Valorisation of spent coffee grounds as CO₂ adsorbents for postcombustion capture applications

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Abstract

In this work spent coffee grounds from single-use capsules were used as the starting material for producing low-cost activated carbons. The activation conditions were selected and optimised to produce microporous carbons with high CO₂ adsorption capacity and selectivity, thus with potential to be used as adsorbents in postcombustion CO₂ capture applications. Two activation methods are compared: physical activation with CO₂ and chemical activation with KOH. The first method is considered less contaminant; however, leads to carbons with lower textural development and thus lower CO₂ adsorption capacity than those obtained by activation with KOH. On the other hand, multicomponent adsorption cyclic experiments pointed out that the CO₂/N₂ selectivity of physically activated carbons is higher than that of chemically activated carbons.

Keywords: CO₂ capture; activated carbon; coffee residues

1. Introduction

Global emissions of carbon dioxide, considered to be the main contributor of global warming, increased by 45% between 1990 and 2010. Consumption of coal and natural gas (responsible for about 40% and 20% of total CO₂ emissions, respectively) both grew in 2010 by 7% and cement production emissions (contributing 4% to the total) by

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11%. Increased energy efficiency, nuclear energy and the growing contribution of renewable energy are not compensating for the globally increasing demand for power and transport. This illustrates the large and joint effort still required for mitigating climate change [1]. IEA analysis suggests that Carbon Capture and Storage (CCS) will play a vital role in worldwide, least-cost efforts to limit global warming, contributing around one-fifth of required emissions reductions in 2050 [2]. Although lower energy penalties can be expected from applying carbon capture (CC) to an integrated gasification combined cycle [3], this technology still seems a risky option to mitigate CO₂ emissions of coal fired power plants due to the cost associated to the integrated gasification combined cycle (IGCC) technology [4]. The main attractive of postcombustion CO₂ capture is that it can be used for retrofitting existing facilities [5-7]. The CO₂ present in the flue gas produced at these sources can be separated for ulterior transport and storage by a number of techniques: absorption, adsorption, separation with membranes, cryogenic distillation, *etc.* [5, 8, 9]. Absorption with aqueous solutions of alkanolamines is a mature technology that has been extensively used in the sweetening of natural gas, and therefore is the natural extension for postcombustion applications, where CO₂ is present at low partial pressures. However, the high energy penalty associated to the regeneration of the solvent (steam consumption accounts for over 50 % of the overall operating costs [10]) has driven much research effort in the search of less energy-intensive alternatives.

Adsorption, also a mature technology used industrially for the separation of air and the purification of H₂ among other applications [11, 12], has been proposed as a candidate to reduce the cost associated to postcombustion CO₂ capture [13-16]. Many adsorbents have been studied for CCS applications: zeolites, activated carbons, calcium oxides, hydrotalcites, MOFs, *etc.* [14, 17-22]. The high pore volume and tailoring properties

makes MOF promising adsorbents for gas separation applications yet they are not mature. Zeolite 13X is a mature adsorbent that presents high CO₂ adsorption capacity and selectivity, but requires relatively high energy for regeneration and its CO₂ adsorption capacity is highly sensitive to moisture [23] which represents an important drawback for post-combustion applications. The heat of adsorption of CO₂ over an activated carbon is *ca.* 20 kJ/mol [24] which is almost half of zeolite 13 X [25] and nearly a quarter of Mg-MOF-74 [26]. Activated carbons present a series of advantages that makes them appealing adsorbents for postcombustion applications: low cost, stability under moisture conditions, and ease of regeneration [12, 16, 27-29].

The production of low-cost activated carbon from biomass residues either by physical or chemical activation is a well-established technology [30-32]. Physical activation is commonly carried out in a two-step process: first a carbonaceous precursor is carbonised in inert atmosphere and subsequently the resulting char is partially gasified with carbon dioxide, steam or air. Usually carbonisation temperature ranges between 673-1123 K, and activation temperature between 873 and 1173 K. Chemical activation makes use of dehydrating agents or oxidants (the most common being KOH, NaOH, K₂CO₃, H₃PO₄, and ZnCl₂), and can be carried out in a single step process at lower temperatures than physical activation. However, the use of chemical products is less desirable in an environmentally friendly scenario.

The consumption of easy-to-use single-cup serving coffee capsules has become very popular in the last few years, driving an increasing public concern about the disposal of the used capsules. Nestlé has addressed the subject by providing dedicated capsule collecting points (over 7000 in 15 countries by the end of 2010) with the final aim of recycling the aluminium [33]. Waste coffee is separated from the aluminium container and used together with other organic residues to form compost. Although the recovery

of the aluminium used to produce the capsules is the most crucial part of this recycling process, the spent coffee grounds might have applications with greater added value than compost production. Of course, spent capsules are not the solely source of coffee grounds. Approximately 20% of the global production of green coffee beans (6.6 million tons in 2001/02) are used for instant coffee production [34]. For each kg of soluble coffee produced, near 0.91 kg of coffee grounds are obtained [35]. Coffee grounds can be considered pollutant due to its high carbon content, which will consume a high amount of oxygen to degrade. Even more, by simply pilling them up, they can ferment and/or combust spontaneously, so they cannot be disposed without being previously treated [35]. Coffee grounds are usually used as fuel in the boilers of the soluble coffee industry, as they present a heat value similar to that of coal [35, 36]. However, it would be highly desirable to find alternative sustainable uses of this abundant residue from the food industry. Apart from burning and compost production, coffee grounds can be used for soil remediation, activated carbon production [37-41] or biodiesel production [42]. In the case of the exploitation of coffee grounds for biodiesel production, the resulting solid waste could still be used for the production of activated carbon [43]. Microwave heat treatment in air has been proposed as an energy-saving method for producing low surface area carbonaceous materials that might be useful for basic dye removal [39]. The production of activated carbon from coffee waste by chemical activation with carbonates for later use in industries of environmental engineering or foodstuff is patented [44]. Activated carbons from coffee grounds have also been obtained by chemical activation with phosphoric acid [37], mixtures of phosphoric acid and zinc chloride [41], and potassium hydroxide [38]. In the present work two different methods are studied for the production of low-cost carbon adsorbents from spent coffee grounds: chemical activation with KOH and

physical activation with CO₂. The properties of the final carbons depend on the preparation conditions: activating agent, temperature, and length of the treatment. Focus was made in developing the narrow microporosity as this has proven to be the key factor in maximizing CO₂ adsorption capacity in postcombustion conditions [45]. The texture of the carbons was characterised by physical adsorption, and their CO₂ adsorption capacity in pure CO₂ flow was evaluated between 298 and 373 K by means of a thermogravimetric analyser. Moreover, adsorption/desorption cycles in pure CO₂ and N₂, and also in diluted CO₂/N₂ and CO₂/He streams were carried out to prove the high selectivity, stability and ease of regeneration of these materials.

2. Materials and methods

Spent Nespresso[®] coffee grounds (from now on referred to as N) were used as the starting material for the development of activated carbons through two different methods: physical activation with CO₂ and chemical activation with KOH. Prior to any treatment, the spent coffee grounds were disposed in large trays and dried in an air forced convection oven at 373 K for 4 h. The proximate and ultimate analyses are shown in Table 1. Table 2 summarises the experimental conditions of the activation processes carried out. To compare the different activation methods, the carbon yield was calculated and referred to the mass of dry coffee grounds (Table 3).

2.1 Activation with KOH

Prior to carry out the activation with KOH, a batch of 20 g of spent coffee grounds were carbonised in a ceramic reactor (i.d. 27 mm) inside a horizontal tube furnace (Carbolite) at 673 K under nitrogen flow (50 cm³ min⁻¹) to reduce the volatile matter content of the starting material. To carry out the activation, 1 g of this low-temperature char (NCL)

was placed forming a fine film over a ceramic tray, and covered with a layer of solid KOH. The mixture was then heated at 5 K min^{-1} up to 673 K under $300\text{ cm}^3\text{ min}^{-1}$ of nitrogen flow in a GSM type furnace from Carbolite. This temperature was held for 1 h to allow KOH to melt, dehydrate and mix intimately with the coffee char [46].

Activation was completed by heating the mixture up to 873 K under $300\text{ cm}^3\text{ min}^{-1}$ of nitrogen flow, and holding this temperature for 1 h. After cooling down in nitrogen flow, the samples were thoroughly washed with distilled water until neutral pH was attained, and dried at 383 K for 24 h in a forced-air convection oven. Several weight ratios KOH/char were used: 1, 2, 3 and 4. The chemically activated samples were denoted as NCLKy, where y accounts for the KOH/char ratio used. It was also intended to activate the coffee grounds in a single stage, departing directly from the coffee grounds (N) instead of the low-temperature carbonised product (NCL), but the obtained carbon yields were excessively low (results not shown). The effect of activation temperature was also assessed at a fixed KOH/char ratio of 3. Only the results for the sample obtained at 973 K are presented (NCLK3b), due to the low carbon yield obtained at 1073 K .

2.2 Activation with CO_2

Prior to carry out the activation with CO_2 , a batch of 20 g of spent coffee grounds were carbonised in a ceramic reactor (i.d. 27 mm) inside a horizontal tube furnace at 873 K under nitrogen flow ($50\text{ cm}^3\text{ min}^{-1}$). This temperature is sufficient to produce a high quality charcoal with reduced volatile matter content (see Figure 1 and Table 1). The resulting char (NCH) was then activated at 973 K using a carbon dioxide flow of $10\text{ cm}^3\text{ min}^{-1}$ in batches of around 3 g in a double jacket quartz reactor (i.d. 20 mm) inside a vertical tube furnace up to three different burn-off degrees (defined as the g lost during activation per 100 g of initial char): 29, 36 and 41%. The samples will be

referred to as: NCHA29, NCHA36 and NCHA41, respectively. The activation conditions were selected according to the results of a non-isothermal reactivity test carried out in a thermogravimetric analyser under CO₂ flow, and the research group experience [47-49]. Higher burn-off degrees were avoided to prevent the widening of the micropores. These activation conditions (low CO₂ flowrate and moderate temperature and burn-off) promote homogeneous gasification throughout the whole porous structure and the desired texture development in the micropore domain.

2.4 Characterisation

The density of the samples was measured through helium picnometry at 308 K in an Accupyc 1330 from Micromeritics. The acid/basic character of the obtained carbons was assessed by measuring the pH of carbon suspensions in equilibrium with distilled water under inert atmosphere: the average pH for the suspensions with 10-18 wt.% solid is taken as the pH_{PZC} [50]. The morphology of the samples was studied by Scanning Electron Microscopy (SEM) using a FEI QuantaTM 650 FEG. The scarce inorganic matter found in the backscattered electron images was analysed by Energy Dispersive X-ray microanalysis (EDX).

The porous texture of the samples was characterised by physical adsorption of N₂ and CO₂ at 77 and 273 K, respectively, in a TriStar 3000 apparatus from Micromeritics. Prior to adsorption measurements, the samples were evacuated overnight at 373 K. CO₂ adsorption at 273 K allows the assessment of narrow microporosity (below 1 nm) whereas N₂ adsorption at 77 K covers wider porosity. The micropore volume was determined making use of the Dubinin-Radushkevich (DR) equation assuming an affinity coefficient of 0.34 for N₂ and 0.36 for CO₂ [51]. The average micropore width (L) was calculated through the Stoeckli-Ballerini equation [52]. The total pore volume

(V_p) was calculated from the amount of N_2 adsorbed at a relative pressure of 0.99, and the BET surface area from the Brunauer-Emmett-Teller equation [53].

2.5 CO₂ adsorption measurements

The CO₂ adsorption capacity of the materials at 298 K and atmospheric pressure was assessed by means of a thermobalance TGA92, from Setaram, in pure CO₂ flow [54]. Prior to the adsorption measurements the samples were dried in 50 cm³ min⁻¹ of Ar flow at 373 K for 1 h, and then allowed to cool down to 298 K. The CO₂ adsorption capacity is assessed from the mass gain experienced by the sample when the gas is switched from Ar to CO₂, and is expressed in terms of mmol of CO₂ adsorbed per g of dry carbon. To assess the effect of temperature upon the CO₂ capture performance, the furnace temperature was raised at 0.5 K min⁻¹ up to 373 K under CO₂ flow once the adsorption equilibrium was attained at 298 K.

The cyclic behaviour of selected adsorbents was evaluated in a thermogravimetric analyser TGA/DSC1 STAR[®] System from Mettler Toledo. After an initial conditioning step carried out in 100 cm³ min⁻¹ of helium at 373 K for 1 h, the samples were subjected to adsorption and desorption cycles at a constant temperature of 323 K and at atmospheric pressure. Adsorption/desorption cycles were carried out by switching automatically the feed gas between helium and the desired adsorbate each 30 min. Four different feed compositions were studied: 100% CO₂, 100% N₂, 10% CO₂ in He and 10% CO₂ in N₂. Due to the use of mixtures (multicomponent adsorption) the mass uptake is expressed as percentage. For each cycle, the initial mass (by the end of the previous desorption step in helium) was taken as reference; thus the value presented here refers to the working capacity of the adsorbent in the evaluated conditions.

3. Results and Discussion

Figure 1 represents the pyrolysis of the starting coffee grounds under N₂ flow at a heating rate of 15 K min⁻¹. Adsorbed water is released at near 400 K. The greater mass loss takes place between 500 and 800 K, corresponding to the decomposition of volatiles present in the biomass. In this temperature range two maxima can be differentiated: the first at near 600 K, due to the decomposition of hemicellulose, with an elbow *ca.* 630 K attributed to cellulose, and the second at near 680 K due to the decomposition of lignin, which will be the main contributor to the final mass of the char [55]. The small and progressive mass loss above 800 K is due to the char consolidation. Oxygen rich feedstocks, with high hemicellulose and cellulose content, such as the present case, are expected to lead to carbons with a predominantly microporous structure [56, 57], which is highly desirable for the adsorption of carbon dioxide. The starting Nespresso[®] coffee grounds present very low ash content (see Table 1), thus showing an adequate precursor for developing activated carbons. The volatile matter content is above 80 wt%, which is typical for lignocellulosic materials commonly used in the preparation of activated carbons [32, 47, 48]. The spent coffee grounds present a mild acidic surface, related with its elevated oxygen content. The elemental analysis is in good agreement with published values for coffee grounds from different origins [35, 39]. The EDX microanalysis of the ash showed variable amounts of Ca, Al, K, Si, and P and lesser amounts of Mg, Fe and Na.

Carbonisation increases the carbon content of the samples, due to the decomposition of hemicellulose, cellulose and lignin, rich in oxygen and hydrogen. Increasing carbonisation temperature from 673 to 873 K decreases the carbon yield from 29 to 23%, due to further primary decomposition of the biomass volatiles (mainly lignin in this temperature range) and through the secondary decomposition and stabilisation of the char [32]. The carbonised coffee grounds present a basic surface with a nitrogen

content of near 5 wt.%, which are *a priori* suitable properties for the adsorption of CO₂ [47, 48, 58-60].

The SEM images of the samples are shown in Figure 2. The release of volatiles leads to a progressively less dense morphology, accompanied by a reduction in particle size. In the images it can be appreciated that physical activation preserves the morphology of the starting char whereas chemical activation causes substantial particle shrinkage. This effect has also been observed in the SEM images from other KOH biomass-based activated carbons [61]. Backscattered electron images showed scarce mineral matter in all the studied samples, and the EDX analysis showed no higher potassium concentration for sample NCLK3.

The carbon yield, helium density and pH_{PZC} of the materials are summarised in Table 3. The carbon yield of the chemically activated samples increased with the ratio KOH/char used at 873 K, but decreased by increasing the temperature for a ratio KOH/char of 3. The carbon yield of physical activation decrease with the burn off attained; that is, with the length of the treatment. For the burn off degrees considered, up to 41%, the yield of physical activation is similar or slightly above that of the chemical activation.

Activation increases the density of the carbons due to the preferential elimination of the disorganised carbon that blocks the entrance of the internal porosity of the chars, and also to the break of bonds and the removal of cross-links and carbon atoms which facilitate the atomic rearrangement and thus the densification of the material.

Densification is favoured with increasing temperature, as can be seen from comparison between samples NCLK3 and NCLK3b. For a given temperature, 973 K, chemical activation leads to denser carbons (NCLK3b) than physical activation (NCHA series). This could be a consequence of the greater particle shrinkage produced by chemical activation. From Table 3 it can also be seen that activation with CO₂ increases slightly

the basicity of the carbon surface, leading to basic carbons, whereas samples treated with KOH are only slightly basic, with near neutral pH_{PZC} . The increase in pH observed for sample NCHA29 compared to that of char NCH can be attributed to the fact that the activation temperature is 100 K above that of carbonisation. The pH increase with burn off is probably due to formation of basic oxygen surface complexes during the activation process [62]. The lower pH observed for NCLK series compared to NCH and NCL might be attributed to the formation of acidic oxygen groups (R-COOH and R-OH) during KOH activation [46].

Figures 3 and 4 show the adsorption isotherms of N_2 and CO_2 at 77 and 273 K, respectively. The shape of the N_2 adsorption isotherms and the nearly absence of hysteresis loops point out that all the carbons are essentially microporous. This is highly desirable, as the micropore volume is intrinsically related to the CO_2 adsorption capacity at atmospheric pressure [45]. NCL char present almost negligible N_2 adsorption due to diffusion limitations at this temperature; however its incipient microporosity results accessible to CO_2 at 273 K. Char NCH, obtained at higher temperature, presents already accessible porosity to the N_2 molecule at 77 K. The samples activated with CO_2 (NCHA series) present an intermediate texture development between the NCH char and the samples activated with KOH (NCLK series), as can be seen from the amount adsorbed of N_2 and CO_2 . CO_2 gasifies the carbon, removing first the most reactive carbon deposits formed during carbonisation and then developing the microporosity of the initial char, NCH. The porosity formed upon KOH activation is believed to be due to the intercalation of potassium compounds in the carbon matrix that causes the separation and deformation of the lamellae [63]. These compounds are removed during the washing step leading to permanent porosity. Carbon can also be consumed in this process by potassium reduction and through gasification with evolved

gases [64]. Table 4 summarises the textural parameters obtained from the analysis of the previously presented adsorption isotherms. It can be observed that the micropore volume (V_{DR}) is in general very close to the total pore volume (V_p); moreover, most of the developed porosity falls in the narrow microporosity domain (with the exception of sample NCLK3b). The average micropore widths calculated from the N_2 adsorption isotherm (L_{DR}) are close to 1 nm (with the exception of samples NCH and NCLK3b). As expected, the pore size widens with the burn off degree for physical activation (NCHA series). No significant differences were observed in the pore volume or pore size by changing the KOH/Char ratio at 873 K. However, an increase in temperature during KOH activation from 873 to 973 K leads to higher BET surface area and total pore volume, formed by wider porosity (see the broader knee of the N_2 adsorption isotherm of sample NCLK3b in Figure 3 and the linear shape of its CO_2 adsorption isotherm in Figure 4). This effect has been previously described [65]. Although higher BET surface areas have been reported for activated carbons obtained from coffee grounds activated with KOH at 1073 K [38], this work focuses on the development of the narrow microporosity to maximise CO_2 adsorption. The BET surface areas of the chemically activated samples presented in this work ($831\text{--}1082\text{ m}^2\text{g}^{-1}$) can be favourably compared to activated carbons produced from coffee grounds by chemical activation with H_3PO_4 [37] and mixtures of $ZnCl_2$ and H_3PO_4 [41]. The narrow micropore volume (W_0), and narrow micropore width (L_0) assessed from the CO_2 adsorption isotherms at 273 K by the DR method are also presented in Table 4. Both values are higher for the chemically activated samples, with the exception of NCLK3b, which presents a lower volume of narrow micropores, probably due to the collapse of pore walls at the higher temperature that leads to wider pores.

Table 5 summarises the CO₂ adsorption capacity of the samples at 273 and 298 K in pure CO₂ at atmospheric pressure. A commercial peat-based steam-activated carbon used for CO₂ adsorption, R2030CO2 from Norit, has also been included for reference purposes. The carbons obtained from Nespresso[®] coffee grounds present CO₂ adsorption capacities up to 4.8 mmol g⁻¹ at 273 K, and 3.0 mmol g⁻¹ at 298 K, which are above that of the reference carbon. Samples activated with KOH present the largest CO₂ adsorption capacities, followed by the samples activated with CO₂ that are in the order of the reference carbon (slightly higher at 298 K). The chars present lower adsorption capacities due to their poor textural development. Note that although NCLK3b is the sample with the greatest adsorption capacity at 273 K, this does not hold at 298 K. As temperature increases (and so the kinetic energy of the gas molecules) only the narrower pores are useful for the adsorption of CO₂.

Figure 5 shows the results from the non-isothermal capture tests carried out in the thermogravimetric analyser: when temperature is raised slowly from 298 to 373 K in CO₂ flow, the amount of CO₂ that remains adsorbed on the different samples falls from 2-3 mmol g⁻¹ to a value close to 0.6 mmol g⁻¹ due to the exothermic nature of the physisorption process. Note that the amount of CO₂ adsorbed on series NCHA seems to be less sensitive to the slow heating than that of series NCLK. This implies that the adsorbent-adsorbate interactions are stronger for the samples activated with CO₂. This can be attributed to their narrower porosity and their greater surface basicity.

Sample NCLK3 was subjected to cyclic adsorption/desorption experiments at 323 K and atmospheric pressure. These conditions can be considered representative of a postcombustion capture process. The corresponding results are summarised in Figure 6: note that the first adsorption step (cycle 0) departs from a different initial state (after the conditioning step at 373 K) and so differs from the following cycles. A cyclic steady

state is progressively reached, in which the mass uptake during the adsorption step equals that released during the desorption step. As expected, the mass uptake is maximum when the sample is exposed to pure CO₂ flow, reaching a steady value of 7.3 wt.% (equivalent to 1.66 mmol CO₂ g⁻¹) from cycle 3 onwards. The mass uptake when the sample is exposed to pure N₂ flow is substantially smaller: 0.9 wt.% (or 0.3 mmol N₂ g⁻¹). The ratio of the adsorption capacities of the pure components at atmospheric pressure is usually taken as a rough estimation of selectivity. The resulting CO₂/N₂ value for NCLK3 is 5 (molar basis). However, in the flue gas the CO₂ represents ordinarily between 3 and 15 % by volume, being the main diluent N₂. Therefore, to assess the adsorption behaviour in a flow with reduced partial pressure of CO₂, more representative of the postcombustion conditions, two different cyclic experiments were carried out: the first with a feed gas consisting in 10% CO₂ in helium, and the second with 10% CO₂ in nitrogen. Obviously, in both cases the mass uptake experienced by the sample is well below that undergone in pure CO₂ flow due to the reduction in the partial pressure. When the diluting gas is helium (considered inert) the mass uptake (1.9 wt.%) is slightly below that experienced under nitrogen dilution (2.4 wt.%). This indicates that N₂ is coadsorbed with CO₂. Assuming that the amount of CO₂ adsorbed is independent of the nature of the diluting gas (only function of the partial pressure of CO₂), the amount of N₂ coadsorbed can be estimated by difference. A more adequate estimation of selectivity is that given by the separation factor, defined as the ratio of the molar fractions in the adsorbed phase to that of the gas phase [27, 66]. The resulting CO₂/N₂ selectivity for sample NCLK3 is 13 at cyclic steady state (cycles 3-5).

The same protocol was followed for sample NCHA29 (see Figure 7). Note that although the working capacity in pure CO₂ is smaller compared to that of NCLK3 (6.6 vs.

7.3 wt.%), the difference seems to diminish at lower partial pressure of CO₂ (1.8 vs. 1.9 wt.% for CO₂ diluted in helium and 2.2 vs. 2.4 wt.% when the diluting agent used is nitrogen). The calculated CO₂/N₂ selectivity of NCHA29 is higher than that of NCLK3: 6 vs. 5 if the data from pure component adsorption are used directly, and 18 vs. 13 using the proper definition of the separation factor and the data from the experiments with 10% CO₂. The higher CO₂/N₂ selectivity of NCHA29 compared to that of NCLK3 can be attributed to the narrower microporosity and/or the more basic character of the physically activated samples. These results, together with the environmental constraints associated to chemical activation, and the higher carbon yield of physical activation for low burn off degrees, encourages the use of physical activation for the production of CO₂ adsorbents from coffee wastes.

Future work will involve testing the materials in a fixed-bed adsorption unit to further study the multicomponent adsorption equilibrium and kinetics. Cyclic performance under different regeneration conditions: vacuum swing adsorption and/or temperature swing adsorption will also be evaluated [67].

4. Conclusions

In this work low-cost microporous carbons were produced departing from spent Nespresso[®] coffee grounds through physical and chemical activation. The obtained carbons presented CO₂ adsorption capacities up to 4.8 mmol g⁻¹ at 273 K, and 3.0 mmol g⁻¹ at 298 K, which are above that of a commercial activated carbon taken as reference. Samples activated with KOH showed superior textural development than samples activated with CO₂. For KOH activation it was found that an increase in the activation temperature increased the wide micro- and mesopore volume of the sample at expenses of the ultramicroporosity.

Adsorption experiments carried out with pure CO₂ at atmospheric pressure showed that activation with KOH leads to higher CO₂ adsorption capacities than activation with CO₂ due to the superior texture development of the chemically activated samples. However, multicomponent adsorption/desorption cyclic tests carried out at 323 K pointed out that the physically activated samples might be more selective towards CO₂ in postcombustion conditions. Moreover, physical activation presents higher carbon yield than chemical activation for low burn off degrees, and also a lower environmental impact (part of the separated CO₂ could even be used for activated carbon production).

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Table 1. Proximate and ultimate analyses of the Nespresso[®] coffee grounds (N) and the carbonised products at 673 and 873K (NCL and NCH, respectively).

Sample	Proximate analysis (% db)		Ultimate analysis (% daf)			
	VM	Ash	C	H	N	O
N	82.9	1.3	56.4	7.0	2.6	34.0
NCL	24.9	3.4	81.2	3.7	4.8	10.3
NCH	4.5	14.6	86.3	2.5	4.9	6.3

Table 2. Description of the activation conditions used to produce activated carbons from spent coffee grounds

Sample	Precursor	Temperature (K)	Heating rate (K min ⁻¹)	KOH/Char (weight ratio)	Gas	Flow rate (cm ³ min ⁻¹)
NCLK1	NCL	873	5	1	N ₂	300
NCLK2	NCL	873	5	2	N ₂	300
NCLK3	NCL	873	5	3	N ₂	300
NCLK4	NCL	873	5	4	N ₂	300
NCLK3b	NCL	973	5	3	N ₂	300
NCHA29	NCH	973	~25 (N ₂)	-	CO ₂	10
NCHA36	NCH	973	~25 (N ₂)	-	CO ₂	10
NCHA41	NCH	973	~25 (N ₂)	-	CO ₂	10

Table 3. Carbon yield, point of zero charge and helium density of the samples

Sample	Yield (g/100g N)	Helium density (g cm ⁻³)	pH _{PZC}
N	100	1.37	5.2
NCL	29	1.31	8.6
NCH	23	1.44	9.6
NCLK1	7	1.76	7.6
NCLK2	12	1.57	7.4
NCLK3	13	1.55	7.9
NCLK4	15	1.79	7.9
NCLK3b	9	2.10	8.4
NCHA29	16	1.89	9.9
NCHA36	15	1.72	10.1
NCHA41	14	1.83	10.0

Table 4. Textural parameters of the samples obtained from the N₂ and CO₂ adsorption isotherms

Sample	N ₂ adsorption at 77 K				CO ₂ adsorption at 273 K	
	S _{BET}	V _{DR}	L _{DR}	V _p	W ₀	L ₀
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(nm)
NCL	-	-	-	0.01	0.09	0.6
NCH	84	0.03	2.1	0.04	0.14	0.5
NCLK1	831	0.34	1.1	0.41	0.41	0.6
NCLK2	876	0.36	1.0	0.40	0.36	0.6
NCLK3	840	0.34	1.0	0.37	0.36	0.6
NCLK4	925	0.38	1.1	0.42	0.33	0.6
NCLK3b	1082	0.44	3.0	0.51	0.22	0.6
NCHA29	593	0.24	0.8	0.24	0.25	0.5
NCHA36	568	0.24	1.0	0.24	0.25	0.5
NCHA41	590	0.24	1.3	0.28	0.27	0.6

S_{BET}: surface area calculated by the BET equation; V_{DR}: micropore volume determined by the DR equation from the N₂ adsorption isotherm at 77 K; L_{DR}: average micropore width calculated through the Stoeckli-Ballerini equation; V_p: total pore volume calculated from the amount of N₂ adsorbed at 77 K at a relative pressure of 0.99; W₀: narrow micropore volume determined by the DR equation applied to the CO₂ adsorption isotherm at 273 K; L₀: width of narrow micropores calculated through the Stoeckli-Ballerini equation.

Table 5. CO₂ adsorption capacity of the samples at 298 K and 101 kPa

Sample	CO ₂ adsorption capacity (mmol g ⁻¹)	
	273 K	298 K
NCL	1.2	0.8
NCH	2.0	1.4
NCLK1	4.9	2.8
NCLK2	4.4	3.0
NCLK3	4.7	3.0
NCLK4	4.5	2.9
NCLK3b	3.2	2.7
NCHA29	3.5	2.2
NCHA36	3.4	2.3
NCHA41	3.6	2.4
R2030CO2	3.7	2.1