro
592 and mesopores are assessed from N₂ adsorption at -196 °C.

593 Table 9 also includes the narrow micropore volume
594 calculated from the CO₂ isotherms by applying the DR
595 equation.

596 Both activated carbons show similar narrow PSD (Fig. b)
597 but again HC-Co displays the largest volume of narrow
598 micropores. These results follow the same trend observed in
599 N₂ adsorption (see

Table 9) .

In summary, a combination of a large amount of ultramicropores that enhance the adsorption of CO₂ at low partial pressures and a significant amount of wider micropores that can enable a rapid mass transport of CO₂, make HC-Co an ideal adsorbent for the envisioned application: CO₂ capture from flue gas.

3.4 Adsorption studies

In order to perform a preliminary test of their adsorption behavior, the CO₂ capture capacities of samples AC-Co and HC-Co were assessed in conditions representative of post-combustion capture (50 °C and 10 kPa partial pressure of CO₂) following the protocol described in Section 0. The estimated CO₂ uptakes are presented in Table 10. HC-Co shows superior performance than AC-Co and an enhancement in adsorption capacity of 10 %.

To evaluate the kinetics of adsorption, the rate of dynamic mass uptake of the samples from the gas mixture was represented vs time, taking as reference mass that of the sample at the end of the conditioning step in N₂ at 50 °C (see Fig.).

Both activated carbons present two stages well defined that can be attributed firstly to the wider pores (above 0.7 nm onwards) and secondly to the narrower microporosity

below 0.7 nm where adsorption potential for the carbon dioxide molecule is higher due to the overlapping effect of the opposite walls of the micropores [31].

Fitting the second stage of each sample to a linear equation and assuming the slope as the rate of adsorption of CO₂ in ultramicropores (below 0.7 nm), we can conclude that HC-Co shows enhanced kinetics, increasing the rate of adsorption in 56 % with respect to AC-Co (See Table 11).

The wider PSD of HC-Co may account for the enhanced kinetics given that it favors the mobility of carbon dioxide towards the narrower microporosity.

4 Conclusions

High-performance post-combustion CO₂ capture adsorbents have been developed by hydrothermal carbonization and CO₂ activation from spent coffee grounds. Preliminary testing showed that the CO₂ capture capacity decreased with the addition of both water and hydrogen peroxide in the HTC treatment.

Response surface methodology determined the HTC temperature as the most influential parameter on the process, while no effect of the dwell time was detected. The maximum value of CO₂ capture capacity at 50 °C and a CO₂ partial pressure of 10 kPa, 2.95 wt.%, was attained at both the lowest temperature and dwell time (120 °C, 3 h).

Analysis of the features of the two ACs produced revealed that HC-Co (HTC followed by CO₂ activation) shows superior performance for CO₂ adsorption under post-combustion capture conditions than AC-Co (single step CO₂ activation, patent ES2526259), which can only be attributed to the HTC process.

The present work concludes that hydrothermal carbonization with subsequent CO₂ activation is a promising route to produce activated carbons from spent coffee grounds, reducing to at least half the time required to produce a CO₂ adsorbent compared with our patent's procedure. Moreover, raw biomass can be used as received without drying pretreatment. All the aforementioned will contribute to big savings in the production costs.

Acknowledgments: This work was carried out with financial support from the Gobierno del Principado de Asturias (PCTI-GRUPIN14-079). N.Q. acknowledges a fellowship from the Gobierno del Principado de Asturias (Programa Severo Ochoa).

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909

910 **Table 1.** Levels of the independent variables, i.e., HTC
 911 temperature (T) and dwell time (t), in the three-level full
 912 factorial design.

	x ₁	x ₂		
	coded	coded	x ₁	x ₂
Run	T	t	T (°C)	t (h)
1	-1	-1	120	3.0
2	-1	0	120	7.5
3	-1	1	120	12.0
4	0	-1	180	3.0
5	0	0	180	7.5
6	0	1	180	12.0
7	1	-1	240	3.0
8	1	0	240	7.5
9	1	1	240	12.0
10	0	0	180	7.5
11	0	0	180	7.5
12	0	0	180	7.5
13	0	0	180	7.5

913

914 **Table 2.** Experimental values of CO₂ capture capacity for all
915 the activated carbons using the three-level full factorial
916 design.

Run	CO ₂ capture capacity (wt. %)
1	3.01
2	2.79
3	2.97
4	2.20
5	2.58
6	2.00
7	2.52
8	2.20
9	2.32
10	2.57
11	2.30
12	2.34
13	2.36

917

918 **Table 3.** Textural characterization performed from physical
919 adsorption of N₂ at -196 °C and of CO₂ at 0 °C

Physical adsorption of N ₂ at -196 °C				
Total pore volume	V _p	Amount of N ₂ adsorbed at a relative pressure of 0.99		
Surface area	BET	Brunauer-Emmett-Teller equation [50]		
Micropore volume	W ₀	Dubinin-Radushkevich (DR)		
Micropore surface area	S _{DR}	equation assuming a density of the adsorbed phase of 0.808 cm ³ g ⁻¹ and a cross sectional area of 0.162 nm ² [51]		
Average micropore width	L ₀	Stoeckli-Ballerini equation [52]		
Pore size distribution	PSD	Quenched Solid State Functional Theory (QSDFT) assuming slit pore model.		
Physical adsorption of CO ₂ at 0 °C				
Micropore volume	W ₀	Dubinin-Radushkevich (DR)		
Micropore surface area	S _{DR}	equation assuming a density of the adsorbed phase of 1.023 cm ³ g ⁻¹ and a cross sectional area of 0.187 nm ² [51]		
Average micropore width	L ₀	Stoeckli-Ballerini equation [52]		
Pore size distribution	PSD	Non-local Density Functional Theory (NLDFE) assuming a slit pore model.		

921 **Table 4.** Severity index calculated for all the conditions
 922 evaluated in the three-level full factorial experimental
 923 design.

x_1	x_2	Severity factor
T (°C)	t (h)	R_0 (log)
120	3.0	1.07
120	7.5	1.46
120	12.0	1.67
180	3.0	2.83
180	7.5	3.23
180	12.0	3.43
240	3.0	4.60
240	7.5	5.00
240	12.0	5.20

924

Table 5. Results of multiple regression analysis and ANOVA used to fit the polynomial model to the CO₂ capture capacity experimental data

	Coded coefficient	Sum of squares	DF ⁽³⁾	p-Value
Intersection	2.359	32.270	1	0.000
T	-0.309	0.571	1	0.002
t	0.048	0.014	1	0.499
Tt	0.047	0.009	1	0.586
T ²	0.237	0.156	1	0.047
t ²	0.065	0.012	1	0.528
Model		0.827	5	0.017
Residual		0.187	7	
Total		1.015	12	
Lack of fit		0.075	3	0.518
Pure error		0.112	4	
R ²	0.815			
Adj-R ² ⁽¹⁾	0.684			
AAD (%) ⁽²⁾	4.49			

⁽¹⁾ Coefficient of determination adjusted by the number of variables; ⁽²⁾ Absolute average deviation; ⁽³⁾ Degrees of freedom

932 **Table 6.** Experimental values of CO₂ capture capacity under
 933 flue gas conditions for the hydrochars prepared at 80 and
 934 100 °C

T (°C)	CO ₂ capture capacity (wt. %)
80	2.76
100	2.75

935

936 **Table 7.** Solid yield values (%) of the activated carbons HC-
 937 Co and AC-Co

Sample	Solid yield value (%)
HC-Co	26.1
AC-Co	21.3

938

939 **Table 8.** Chemical analysis of the samples.

Sample	Proximate Analysis (wt.%)		Ultimate Analysis (wt.%, daf ¹)			
	Ash	Humidity	C	H	N	O
HC-Co	7.5	13.3	88.9	0.7	4.0	6.4
AC-Co	7.1	5.7	82.4	1.4	4.1	12.1

940 ¹ dry ash free basis.

941

942 **Table 9.** Textural parameters of the samples obtained from
 943 the N₂ and CO₂ adsorption isotherms.

Sample	N ₂ Adsorption (-196 °C)						CO ₂ Adsorption (0 °C)			
	V _p ¹	S _{BET} ²	W ₀ ¹	E ₀ ³	L ₀ ⁴	S _{mi} ²	W ₀ ¹	E ₀ ³	L ₀ ⁴	S _{mi} ²
HC-Co	0.34	801	0.30	27.97	0.65	934	0.29	31.43	0.54	1078
AC-Co	0.23	534	0.21	28.62	0.63	658	0.23	32.09	0.52	866

944 ¹ V, W [=] cm³·g⁻¹; ² S [=] m²·g⁻¹; ³ E₀ [=] kJ·mol⁻¹; ⁴ L₀ [=]

945 nm.

946

947 **Table 10.** Experimental values of CO₂ capture capacity for
 948 the activated carbons prepared from spent coffee grounds.

Sample	CO ₂ capture capacity (wt. %)
HC-Co	3.01
AC-Co	2.71

949

950 **Table 11.** Experimental values of the rate of CO₂ adsorption
 951 for the activated carbons prepared

Sample	Slope (mmol g ⁻¹ s ⁻²)
HC-Co	4.01E-04
AC-Co	2.57E-04

952

953

954

955 **Fig. 1.** Scheme of the preliminary testing to fit the number
 956 of independent variables involved in the HTC process and
 957 optimize the development of microporosity in the hydrochar
 958 derived activated carbons.

959

961 **Fig. 2.** Total mass uptake vs. time (full experiment). Scheme
 962 of the different stages performed during the CO₂ capture
 963 capacity experiment.

964 **Fig. 3.** CO₂ mass uptake (wt.%) under a gas stream composed
 965 of 90% N₂ and 10% CO₂ at 50 °C. Effect of: (a) activation
 966 temperature and (b) biomass/water ratio during HTC.

Fig. 4. CO₂ mass uptake (wt.%) under a gas stream composed of 90% N₂ and 10% CO₂ at 50 °C. Effect of holding time on activation.

Fig. 5. CO₂ mass uptake (wt.%) under a gas stream of 90% N₂ and 10% CO₂ at 50 °C, corresponding to the addition of H₂O₂ to the HTC process (a) uptake values and (b) kinetic performance.

Fig. 6. Hydrochar yield (wt.%) at different HTC temperatures (120, 180 and 240 °C) and dwell times (3, 7.5 and 12 h).

Fig. 7. Response surface and contour plots for CO₂ capture capacity under flue gas conditions of the hydrochar derived activated carbons as a function of the HTC temperature and dwell time.

(a)

(b)

982 **Fig. 8.** (a) N₂ adsorption isotherms at -196 °C and (b) N₂
983 adsorption QSDFT PSD of ACs.

(a)

(b)

984 **Fig. 9.** (a) CO₂ adsorption isotherms at 0 °C and (b) CO₂
985 adsorption NLDFT PSD of ACs.

986 **Fig. 10.** Rate of CO₂ uptake of activated carbons HC-Co and
 987 AC-Co.

988