Precombustion CO₂ capture by means of phenol-formaldehyde resin-derived carbons: from equilibrium to dynamic conditions

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Abstract

The performance of two phenol-formaldehyde resin-based activated carbons prepared in our laboratory, as potential adsorbents for precombustion CO₂ capture has been evaluated under static (adsorption isotherms) and dynamic (adsorption-desorption cycles conducted in a fixed bed) conditions. Most of the literature on CO₂ capture with solid sorbents is based on equilibrium CO₂ adsorption capacities, determined from CO₂ adsorption isotherms at the desired temperature. However, dynamic testing is required to ascertain the extent to which the equilibrium uptake may be translated into breakthrough capacity. CO₂ and H₂ adsorption isotherms up to 30 bar were determined in a high-pressure magnetic suspension balance. Equilibrium CO₂ uptakes at 15 bar of up to 8.5 mmol g⁻¹ at 298 K and 7 mmol g⁻¹ at 318 K were attained. Adsorption-desorption cycles by means of pressure and temperature swings were conducted with a simulated shifted-syngas in a purpose-built fixed-bed set-up. With a ternary mixture of CO₂/H₂/N₂, breakthrough capacities at a total pressure of 15 bar reached 6.5 mmol g⁻¹ at 298 K and 5.8 mmol g⁻¹ at 318 K. These figures point out the suitability of these adsorbents to be applied to precombustion CO₂ capture by means of a PSA process.

keywords: phenol-formaldehyde resin, CO₂ capture, H₂ purification

1. Introduction

Carbon dioxide capture and storage (CCS) is a critical technology to significantly reduce CO₂ emissions from large-point stationary sources. The purpose of CO₂ capture is to produce a concentrated stream that can be readily transported to a CO₂ storage site. A number of different carbon capture processes for post and precombustion applications have been tested and deployed at various scales, but no particular technology has emerged yet as the chosen one for CO₂ capture. While the retrofitting of existing power

plants using postcombustion capture methods presents the closest marketable technology, precombustion capture and oxyfuel processes are projected to attain higher efficiencies for CO₂ separation and capture than postcombustion capture processes, which will offset their extensive capital investments in the longer term [1]. Hence, all the aforementioned approaches might be needed in a future decarbonised energy system.

Precombustion CO₂ capture within integrated gasification combined cycle (IGCC) plants offers the opportunity to remove CO₂ from the fuel gas before it is combusted in the turbine, and could become the technology of choice for new-build power plants. Precombustion capture involves partial oxidation (gasification) of fuel to produce syngas (or fuel gas) composed mainly of carbon monoxide and hydrogen. The carbon monoxide is reacted with water vapour in a shift converter to increase carbon dioxide and hydrogen yield. CO₂ is then concentrated from this H₂/CO₂ mixture, resulting in a hydrogen-rich fuel and a CO₂-rich stream ready for storage. The significant advantage of precombustion capture is that the high CO₂ concentrations (typically 15 to 60% by volume on a dry basis) and elevated pressures encountered after the shift reactor, reduce the energy capture penalty of the process to 10–16%, roughly half that for postcombustion CO₂ capture [2]. Hydrogen production with capture and storage of CO₂ will “bridge-the-gap” towards the renewable hydrogen economy and make a more economical viable transition [2].

In a typical IGCC plant, the crude fuel gas is first fed to a facility to remove the particulates from the gas stream. The gas leaving the particulates scrubber is then cooled and dewatered and, at this point, consists mainly of CO, H₂, and CO₂. It also contains H₂S, which will be removed in the desulphurisation system. The acid gas scrubbing process is generally designed for the removal of sulphur-bearing compounds with very little CO₂ removed in the process, e.g. Selexol® process. Acid gas cleaning can also be conducted within a warm gas clean-up system, rather than with the previously described cold gas clean-up route. The main advantage in cleaning the gas at higher temperature is that the thermal plant efficiency will be as much as 2–3% greater as compared to the lower temperature acid gas cleaning scenario [3].

While no commercial IGCC plants with CCS are yet in operation, the largest proposed projects include the recently re-instated 275 MW FutureGen plant in the U.S. and China's 250 MW GreenGen project [4]. These are based on the world's first precombustion CCS pilot-plant (14 MWth) operating from 2010 at ELCOGAS IGCC

(335 MW), in Spain, which will be our reference for the present work. The CCS pilot-plant, including shifting, gas conditioning and capture units, is installed right after the desulphurisation step. The shifted-syngas that is fed to the amine-based CO₂ capture unit is at around 318 K and 15 bar and contains mainly H₂, CO₂ and N₂.

There are a number of different separation technologies which can be integrated into the precombustion carbon dioxide capture system including solvent, membrane, and adsorbent based processes. The commercial CO₂ capture technology is UOP's liquid absorption Selexol® process for the removal of H₂S and simultaneous capture of CO₂ from an IGCC. This process, used as the benchmark for comparison between different capture technologies, is expensive and entails a significant amount of utility consumption. Hence, improved technologies are necessary to achieve higher performances at reduced costs in the CO₂ capture process.

Physical solvents for CO₂ removal at high temperatures (423-473 K) in IGCC applications are being studied. The higher temperature of operation for these solvents enhances the thermal efficiency of the IGCC power generation system. Depressurisation or flashing of the CO₂ from the rich solvent is the means for regeneration. A temperature swing is another means for regenerating the solvent, although vapour pressure and thermal degradation of the solvent must be considered.

Membranes are also an appealing option for CO₂ separation, mainly because of the inherent permeating properties of these species. This technology does not require a separating agent nor does it involve phase changes. As a consequence, the elevated processing costs associated with regeneration and phase change are eliminated. However, a membrane combining high flux, high selectivity and stability is not yet realistic at this stage. Currently, the membrane market devoted to CO₂ separation from natural gas is about 20%, which is only 2% of the total separations market for natural gas. Amine based absorption processes dominate this market. Membranes for large-scale recovery of CO₂ are a relatively recent development; current membranes have been designed generally to remove unwanted CO₂ from a desired product, rather than to recover CO₂ for its own value [5]. An alternative technology is the non-dispersive absorption process using porous membranes to perform the separation. The membrane does not provide selectivity to the separation since its role is to act merely as a barrier between the two phases. However, the long-term stability of the membranes along with their wetting and some other aspects must be addressed to make this technology competitive with the conventional absorption process for CO₂ capture [6].

Adsorption is considered a promising technology for CO₂ capture applications, both in pre and postcombustion processes, since adsorbents present high adsorption capacity, great selectivity, good mechanical properties and they remain stable over repeated adsorption-desorption cycles [7-13]. Selective adsorption of CO₂ on inorganic and organic adsorbents like zeolite, silica gel, alumina and activated carbon is used commercially for separation of bulk CO₂ from gas mixtures and removal of trace CO₂ from a contaminated gas [14]. Different types of solid sorbents have been or are currently being investigated as potential adsorbents for CO₂ capture [7-9, 15-30]. Past work has included alkali and alkaline earth metals as the basic component of sorbent structures [31]. These sorbents could be used in high temperature (>423 K) sorption processes. Recent work has included lower temperature (<423 K) adsorbents for potential use as a substitute for the Selexol® process [13, 19] in precombustion CO₂ capture. The regeneration step is crucial for these types of sorbents, and pressure swing and/or temperature swing can be effectively utilised. Pressure swing adsorption (PSA) offers significant advantages for precombustion CO₂ capture in terms of performance, energy requirements, and operating costs. PSA is a well developed technology that achieves gas separation by means of adsorption and desorption cycles and, therefore, operates in a solvent-free manner. Moreover, only feed compression constitutes the key energy requirements for the process, which can be significantly low for precombustion capture since feed is already available at high pressure [32-34]. An overview of how the PSA units can be integrated in complex flowsheets of power plants and steam reformers for precombustion CO₂ capture is presented in the work of Voss [35].

Owing to their low cost, high surface area, high amenability to pore structure modification and surface functionalisation, and relative ease of regeneration, carbon-based materials are considered to be one of the most promising adsorbents for capturing CO₂ in IGCC processes for energy generation and hydrogen production [36]. Activated carbon adsorbents are ideally suited for CO₂ capture after the water-gas-shift reaction where CO₂ is at high pressure and physical adsorbents with weak basic functionalities are required for CO₂ capture, as opposed to the strong basic functionalities required at low pressures. Phenolic resin-derived activated carbons offer further advantages in that they can be produced in a wide variety of physical forms, allow a close control of porosity, and present a very low level of impurities and good physical strength [37, 38]. In this contribution, the performance of two phenol-formaldehyde resin-based activated carbons prepared in our laboratory as potential adsorbents for precombustion CO₂

capture has been evaluated under static (adsorption isotherms) and dynamic (adsorption-desorption cycles conducted in a fixed bed) conditions. Most of the literature on CO₂ capture with solid sorbents is based on equilibrium CO₂ adsorption capacities determined from CO₂ adsorption isotherms at the desired temperature. However, the suitability of a selected adsorbent for CO₂ capture relies on efficient regeneration and cycling. Thus, analyses using a dynamic test set-up are required to ascertain the extent to which the equilibrium uptake may be translated into breakthrough capacity.

2. Experimental

2.1. Materials

Two activated carbons prepared in our laboratory from *Resol*, PFNA, and *Novolac*, PFCLA, phenol-formaldehyde resins have been tested as CO₂ adsorbents under precombustion capture conditions. These two adsorbents have been prepared following an activated carbon production procedure consisting in a first step of carbonisation under inert atmosphere followed by a second step of activation under CO₂ atmosphere up to around 40 % burn off. Table 1 summarises the main characteristics of these materials. Details on the synthesis and characterisation can be found elsewhere [39]. These adsorbents present high carbon contents (~ 97 wt.%) and well-developed microporosity (total micropore volume ~ 0.5 cm³ g⁻¹, assessed from the Dubinin-Radushkevich relation applied to the N₂ adsorption isotherms at 77 K). Previous works in our research group have demonstrated that the equilibrium CO₂ uptake at elevated pressure is limited to the presence of microporosity in the carbon [40].

2.2. Adsorption isotherms of pure gases

CO₂ and H₂ adsorption isotherms up to 30 bar were determined in a high pressure magnetic suspension balance, Rubotherm-VTI. This instrument allows the elimination of most of the disadvantages of the gravimetric technique by physically separating the sample and the high resolution balance by means of a magnetic suspension coupling. The sample is exposed to the measuring atmosphere while the balance is located under ambient conditions [41]. High resolution (0.01 mg) sorption measurements can be performed in the pressure range from ultra high vacuum to 500 bar at temperatures between 270 and 500 K.

Carrying out an adsorption measurement with a gas at one temperature involves three steps:

- i) the sample container is filled with the adsorbent (~ 300 mg) which is then weighed with the magnetic suspension balance,
- ii) the measuring cell is evacuated several times and flushed with helium. After this, the measuring cell is filled with He up to a certain pressure (~1 MPa) and heated up to 373 K and held at this temperature for a maximum of 120 min. Next, the cell is evacuated and cooled down to the measuring temperature.
- iii) the measuring cell is pressurized with the desired measuring gas and the process of equilibration observed with the magnetic suspension balance. After the adsorption equilibrium is reached, the pressure is increased (pressure steps ~ 2.5 bar) to the next desired value. This carries on until the maximum pressure of the isotherm is reached (here 30 bar). After measuring the last point of the isotherm the pressure is reduced stepwise and the desorption isotherm measured.

Commonly used measuring techniques for adsorption equilibrium allow only differences to be measured, i.e., the mass of adsorbate minus the product of the volume of the atmosphere displaced by the adsorbent and the density of the atmosphere surrounding it. Thus, to obtain the quantity of interest, the mass of adsorbate (m), from the measured data, a buoyancy correction has to be performed:

$$m(P, T) = \Delta m(P, T) + (V_{SC} + V) \rho(P, T) \quad (1)$$

where Δm is the reading of the balance, ρ is the density of the atmosphere surrounding the sample, V the volume of the adsorbent sample displacing the atmosphere and V_{SC} is the volume of the balance components holding the sample. Assuming that V characterises only the volume of the adsorbent, m may account for the surface excess adsorbed.

In order to obtain a value for the volume of the adsorbent, the so-called helium-volume was determined. Therefore, we have performed measurements with He as adsorptive gas. Applying eq. (1), assuming He is not adsorbed, the volume of the adsorbent can be calculated from the measured data.

From the high-pressure H₂ and CO₂ adsorption isotherms at 298 K the selectivity of the studied carbons to separate CO₂ from CO₂/H₂ mixtures together with the maximum CO₂ adsorption capacity at different pressures were evaluated.

High pressure CO₂ adsorption isotherms at 318 and 338 K were also determined for sample PFCLA. Experimental data were fitted with the Toth model, considering the effect of temperature. This is an empirical equation that satisfies both the low and high pressure ranges and has the following form:

$$q = q_s \frac{bP}{[1 + (bP)^t]^{1/t}} \quad (2)$$

where q represents the concentration of the adsorbed specie and q_s the saturation capacity, P the pressure of adsorptive and T the temperature. The parameters b and t (usually < 1) and q_s are temperature dependent; b usually takes the form of the adsorption affinity whereas t and q_s attain empirical functional forms (see eqs. (3)-(5)):

$$b = b_0 \exp \left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right] \quad (3)$$

$$t = t_0 + \alpha \left(1 - \frac{T_0}{T} \right) \quad (4)$$

$$q_s = q_{s,0} \exp \left[c \left(1 - \frac{T}{T_0} \right) \right] \quad (5)$$

where b_0 , t_0 , and $q_{s,0}$ stand for the corresponding parameters at a selected reference temperature, T_0 ; Q is a measure of the heat of adsorption and α and c are fitting parameters.

2.3. Breakthrough experiments with multi-component gas mixtures

Breakthrough tests with a ternary gas mixture of CO₂, H₂ and N₂, representative of the shifted-syngas that is fed to ELCOGAS IGCC CCS pilot-plant (43 % v/v CO₂, 47 % H₂, N₂ balance on a dry basis) were conducted in a purpose-built bench-scale system. ELCOGAS IGCC is running the world's first precombustion CCS pilot-plant (14 MWth) from 2010. The bench-scale system consists in a stainless steel adsorption column (157 mm height, 9 mm inner diameter). Pressure and temperature are continuously monitored and controlled by means of a back-pressure regulator and a PID control, respectively. Feed gas flows are measured and controlled with Bronkhorst high-tech mass flow controllers. The composition of the outlet gas was monitored by a gas micro-chromatograph, Varian CP-4900, equipped with a thermal conductivity detector (TCD). A scheme of the experimental set-up can be found elsewhere [42]. Six consecutive adsorption-desorption cycles were carried out. Adsorption was conducted at 298 and 318 K and a total pressure of 15 bar while desorption was carried out at 353 K

and atmospheric pressure until complete regeneration. Table 2 summarises the experimental conditions of these experiments and the main characteristics of the adsorbent beds.

The CO₂ capture capacity under these conditions was evaluated as an average of the capture performance of the adsorbents after six consecutive adsorption-desorption PSA cycles. A mass balance was applied to each adsorption-desorption cycle to calculate the amount of CO₂ adsorbed (q_{CO_2}).

$$q_{CO_2} = \int_0^{t_s} (F_{CO_2,in} - F_{CO_2,out}) dt - \frac{y_{CO_2,in} P}{ZRT} (\varepsilon_T V_b - V_d) \quad (6)$$

where q_{CO_2} stands for the mol of CO₂ adsorbed; $F_{CO_2,in}$ and $F_{CO_2,out}$ refer to the molar flowrates of CO₂ in the inlet and outlet streams; t_s refers to the time to reach saturation; $y_{CO_2,in}$ is the molar fraction of CO₂ in the inlet stream; P and T are the pressure and temperature of the bed at equilibrium; ε_T is the total bed porosity; V_b is the bed volume; V_d is the dead volume of the bed; R is the universal gas constant and Z the compressibility factor for CO₂ at T and P .

It should be taken into account that the CO₂ stored in the bed voidage, including the dead volume and the intraparticle voids (second term in eq. (6)), is subtracted from the total quantity of CO₂ accumulated in the bed to calculate the actual CO₂ adsorbed. The capacity to capture CO₂ is then expressed in terms of mass of CO₂ adsorbed (mol CO₂) per mass of adsorbent in the bed.

3. Results and discussion

3.1. High-pressure adsorption of CO₂

Figure 1 shows the CO₂ and H₂ adsorption isotherms at 298 K up to 30 bar. The shape of the isotherms indicates that interactions adsorbate-adsorbent are stronger for CO₂ than for H₂. The CO₂ isotherms show a pronounced curvature compared to the linear H₂ isotherms. In addition, CO₂ adsorption is significantly greater (nearly two orders of magnitude at pressures > 5 bar) than H₂ adsorption along the tested pressure range.

The maximum CO₂ uptake corresponds to sample PFCLA that reaches ~ 10 mmol g⁻¹ at 30 bar. This value is superior to those found in the literature for commercial activated carbons like Calgon BPL (8.4 mmol g⁻¹ at 55 bar) [43] or Norit RB2 (9.5 mmol g⁻¹ at 40 bar) [44] and zeolites (5-8 mmol g⁻¹ at 40 bar) [27, 45]. In the low pressure range (up to 2 bar), both carbons show similar CO₂ uptakes (~3 mmol g⁻¹) in agreement with their

similar narrow micropore volume and size ($\sim 0.3 \text{ cm}^3 \text{ g}^{-1}$ and 0.7 nm). However, at higher pressures differences in the CO_2 capture capacity between these two samples appear. This may be attributed to the slightly greater micropore volume of PFCLA and, mainly, to the different average micropore sizes (1.26 nm for PFNA and 1.45 nm for PFCLA, determined from the Stoeckli-Ballerini relation [46]).

To determine the effect that the isotherm shape has on the expected performance of the adsorbent in an adsorption cycle, three temperatures, 298, 318 and 338 K, were selected and the corresponding CO_2 adsorption isotherms were determined for sample PFCLA. In order to evaluate the fitting parameters of the temperature-dependent form of the Toth equation, a non-linear regression was performed, considering all the data points at the three temperatures. This approach was based on a Generalized Reduced Gradient (GRG2) nonlinear optimisation code. This nonlinear regression was programmed on an Excel spreadsheet by means of the *Solver* tool. Table 3 summarises the CO_2 adsorption data for sample PFCLA at 298, 318 and 338 K. The comparison of experimental adsorption data and the temperature-dependent Toth equation fitting is graphically displayed in Figure 2. As expected, the CO_2 adsorption capacity decreases with increasing temperature. Data are presented on a logarithmic scale for low pressure clarity. The quality of the fit was determined by an error function based on the normalised standard deviation:

$$\Delta_q (\%) = \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{fit}})/q_{\text{exp}}]^2}{N - 1}} \times 100 \quad (7)$$

where Δq (%) is the error function, q_{exp} is the amount adsorbed determined experimentally, q_{fit} is the amount adsorbed as predicted by the Toth model and N is the total number of experimental points. Errors below 4 % were obtained.

When $t = 1$ the Toth equation reduces to the Langmuir's. Thus, this parameter is said to characterise the heterogeneity of the system. Fitted t values between 0.6 and 0.63 indicate that the surface of PFCLA is heterogeneous. However, temperature seems to slightly influence the heterogeneity parameter. b is related to the adsorption affinity at low pressures and fitted values decrease with increasing temperature. At zero loading the Toth equation reduces to the Henry's law being $b \times q_s$ the Henry's constant (k_H). Values between $4.16 \text{ mmol g}^{-1} \text{ bar}^{-1}$ at 298 K and $1.85 \text{ mmol g}^{-1} \text{ bar}^{-1}$ at 338 K were obtained for k_H . These figures are in good agreement with those found in the literature for commercial activated carbons [47].

Using the temperature dependence of b (eq. (3)) and t (eq. (4)) and applying the van't Hoff equation, the following isosteric heat equation for the Toth model is derived:

$$(-\Delta H) = Q - \frac{1}{t}(\alpha RT_0) \left\{ \ln(bP) - \left[1 + (bP)^t \right] \ln \left[\frac{bP}{(1 + (bP)^t)^{1/t}} \right] \right\} \quad (8)$$

From this equation (eq. (8)) it is deduced that Q is equal to the isosteric heat when the fractional loading is zero. In Figure 3 the isosteric heat of CO₂ adsorption determined from the Toth model is plotted versus the CO₂ fractional loading for sample PFCLA. At zero loading $\Delta H \approx 16.7 \text{ kJ mol}^{-1}$. This value is in agreement with those found in the literature for commercial activated carbons, like Calgon BPL (24.3 kJ mol⁻¹) [48] or Maxsorb carbon (14.7 kJ mol⁻¹) [49]. It can be observed that the isosteric heat increases with fractional loading up to ~0.4 and then decreases. This may suggest that interaction between CO₂ molecules become more significant up to certain loadings. In addition, it shows very weak temperature dependence over the studied 298-338 K range.

The results assessed with the temperature-dependent form of the Toth equation show and excellent fit to the experimental data. Therefore, it may be assumed that the Toth isotherm can be used as an accurate model of the CO₂ adsorption equilibrium.

3.2. Selectivity to separate CO₂ from high-pressure CO₂/H₂ mixtures

Gas adsorption selectivities are often reported as the ratio of number of moles of each component adsorbed at the relevant partial pressures in the pure-component isotherms. For a particular application, it is important to determine selectivity factors at conditions relevant to that application. For precombustion CO₂ capture under the above specified conditions, selectivity factors should be calculated for a mixture of approximately 6 bar CO₂ and 9 bar H₂. Selectivity factors should also be normalized to the composition of the gas mixture as shown in eq. (9), where q_i is the uptake and P_i is the partial pressure of component i [50]:

$$S_{ads} = \frac{q_1 / q_2}{P_1 / P_2} \quad (9)$$

According to eq. (9) the selectivity CO₂/H₂ of the studied carbons at 298 K for a mixture of 6 bar CO₂ and 9 bar H₂ would result in values of 96 (PFNA) and 92 (PFCLA). These values were estimated from the experimental pure gas adsorption isotherms. To describe multi-component adsorption, one common approach is to use experimental pure gas adsorption isotherms to predict multi-component adsorption

isotherms and selectivities by means of Ideal Adsorbed Solution Theory (IAST) [51]. The performance of IAST only depends on the quality of the pure isotherm data of each species and is independent of the assumptions underlining the isotherm model. IAST calculations for a 40% CO₂-60% H₂ mixture resulted in CO₂ adsorption isotherms overlapping those determined experimentally with pure CO₂ at the same partial pressure. Similar results were attained by applying the extended Langmuir-Freundlich equation to predict multi-component adsorption.

Cao et al. reported a decrease in the selectivity of CO₂ relative to H₂ with the increase in pore width for activated carbons [52]. This may account for the difference in CO₂ selectivity of PFNA and PFCLA (see Table 1). Under these particular conditions, selectivities determined from pure gas adsorption isotherms were in good agreement with those estimated from multi-component prediction equations. For other CO₂ adsorbents (i.e., MOFs) inconsistencies have been reported in the trend in selectivity (estimated from single and multi-component adsorption) as function of temperature when high-energy binding sites are involved [50].

As could be seen from the equilibrium adsorption isotherms (Figure 1) preferential adsorption of CO₂ over H₂ takes place at high pressures. Thus, the estimated values corroborate that the studied carbons are very selective to CO₂. Lower selectivities have been reported for common PSA activated carbons applied to hydrogen purification under similar experimental conditions [13, 52]. MOFs have been recently proposed as adsorbents for hydrogen purification and CO₂ precombustion capture since they present significant CO₂ uptakes at high pressure and great selectivity CO₂/H₂ [13]. However, in their study, these authors conclude that the high surface areas and concomitant extraordinary CO₂ uptake of many metal-organic frameworks do not necessarily make them ideal for CO₂/H₂ separations. Industrially, adsorbents for this separation are tailored and optimized for each specific PSA system. Thus, in order to validate the efficiency of these materials, additional tests, such as regeneration studies, will be needed.

3.3. Breakthrough tests with a simulated shifted-syngas

Previous tests were conducted under pure CO₂ flow until equilibrium. Thus, they allow the assessment of the maximum CO₂ capture capacities at high pressure. For the breakthrough tests, a ternary mixture of CO₂, H₂ and N₂ was fed to the adsorption column. A feed flow rate of 100 mL min⁻¹ was used which resulted in an empty-bed retention time between 4.5 and 5.1 s, depending on the height of the adsorbent bed.

Consecutive adsorption-desorption cycles by means of pressure and temperature swings were conducted. In Figure 4 the gas outlet concentrations, pressure and temperature profiles of the three-step cycle configuration selected to conduct the breakthrough tests is depicted. The first step (1) corresponds to the conditioning of the adsorbent bed which implies a decrease in temperature and pressure rise under N₂ flow. The adsorption step (2) is characterised by zero CO₂ outlet concentration at the beginning, while the adsorbent bed is not yet saturated. N₂ and H₂ profiles indicate that adsorption of these two gases is negligible. Once the bed is fully saturated with CO₂ the outlet gas concentrations return to the inlet conditions. The break point is often taken at a relative concentration ($\text{CO}_{2,\text{outlet}}/\text{CO}_{2,\text{feed}}$) of 0.01. In these experiments the adsorption step was carried out at 15 bar and 298 and 318 K. Following the adsorption step the bed is heated up to 353 K and pressure is reduced down to 1 bar under N₂ flow to achieve complete regeneration of the adsorbent bed. The desorption step (3) is characterised by a sharp increase in the outlet CO₂ concentration that progressively tends to zero.

Figure 5a presents the CO₂ breakthrough curves for samples PFNA and PFCLA, during the breakthrough tests conducted under the above specified conditions. The adsorption of H₂ by the activated carbon beds was negligible and it is not presented. Longer breakthrough times (t_b) were obtained during the 298 K tests. This is due to the drop in the CO₂ capture capacity at 318 K compared to 298 K. As shown in Figure 5b for sample PFCLA during the test at 318 K, CO₂ breakthrough curves overlap showing that regeneration is homogeneous over the consecutive cycles and the performance of the adsorbent bed is not altered. Thus, CO₂ capture over the six consecutive PSA cycles can be considered stable.

In Table 4 the CO₂ capture capacities of the adsorbents assessed from the breakthrough tests are presented. These values stand for the average capacity of the cycles conducted in each experiment. While gravimetric capacities (mmol of CO₂ adsorbed per g of adsorbent) are normally reported when evaluating materials for a CO₂/H₂ separation, the volumetric capacities (kg of CO₂ adsorbed per m³ of adsorbent) were also calculated, since both parameters are critical in designing a PSA separation process. Capture capacities up to 6.5 mmol g⁻¹ at 298 K and 5.8 mmol g⁻¹ at 318 K were achieved. On a mass basis, capacities are similar for both activated carbon beds and differences are only apparent at 318 K. However, on a volumetric basis PFNA shows enhanced performance at both temperatures due to the greater bed density.

In Table 4 the values corresponding to the length of unused bed (LUB) are also reported. The scale-up principle in an adsorption process is that the length of unused bed does not change with the total bed length. To calculate this parameter the ratio between the amount of CO₂ adsorbed up to the break point and the total amount of CO₂ adsorbed should be determined. Thus, *LUB* is evaluated by the following expression [53]:

$$LUB = L \left(1 - \frac{q_{CO_2,b}}{q_{CO_2}} \right) \quad (10)$$

where *L* represents the length of the bed and *q*_{CO₂,b} and *q*_{CO₂} refer to the mol of CO₂ adsorbed up to the break point and to saturation of the bed (eq. (6)), respectively. According to eq. (10), *LUB* may evaluate the efficiency of the adsorbent bed, because the similar is *q*_{CO₂,b} to *q*_{CO₂} the narrower the mass transfer zone is. *LUB* diminishes with the increase in temperature from 298 to 318 K. Temperature favours mass transfer along the adsorbent bed and thus improves the efficiency of utilization.

PFNA seems to lose less capacity than PFCLA with the increase in temperature from 298 to 318 K while the efficiency of the adsorbent bed, here represented by *LUB*, is significantly greater at 318 K for PFCLA.

The design and efficiency of an adsorption process are controlled by the overall dynamics of the packed-bed, rather than the adsorption kinetics for a single particle. Thus, the importance of breakthrough tests to properly assess the dynamics of a fixed-bed adsorption column. Literature on the dynamic performance of adsorbent beds under precombustion CO₂ capture conditions is scarce. In a previous work from our research group [42], a commercial activated carbon, Norit R2030CO2, was tested for precombustion capture at different CO₂ partial pressures and temperatures. The maximum capacity attained was ~4 mmol g⁻¹ at a CO₂ partial pressure of 3 bar (15 bar total pressure) and 298 K. Most of the working capacities under precombustion CO₂ capture conditions reported so far are estimated from multi-component gas adsorption isotherms. For instance, to the best of our knowledge, *Herm et al.* have reported the maximum CO₂ working capacity of 7 mmol g⁻¹ for a 40% CO₂-60 % H₂ mixture at 313 K and 15 bar for MOF Cu-BTtri [13]. However, this material has not yet been validated under cyclic operation in order to evaluate its efficiency. On the other hand, they reported the performance of other commercial adsorbents. The best performance of a commercial activated carbon corresponds to Calgon BPL that showed a CO₂ capture

capacity of 4.5 mmol g^{-1} at 303 K and 15 bar for a 40% CO_2 -60 % H_2 mixture. For zeolite 13X the working capacity dropped down to 2 mmol g^{-1} under the same conditions. Comparison of our results to those available in the literature is not straightforward since adsorption isotherms do not consider any dispersive effect due to the packing of the adsorbent in the fixed-bed. Moreover, when capacities are expressed on a volumetric basis it must be born in mind that particle densities are usually greater than bed densities.

4. Conclusions

Two phenol-formaldehyde derived activated carbons have been tested as CO_2 adsorbents under precombustion capture conditions. In this study we have shown the importance of dynamic tests to accurately evaluate the performance of adsorbents to be applied to precombustion CO_2 capture. Both carbons showed similar CO_2 uptakes under equilibrium at 15 bar and 298 K: 8.5 mmol g^{-1} for PFCLA and 8 mmol g^{-1} for PFNA. H_2 adsorption did not exceed 0.15 mmol g^{-1} . Nevertheless, for a mixture of 40% CO_2 -60% H_2 at 15 bar and 298 K, PFNA showed greater CO_2/H_2 selectivity than PFCLA that may be attributed to its narrower average pore width. Breakthrough tests in a fixed-bed column with a simulated shifted-syngas at a total pressure of 15 bar resulted in CO_2 capture capacities of 6.5 and 6.4 mmol g^{-1} at 298 K and 5.3 and 5.8 mmol g^{-1} at 318 K for PFCLA and PFNA, respectively. Moreover, both carbons showed good cyclability and regenerability over consecutive pressure swing adsorption cycles. Most of capture capacities reported in the literature are based on predicted multi-component adsorption isotherms that do not consider the performance of the adsorbent in the packed bed. However, from the results presented it can be concluded that the tested carbons show great potential to be applied to precombustion CO_2 capture by means of a PSA process.

5. Acknowledgements

This work was carried out with financial support from the Spanish MICINN (Project ENE2008-05087). C.F.M. and D.B. acknowledge support from the CSIC JAE-Predoc Program co-financed by the European Social Fund.

Table 1 Characteristics of the phenol-formaldehyde activated carbons.

	PFCLA	PFNA
Particle density (kg m^{-3}) ¹	928	894
Skeletal density (kg m^{-3}) ²	2,110	2,080
Particle size (mm)	1-3	1-3
Particle porosity	0.56	0.57
BET surface area ($\text{m}^2 \text{g}^{-1}$)	1,211	1,381
Micropore volume ($\text{cm}^3 \text{g}^{-1}$) ³	0.45	0.51
Average micropore width (nm) ⁴	1.45	1.26

¹determined by Hg porosimetry; ²determined by He picnometry; ³evaluated with the Dubinin-Radushkevich equation; ⁴determined with the Stoeckli-Ballerini relation

Table 2 Experimental conditions and characteristics of the breakthrough experiments on the phenol-formaldehyde activated carbon beds

	Units	PFCLA		PFNA	
<i>Experimental conditions</i>					
Feed flow, STP	mL min ⁻¹	100			
Feed composition	% v/v	40% CO ₂ , 50% H ₂ , N ₂ balance			
Pressure (ads.)	bar	15			
Pressure (des.)	bar	1			
Temperature (ads.)	K	298	318	298	318
Temperature (des.)	K	353			
<i>Bed parameters</i>					
diameter	m	0.009			
height (<i>h</i>)	m	0.130	0.121	0.135	0.113
mass of adsorbent	kg	3.54x10 ⁻³	3.53x10 ⁻³	3.61x10 ⁻³	3.45x10 ⁻³
density (ρ_b)	kg m ⁻³	432		454	
total porosity (ϵ_T)	-	0.80	0.79	0.80	0.78
porosity (ϵ_b)	-	0.55	0.52	0.54	0.48
Z^*	-	0.92	0.94	0.92	0.94

* Compressibility factor for CO₂ at adsorption pressure and temperature

Table 3 CO₂ adsorption data at 298, 318 and 338 K for sample PFCLA: Experimental data,
Toth isotherm fits and Toth parameters.

298 K			318 K			338 K		
P (bar)	q (mmol g ⁻¹)		P (bar)	q (mmol g ⁻¹)		P (bar)	q (mmol g ⁻¹)	
	Exp	Toth		Exp	Toth		Exp	Toth
0.2	0.760	0.643	0.2	0.484	0.429	0.2	0.316	0.300
0.7	1.753	1.698	0.7	1.180	1.168	0.7	0.815	0.838
1.1	2.356	2.357	1.1	1.652	1.688	1.1	1.163	1.219
1.3	2.774	2.714	1.3	1.886	1.938	1.3	1.346	1.417
4.0	5.084	5.098	4.0	3.801	3.882	4.0	2.900	2.975
6.7	6.416	6.408	6.5	4.912	4.970	6.7	3.883	3.928
9.2	7.255	7.219	9.2	5.735	5.767	9.3	4.626	4.631
10.8	7.674	7.625	10.8	6.144	6.164	10.8	4.983	4.967
13.3	8.225	8.157	13.1	6.629	6.638	13.4	5.486	5.441
15.9	8.660	8.583	15.7	7.071	7.071	15.9	5.906	5.840
18.3	8.986	8.914	18.3	7.427	7.434	18.5	6.259	6.181
21.0	9.286	9.232	21.1	7.743	7.766	21.1	6.558	6.480
24.9	9.606	9.602	24.9	8.093	8.150	24.9	6.915	6.857
28.8	9.831	9.907	29.4	8.399	8.528	29.4	7.250	7.238
Toth isotherm fit parameters					Toth T-dependent parameters			
T(K)	q_s (mmol g ⁻¹)	b (bar ⁻¹)	t	Δq (%)	q_{s0}	13.99		
					b_0	0.19		
298	14.33	0.29	0.63	4.13	$Q/R \times T_0$	5.98		
318	13.99	0.19	0.61	3.26	t_0	0.61		
					c	0.381		
338	13.66	0.14	0.59	2.63	α	-0.395		

Table 4 CO₂ adsorption capacities from the breakthrough tests at 298 and 318 K. Experimental conditions of the adsorption step: P = 15 bar, Feed composition = 43 % CO₂, 47 % H₂, N₂ balance, 100 mL min⁻¹ STP

Sample	T _{ads} (K)	t _b [*] (min)	LUB (cm)	CO ₂ adsorption capacity		
				(mmol g ⁻¹)	(wt.%)	(kg m ⁻³)
PFCLA	298 K	12.1	2.6	6.5	28.6	123.5
	318 K	11.7	0.6	5.3	23.4	101.1
PFNA	298 K	12.5	2.4	6.4	28.1	127.6
	318 K	11.3	1.7	5.8	25.4	115.3

*t_b is determined at a ratio of concentrations CO₂ outlet/ CO₂ feed of 0.01.

Figure 1

Figure 1. CO₂ and H₂ adsorption isotherms evaluated at 298 K up to 30 bar.

Figure 2

Figure 2. CO₂ adsorption isotherms at 298, 318 and 338 K and up to 30 bar for sample PFCLA
(symbols: experimental data; lines: Toth isotherm fits)

Figure 3

Figure 3. Isosteric heat of adsorption of pure CO_2 on sample PFCLA.

Figure 4

Figure 4. Three-step adsorption-desorption cycle during a breakthrough test: (1) conditioning, (2) adsorption and (3) desorption.

Figure 5

Figure 5. CO₂ breakthrough curves: a) tests carried out at two temperatures: 298 and 318 K for samples PFCLA and PFNA, and b) consecutive adsorption-desorption cycles for sample PFCLA at 318 K.

6. References

- [1] IPCC, IPCC Special Report on Carbon Dioxide Capture and Storage, 2005.
- [2] L.I. Eide, D.W. Bailey, Capture précombustion, *Oil & Gas Science and Technology - Rev. IFP*, 60 (2005) 475-484.
- [3] H.W. Pennline, D.R. Luebke, K.L. Jones, C.R. Myers, B.I. Morsi, Y.J. Heintz, J.B. Ilconich, Progress in carbon dioxide capture and separation research for gasification-based power generation point sources, *Fuel Processing Technology*, 89 (2008) 897-907.
- [4] R.S. Haszeldine, Carbon capture and storage: how green can black be?, *Science*, 325 (2009) 1647-1652.
- [5] A.D. Ebner, J.A. Ritter, State-of-the-art adsorption and membrane separation processes for carbon dioxide production from carbon dioxide emitting industries, *Separation Science and Technology*, 44 (2009) 1273-1421.
- [6] P. Luis, B. Van der Bruggen, T. Van Gerven, Non-dispersive absorption for CO₂ capture: from the laboratory to industry, *Journal of Chemical Technology & Biotechnology*, 86 (2011) 769-775.
- [7] Z. Yong, V. Mata, A.E. Rodrigues, Adsorption of carbon dioxide at high temperature—a review, *Separation and Purification Technology*, 26 (2002) 195-203.
- [8] S. Choi, J.H. Drese, C.W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, *ChemSusChem*, 2 (2009) 796-854.
- [9] Q. Wang, J. Luo, Z. Zhong, A. Borgna, CO₂ capture by solid adsorbents and their applications: current status and new trends, *Energy & Environmental Science*, 4 (2011) 42-55.
- [10] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO₂ capture technology—the U.S. department of energy's carbon sequestration program, *International Journal of Greenhouse Gas Control*, 2 (2008) 9-20.
- [11] S. Sjostrom, H. Krutka, Evaluation of solid sorbents as a retrofit technology for CO₂ capture, *Fuel*, 89 (2010) 1298-1306.
- [12] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-combustion CO₂ capture using solid sorbents: a review, *Industrial & Engineering Chemistry Research*, 51 (2012) 1438-1463.
- [13] Z.R. Herm, J.A. Swisher, B. Smit, R. Krishna, J.R. Long, Metalorganic frameworks as adsorbents for hydrogen purification and precombustion carbon dioxide capture, *Journal of the American Chemical Society*, 133 (2011) 5664-5667.
- [14] D.M. Ruthven, Principles of adsorption and adsorption processes, John Wiley & Sons, New York, 1984.
- [15] T.C. Drage, J.M. Blackman, C. Pevida, C.E. Snape, Evaluation of activated carbon adsorbents for CO₂ capture in gasification, *Energy & Fuels*, 23 (2009) 2790-2796.
- [16] M.L. Gray, Y. Soong, K.J. Champagne, J. Baltrus, R.W. Stevens Jr, P. Toochinda, S.S.C. Chuang, CO₂ capture by amine-enriched fly ash carbon sorbents, *Separation and Purification Technology*, 35 (2004) 31-36.
- [17] G.P. Knowles, S.W. Delaney, A.L. Chaffee, Diethylenetriamine[propyl(silyl)]-functionalized (DT) mesoporous silicas as CO₂ adsorbents, *Industrial and Engineering Chemistry Research*, 45 (2006) 2626-2633.
- [18] M.M. Maroto-Valer, Z. Tang, Y. Zhang, CO₂ capture by activated and impregnated anthracites, *Fuel Processing Technology*, 86 (2005) 1487-1502.
- [19] C.F. Martin, E. Stockel, R. Clowes, D.J. Adams, A.I. Cooper, J.J. Pis, F. Rubiera, C. Pevida, Hypercrosslinked organic polymer networks as potential adsorbents for pre-combustion CO₂ capture, *Journal of Materials Chemistry*, 21 (2011) 5475-5483.
- [20] C. Pevida, M.G. Plaza, B. Arias, J. Feroso, F. Rubiera, J.J. Pis, Surface modification of activated carbons for CO₂ capture, *Applied Surface Science*, 254 (2008) 7165-7172.

- [21] C. Pevida, C.E. Snape, T.C. Drage, Templated polymeric materials as adsorbents for the postcombustion capture of CO₂, *Energy Procedia*, 1 (2009) 869-874.
- [22] M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, CO₂ capture by adsorption with nitrogen enriched carbons, *Fuel*, 86 (2007) 2204-2212.
- [23] M.G. Plaza, C. Pevida, B. Arias, M.D. Casal, C.F. Martín, J. Fermoso, F. Rubiera, J.J. Pis, Different approaches for the development of low-cost CO₂ adsorbents, *Journal of Environmental Engineering - ASCE*, 135 (2009) 426-432.
- [24] M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, A. Arenillas, F. Rubiera, J.J. Pis, Application of thermogravimetric analysis to the evaluation of aminated solid sorbents for CO₂ capture, *Journal of Thermal Analysis and Calorimetry*, 92 (2008) 601-606.
- [25] M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, M.D. Casal, C.F. Martín, F. Rubiera, J.J. Pis, Development of low-cost biomass-based adsorbents for postcombustion CO₂ capture, *Fuel*, 88 (2009) 2442-2447.
- [26] M.G. Plaza, C. Pevida, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, A comparison of two methods for producing CO₂ capture adsorbents, *Energy Procedia*, 1 (2009) 1107-1113.
- [27] S. Cavenati, C.A. Grande, A.E. Rodrigues, Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolite 13X at high pressures, *Journal Chemical Engineering Data*, 49 (2004) 1095-1101.
- [28] D. Ko, R. Siriwardane, L.T. Biegler, Optimization of a pressure-swing adsorption process using zeolite 13X for CO₂ sequestration, *Industrial Engineering Chemistry Research*, 42 (2003) 339-348.
- [29] J. Merel, M. Clausse, F. Meunier, Experimental investigation on CO₂ post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites, *Ind. Eng. Chem. Res.*, 47 (2008) 209-215.
- [30] N. Shigemoto, T. Yanagihara, S. Sugiyama, H. Hayashi, Material balance and energy consumption for CO₂ recovery from moist flue gas employing K₂CO₃-on-activated carbon and its evaluation for practical adaptation, *Energy & Fuels*, 20 (2006) 721-726.
- [31] R.V. Siriwardane, C. Robinson, M. Shen, T. Simonyi, Novel regenerable sodium-based sorbents for CO₂ capture at warm gas temperatures, *Energy & Fuels*, 21 (2007) 2088-2097.
- [32] D.M. Ruthven, S. Farooq, K.S. Knaebel, *Pressure Swing Adsorption*, John Wiley & Sons, Inc., 1994.
- [33] R.T. Yang, *Gas separation by adsorption processes*, Imperial College Press, 1997.
- [34] A. Agarwal, L.T. Biegler, S.E. Zitney, Superstructure-based optimal synthesis of pressure swing adsorption cycles for precombustion CO₂ capture, *Industrial & Engineering Chemistry Research*, 49 (2010) 5066-5079.
- [35] C. Voss, Applications of pressure swing adsorption technology, *Adsorption*, 11 (2005) 527-529.
- [36] T.C. Drage, O. Kozynchenko, C. Pevida, M.G. Plaza, F. Rubiera, J.J. Pis, C.E. Snape, S. Tennison, Developing activated carbon adsorbents for pre-combustion CO₂ capture, *Energy Procedia*, 1 (2009) 599-605.
- [37] S.R. Tennison, Phenolic-resin-derived activated carbons, *Applied Catalysis A: General*, 173 (1998) 289-311.
- [38] A.I. Foster, H.J. Linney, S.R. Tennison, R.A. Cory, D.P. Swan, The use of carbons produced from phenolic resins for flue gas desulphurization, *Fuel*, 72 (1993) 337-342.
- [39] C.F. Martín, M.G. Plaza, S. García, J.J. Pis, F. Rubiera, C. Pevida, Microporous phenol-formaldehyde resin-based adsorbents for pre-combustion CO₂ capture, *Fuel*, 90 (2011) 2064-2072.
- [40] C.F. Martín, M.G. Plaza, J.J. Pis, F. Rubiera, C. Pevida, T.A. Centeno, On the limits of CO₂ capture capacity of carbons, *Separation and Purification Technology*, 74 (2010) 225-229.

- [41] F. Dreisbach, H.W. Lösch, P. Harting, Highest pressure adsorption equilibria data: measurement with magnetic suspension balance and analysis with a new adsorbent/adsorbate-volume, *Adsorption*, 8 (2002) 95-109.
- [42] S. Garcia, M.V. Gil, C.F. Martin, J.J. Pis, F. Rubiera, C. Pevida, Breakthrough adsorption study of a commercial activated carbon for pre-combustion CO₂ capture, *Chemical Engineering Journal*, 171 (2011) 549-556.
- [43] H. Furukawa, O.M. Yaghi, Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications, *Journal of the American Chemical Society*, 131 (2009) 8875-8883.
- [44] A.R. Millward, O.M. Yaghi, Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature, *Journal of the American Chemical Society*, 127 (2005) 17998-17999.
- [45] S. Bourrelly, G. Maurin, P.L. Llewellyn, Adsorption microcalorimetry of methane and carbon dioxide on various zeolites, in: *Studies in Surface Science and Catalysis*, Elsevier, 2005, pp. 1121-1128.
- [46] F. Stoeckli, L. Ballerini, Evolution of microporosity during activation of carbon, *Fuel*, 70 (1991) 557-559.
- [47] B. Mu, K.S. Walton, High-pressure adsorption equilibrium of CO₂, CH₄, and CO on an Impregnated activated carbon, *Journal of Chemical & Engineering Data*, 56 (2011) 390-397.
- [48] S. Sircar, T.C. Golden, M.B. Rao, Activated carbon for gas separation and storage, *Carbon*, 34 (1996) 1-12.
- [49] K.B. Lee, M.G. Beaver, H.S. Caram, S. Sircar, Reversible chemisorbents for carbon dioxide and their potential applications, *Industrial & Engineering Chemistry Research*, 47 (2008) 8048-8062.
- [50] J.A. Mason, K. Sumida, Z.R. Herm, R. Krishna, J.R. Long, Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption, *Energy & Environmental Science*, 4 (2011) 3030-3040.
- [51] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, *AIChE Journal*, 11 (1965) 121-127.
- [52] D. Cao, J. Wu, Modeling the selectivity of activated carbons for efficient separation of hydrogen and carbon dioxide, *Carbon*, 43 (2005) 1364-1370.
- [53] W.L. McCabe, J.C. Smith, P. Harriott, *Unit operations of chemical engineering*, seventh ed., McGraw-Hill Companies Inc., Singapore, 2005.