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Developing activated carbon adsorbents for pre-combustion CO_2 capture

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Abstract

This paper describes the development of carbon-based adsorbents for CO_2 separation in integrated gasification combined cycle (IGCC) processes for energy generation and hydrogen production. The research presented forms part of a Research Fund for Coal and Steel funded project "Hydrogen separation in advanced gasification processes" (HYDROSEP) with the ultimate aim of developing technologies to reduce the costs for the capture of CO_2 when compared to existing absorption processes.
A range of carbon adsorbents were developed by MAST Carbon. They present significant microporosity and in some cases also meso or macroporosity. CO_2 adsorption isotherms have been determined using a dual limb differential pressure apparatus under realistic operating conditions. CO_2 and H_2 high pressure adsorption isotherms at room temperature have also been evaluated in a high pressure adsorption balance. Maxima CO_2 uptakes of 58 wt.% at 3 MPa and H_2 uptakes of 0.3 wt.% at 4 MPa were obtained. The significant differences observed in CO_2 and H_2 adsorption at high pressures showed the high selectivity for CO_2 of the tested MAST Carbon adsorbents.

Keywords: CO_2 capture; Adsorption; Carbon materials; IGCC; H_2 purification

1. Introduction

Power generation, mainly based on fossil fuel combustion, is responsible for about one third of all anthropogenic CO_2 emissions. Moreover, related emissions are increasing rapidly due to the current growth in global energy demand. At the same time, there is an urgent need to stabilize the concentration of CO_2 in the atmosphere before permanent and severe damage to the climate system is done. Consequently, CO_2 capture from large stationary sources has recently focused the attention as a potential means of mitigating fossil fuel CO_2 emissions.

Gasification, for example integrated gasification combined cycles (IGCC), offers potential benefits over conventional coal fired power plants, especially with regards to the environment and feedstock flexibility. Gasification plant offers the potential to selectively capture and remove CO_2 from the syngas stream prior to

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combustion and electricity generation (pre-combustion capture). The current state of the art technologies for the capture of CO_2 from fossil fuel gasification derived syngas are based on physical solvent washing systems, for example Rectisol [1] and Selexol [2] processes. Both of these technologies are mature technologies with gas separation plants, and currently being demonstrated for operation with gasification plants. As an alternative method for CO_2 capture, adsorption can be considered to be one of the more promising methods, offering potential energy savings compared to absorbent systems, especially with respect to compression costs [3]. Pressure swing adsorption (PSA) using solid sorbents has gained interest due to its low energy and capital investment costs [4-5].

This paper describes the development of carbon-based adsorbents for CO_2 separation in integrated gasification combined cycle (IGCC) processes for energy generation and hydrogen production. The research presented forms part of a Research Fund for Coal and Steel funded project "Hydrogen separation in advanced gasification processes" (HYDROSEP) with the ultimate aim of developing technologies to reduce the costs for the capture of CO_2 when compared to existing absorption processes.

Activated carbon adsorbents are ideally suited for CO_2 capture after the water gas shift reaction where CO_2 is at high pressure and "physical" adsorbents with weak basic functionalities are required for CO_2 capture, as opposed to the strong basic functionalities required at low pressures. A range of carbon adsorbents have been developed by MAST Carbon to determine the optimal textural and chemical properties for CO_2 capture. High pressure CO_2 adsorption isotherms have been determined using a volumetric and a gravimetric apparatus and the results obtained with both methodologies have been compared. In addition, H_2 high pressure adsorption isotherms have been evaluated in order to determine the selectivity of the prepared adsorbents to separate CO_2 from CO_2/H_2 mixtures. The performance of the adsorbents has been discussed in terms of their application to separate CO_2 in gasification streams by means of pressure swing adsorption (PSA) processes.

2. Experimental

2.1. Materials

MAST Carbon has developed and produced carbon adsorbents based on phenolic resin (Novolak). Carbon beads were produced by dissolving a Novolak resin and a curing agent (hexamethylene tetramine) in ethylene glycol. After dispersion into oil the beads were recovered and the majority of the glycol was removed either by washing or by vacuum drying. This produced a mesoporous resin bead in which the porosity was controlled primarily by the resin to glycol ratio but also by the curing agent content and the glycol recovery process. The resin beads were then carbonized and activated to generate the micropore structure. To explore the influence of porosity on CO_2 adsorption three sets of carbons (microporous, micro/mesoporous and micro/macroporous) each comprising examples of low (~ 600 $m^2 g^{-1}$), medium (~ 1000 $m^2 g^{-1}$) and high (> 1200 $m^2 g^{-1}$) surface area were prepared and tested. A total of nine carbons were tested in this work and denoted as MC-X-Y where "X" stands for the resin type and "Y" for the burn-off degree.

The prepared carbons were characterized in terms of chemical composition (elemental analysis) and texture (N_2 adsorption isotherms at -196 ºC).

2.2. High pressure adsorption measurements

CO_2 adsorption at high pressures was evaluated in two apparatus, volumetric and gravimetric. In addition, H_2 high pressure adsorption isotherms were evaluated in the gravimetric apparatus to assess the selectivity of the carbons towards CO_2. The adsorption isotherms were determined at ambient temperature and carbons were outgassed prior to any measurement.

2.2.1. Volumetric method: dual limb differential pressure apparatus

Equilibrium uptake measurements have been conducted in a dual limb differential pressure apparatus [6] at up to 4.1 MPa pressure at ambient temperature (30 °C). Briefly, the system comprises of two identical limbs, monitored using a differential pressure transducer ± 0.5 MPa operational range (accuracy 0.1 %). The volume of the system was calibrated by attaching sample cells of known volume and performing helium expansions, from which the

reservoir volumes were calculated. The temperature of the enclosure was maintained at a constant 30 ± 0.1 °C using a heat-cool control system. Three adsorbent pre-treatment conditions were used: as received, dried at 150 ºC for 1 hour and dried at 150 ºC for 1 hour with partial vacuum (0.001 kPa). I this way the influence of pre-treatment conditions on the CO_2 adsorption capacity was evaluated.

2.2.2. Gravimetric method: magnetic suspension balance

In this method the change of the weight of a sorbent sample due to adsorption of molecules from a gas is observed. High pressure adsorption isotherms were measured in a Rubotherm-VTI magnetic suspension balance at ambient temperature and under static conditions. CO_2 and H_2 adsorption isotherms were determined up to 3 and 4 MPa, respectively. Prior to any measurement the samples were outgassed at 100 ºC under high vacuum (~ 10^{-7} kPa) for 120 min. Equilibrium weights were achieved in 15-30 min. Buoyancy effects were corrected by means of He adsorption.

3. Results and discussion

The elemental analysis of the prepared carbons and basic textural parameters calculated from the N_2 adsorption isotherms at -196 ºC are included in Table 1. The total pore volume (Vp) was estimated from the N_2 adsorbed volume, as a liquid, at a relative pressure of approximately 0.99 and the apparent surface area (S_{BET}) from the BET equation applied to the N_2 adsorption isotherms in the relative pressure range between 0.01 and 0.1.

Table 1 Characteristics of the prepared carbons

Samples	Elemental analysis (wt.%, daf)				N_2 adsorption at -196 ºC	
	C	H	N	O*	V_p ($cm^3\ g^{-1}$)	S_{BET} ($m^2\ g^{-1}$)
MC-A-00	95.1	1.7	0.9	2.3	0.02	14
MC-A-22	97.2	0.4	1.2	1.2	0.35	851
MC-A-38	97.2	0.4	1.1	1.3	0.54	1247
MC-B-00	97.1	0.9	0.7	1.3	0.61	730
MC-B-22	97.8	0.3	1.0	0.9	0.82	1112
MC-B-40	98.0	0.3	1.0	0.7	1.21	1722
MC-C-00	95.6	0.7	0.7	3.0	0.48	640
MC-C-20	97.4	0.4	0.9	1.3	0.71	1055
MC-C-30	97.6	0.3	0.8	1.3	0.96	1377

* Calculated by difference; daf: dry ash free basis

All MC carbons present similar elemental analyses characterized by carbon contents greater than 95 wt.% and nitrogen contents around 1 wt.%. The oxygen and hydrogen contents decrease with the activation step although there are not substantial differences between the oxygen and hydrogen contents of samples in the same MC series obtained at two degrees of burn-off. With respect to the textural development, it can be observed a significant increase in V_p and S_{BET} of the activated samples with respect to the respective un-activated ones. In addition, the greater the burn-off degree the higher the V_p and S_{BET} values. Maximum V_P of 1.21 $cm^3\ g^{-1}$ and S_{BET} of 1722 $m^2\ g^{-1}$ were obtained for MC-B-40. These three series of adsorbents present a wide range of textural properties. All produced MC carbons are microporous, as can be deduced from the great S_{BET} values of the activated samples, but for MC-B and MC-C the higher V_p values may only be justified by the presence of additional meso or macroporosity.

CO_2 adsorption capacity determined by the volumetric dual limb apparatus is observed to be dependent upon outgassing conditions with the greatest adsorption capacity achieved by drying and vacuum treatment of the

adsorbents. However, appreciable uptake is still achieved from atmospheric pressure with or without drying of the sample (Figure 1). The shape of the adsorption isotherms are also dependent upon sample outgas conditions, with the decrease in adsorption capacity being more pronounced at lower pressure (Figure 1). The isotherm shape is important for PSA operation and determines the possible cyclic PSA capacity that can be achieved [7].

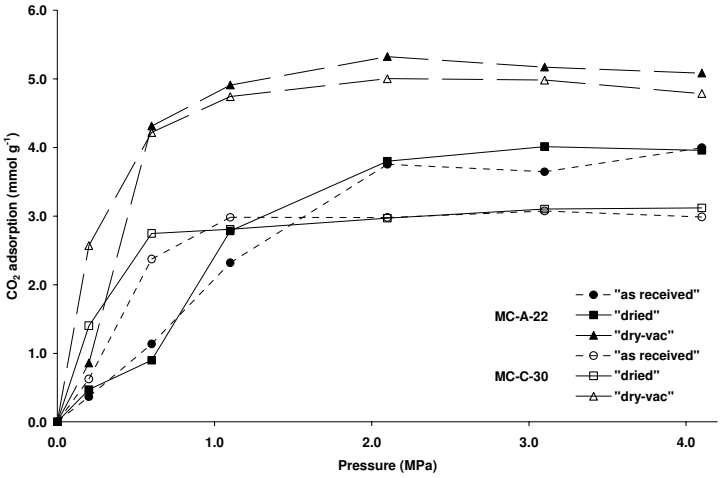

Figure 1. Adsorption isotherms for MC-B-22 and MC-C-30 for the three different analysis conditions..

Figure 2 presents isotherms for all the adsorbents tested from drying and vacuum pre-treatment. Equilibrium adsorption capacity is achieved over a range of pressures, from 1 to 3 MPa, for the different adsorbents. Isotherm shape to some extent can be attributed to the textural properties of the adsorbent, with carbons containing a significant amount of mesoporosity (MC-B) continuing to increase in capacity above 2 MPa, whilst predominantly microporous carbons do not (MC-A). This change in isotherm shape agrees with predicted isotherms for materials with simulated micro and mesoporous structures [8] and adsorption isotherms at 273 K [9].

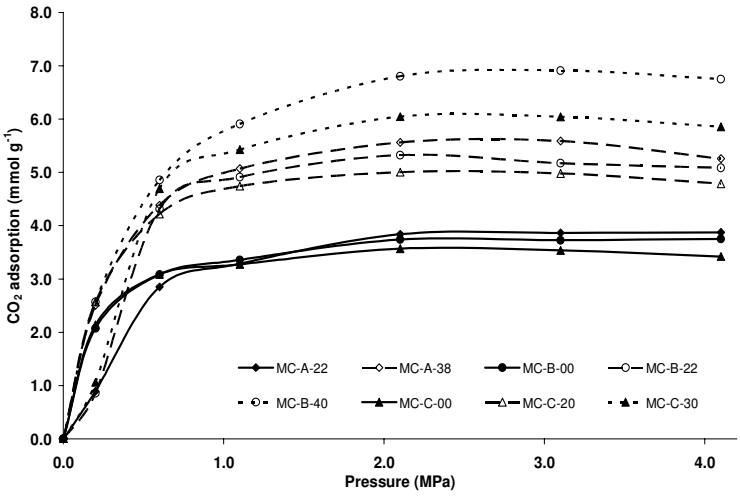

Figure 2. CO_2 adsorption isotherms of adsorbents tested from “dry-vac” pre-treatment

The variation of equilibrium CO_2 uptakes at 4.1 MPa with BET surface area for the carbons tested are shown in Figure 3. As a general trend CO_2 adsorption capacity increases concomitantly with surface area / degree of activation, which in turn results in an increase in microporosity. MC-B-40 adsorbent has the best performance on a mass basis of all of the materials presented.

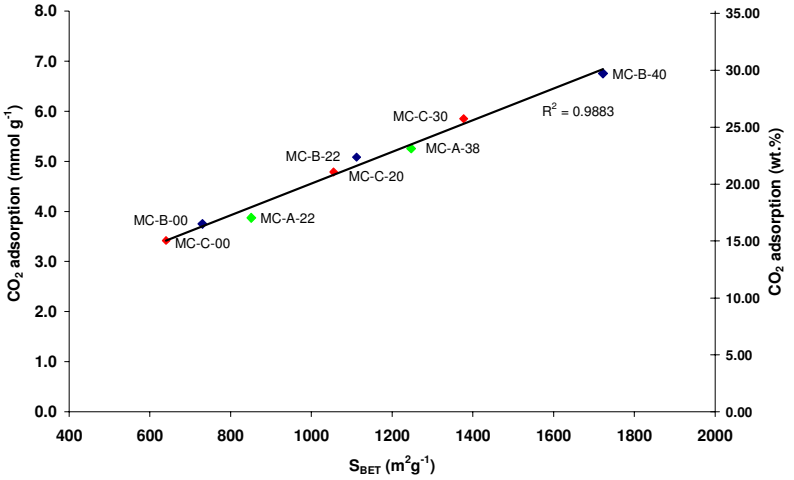

Figure 3. Relationship between CO_2 adsorption capacity, at 4.0 MPa, and BET surface area.

High pressure CO_2 and H_2 adsorption isotherms at ambient temperature and up to 3 and 4 MPa, respectively, determined in the magnetic suspension balance are presented in Figure 4. The shape of the isotherms suggests that interactions adsorbate-adsorbent are different for CO_2 and H_2. The presence of a noticeable elbow in the CO_2 adsorption isotherms at low pressures ($p < 1$ MPa) may imply specificity in the CO_2-carbon interaction. CO_2 uptake is significantly greater than H_2 uptake for all tested carbons. This fact clearly evidences the selectivity of the adsorbents towards CO_2.

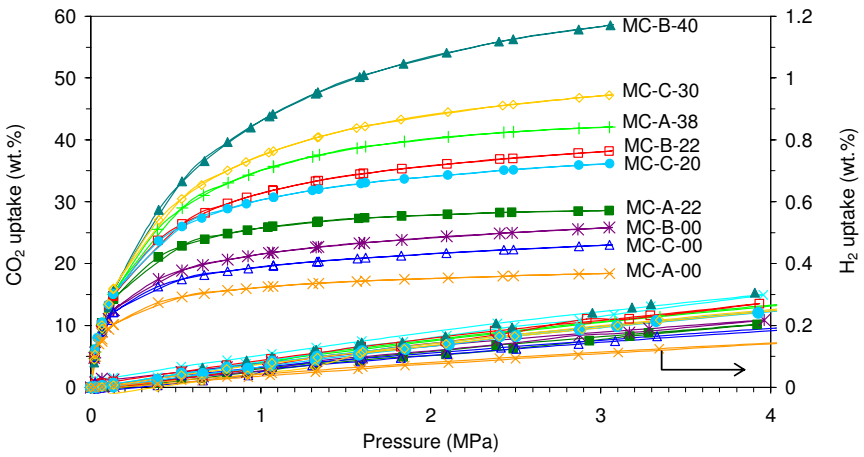

Figure 4. High pressure CO_2 and H_2 adsorption isotherms evaluated in the gravimetric apparatus.

Comparing the behavior of the series of carbons to adsorb CO_2 it can be observed that MC-B carbons present the better performance with MC-B-40 showing the greatest CO_2 uptakes along the tested pressure range. The maximum CO_2 adsorption capacity is attained for this sample. Globally it is observed that the higher the percentage of activation the greater the CO_2 uptake, being the un-activated samples the ones with the lowest CO_2 adsorption capacities and with the most pronounced low pressure elbows. H_2 adsorption is very poor for all tested samples (< 0.3 wt.%), there being minor differences in the performance of the carbons. MC-B-40 presents the highest CO_2 and H_2 adsorption capacities: 58 wt.% at 3 MPa for CO_2 and 0.3 wt.% at 4 MPa for H_2. Therefore, the observed differences in CO_2 and H_2 adsorption suggest that applicability of these carbons for CO_2/H_2 separation processes, particularly at high pressures (p > 1 MPa), could be envisaged.

CO_2 adsorption capacities, in molar basis, attained at low, medium and high pressures by gravimetric analysis have been summarized in Table 2. It can be observed that there is a considerable increase in CO_2 adsorption for the activated carbons in the pressure range between 0.1 and 1.3 MPa. Capacities at 1.3 MPa of the carbons activated to the highest burn-off degree in each series are three times those achieved at 0.1 MPa. This significant difference clearly suggests that PSA processes to capture CO_2 from gasification streams would be feasible for these carbons.

Moreover, CO_2 adsorption capacities estimated by gravimetric analysis are in all cases greater than those evaluated by volumetric analysis. These differences become more apparent at higher pressures. The different outgassing conditions, more stringent in the case of the magnetic suspension balance, could result in an underestimation of the adsorption capacity evaluated in the dual limb. In addition the adsorption isotherms were determined at 30 ºC in the dual limb and at 25 ºC in the magnetic suspension balance, higher temperatures acting to the detriment of the adsorption.

Table 2 CO_2 adsorption capacities at low, medium and high pressures determined with the magnetic suspension balance

Samples	CO_2 adsorption capacity (mmol g^{-1})		
	0.1 MPa	1.3 MPa	3 MPa
MC-A-00	2.1	3.8	4.2
MC-A-22	2.9	6.1	6.5
MC-A-38	3.0	8.5	9.6
MC-B-00	2.5	5.1	5.9
MC-B-22	3.0	7.6	8.7
MC-B-40	3.0	10.8	13.3
MC-C-00	2.5	4.6	5.3
MC-C-20	3.0	7.2	8.2
MC-C-30	3.1	9.2	10.7

Conclusions

Nine carbons with tailored textural properties have been developed and produced by MAST Carbon using a phenolic resin as precursor material. These carbons have been tested for CO_2 adsorption at high pressures (pre-combustion CO_2 capture) by means of a dual limb differential pressure apparatus (volumetric) and a magnetic suspension balance (gravimetric). Maximum CO_2 adsorption capacity of 58 wt.% (13 mmol g^{-1}) at 3 MPa was attained. In addition, carbons showed great selectivity to CO_2 with maximum H_2 uptakes of 0.3 wt.%.

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