ACTIVATED CARBON MONOLITHS WITH HIERARCHICAL PORE STRUCTURE FROM TAR PITCH AND COAL POWDER FOR THE ADSORPTION OF CO_2, CH_4 AND N_2

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Abstract

Activated carbon monoliths with hierarchical pore structures were prepared from petroleum tar pitch and powdered coal in a low pressure foaming process with potassium hydroxide activation. The effects of coal to tar pitch ratio and of the amount of potassium hydroxide on the stability of tar pitch during the foaming process, the product's density and the micropore structure were studied. The carbon monolith prepared with adding 50 %wt coal to pitch retained the shape of the cylindrical foam mould. This carbon monolith featured an open-cell structure with cell widths of around 2 μm and a well-developed microporosity that presented a BET specific surface area of 1044 $m^2 \cdot g^{-1}$. The apparent density of this structure was 0.42 $g \cdot cm^{-3}$. The adsorption capacity of the carbon monolith for CO_2, N_2 and CH_4 were evaluated by the volumetric sorption method at pressures up to 130 kPa and by a gravimetric sorption method for pressures up to 4500 kPa. At 298 K and pressures close to 3500 kPa the adsorption capacities of the carbon monolith prepared with 50 %wt coal to pitch were 7.398 $mol \cdot kg^{-1}$ CO_2, 5.049 $mol \cdot kg^{-1}$ CH_4 and 3.516 $mol \cdot kg^{-1}$ N_2. The sorption results suggest these activated carbon monoliths have potential as monolithic adsorbents for gas separation or storage applications.

1   *Introduction*

Carbon foams are sponge-like carbonaceous materials with cellular microstructures and hierarchical pore structures that may be attractive for numerous applications including as high temperature insulation, electrodes and catalyst supports [1, 2]. For packed reactors and adsorbent towers, some potential advantages of structured foams and honeycomb-type monoliths over random packings (e.g extruded pellets, granules, powders) are lower pressure drop and high bed porosity, which allow operation of the bed at high superficial velocities [3-6]. Furthermore, an open cellular foam structure may allow improved radial mixing of fluids, which leads to improved heat and mass transfer, compared to pellets or honeycomb monoliths that typically consist of linear macrochannels. Carbon foams also facilitate operation at low contact time (fast periodic processes) as an adsorbent in the gas separation or storage applications. However, to realise the potential advantages of carbon foams in adsorption and catalyst-support applications there is a need to improve production methods to obtain foams with high specific surface area, controlled microporosity and high adsorbent density [7].

Carbon foams have been prepared from coal and petroleum tar pitch [8], polymeric precursors [9], sucrose [1, 10] and biomass materials [11, 12]. Petroleum tar pitch is one of the most commonly used raw materials in the carbon manufacturing industry due to its high carbon content, low price, availability and properties that allow a variety of carbon structures to be produced [13]. Typically carbon foams produced at low pressures from pre-treated pitch without any additional foam stabilization steps contain large pore volumes after carbonization but have low bulk density [13-17]. To use these foam materials in an adsorption process, their concentration of adsorbent sites in the adsorption bed needs to be enhanced (if carbon foams are to be competitive with pellets or granular packed beds). One approach to improve the

adsorption capacity of foams or monoliths is to coat a high surface area adsorbent on the foam surface [18]. Another approach is to design composite foam materials consisting of carbon filler particles, such as coal, graphene or carbon nanotubes, and the foam phase [19-21]. Filler particles may be selected to serve multiple functions in the composite foam as high surface area particles can provide additional adsorption sites, modify the density of the produced foam, and act to stabilize the pitch in low pressure foam preparation processes. In this context, the term stabilisation of the foam refers to restriction of bubble growth in the pitch during heat treatment to control the expansion and prevent overflow from the foaming mould (others have used the term *stabilisation* in reference to maximising bubble size).

In this study, we prepared activated carbon monoliths (ACM) with foam-like features from petroleum tar pitch at ambient pressure and used coal powder to stabilize the liquified pitch, and so prevent overflow of pitch from a foam mould during the high temperature foaming process. The effect of coal to pitch ratio on foam morphology and micropore development was investigated. Activation of the carbon monoliths with KOH was also investigated as a method to increase the surface area of the monolith for use in gas adsorption processes. The potential of the pitch + coal derived ACMs with hierarchical pore structure as adsorbents for separation of mixtures containing CO_2, N_2 and CH_4 using PSA were evaluated by pure fluid adsorption measurements at pressures up to 4500 kPa. The separation of $CO_2 + N_2$, $CO_2 + CH_4$ and $CH_4 + N_2$ mixtures represent challenging industrial separations in carbon dioxide capture from combustion flue gases and in liquefied natural gas production plants. We report here a preliminary screening of the ACMs for gas separation applications based on pure fluid adsorption measurements and predictions from Toth and Multi-site Langmuir isotherm models. Measurements of equilibrium and kinetics of adsorption from binary gas mixtures will form part of a future study.

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2 *Experimental methodology*

2.1 Materials and pre-treatment of tar pitch

Paving grade Bitumen Class 170 (BP Bitumen Australia), which has a softening point of 320 K [22], was first pre-treated to adjust its viscosity and degree of anisotropy, because these properties are reported to be critical in the formation of stable foams [15]. The pitch modification was performed in two steps: (1) acid initiated polymerisation and de-volitization, followed by (2) thermal treatment. In the acid treatment step, 15 M nitric acid was added drop wise to the melted pitch at 393 K using a low stirring speed (150 rpm). The polymerisation and de-volatilization reactions between the nitric acid and the hydrocarbon pitch components lead to evolution of gases, which expand to swell the pitch. Simultaneously, the pitch viscosity increases with the increase in the average molecular weight of the hydrocarbons in solution and the pitch temperature must be increased to continue stirring the fluid. On this basis, we defined the end-point for the acid treatment step to be when the pitch's viscosity increased to such a point that the pitch could no longer be stirred at 433 K. In the thermal treatment step, the acid-treated pitch (TP) was heated to 623 K and held at this temperature for 2 hours. The product obtained after this two-step treatment process was a solid and brittle tar pitch at room temperature. This solid was ground and sieved to a particle size less than 250 µm.

Coal from the Blackwater coal mine (Queensland, Australia) was ground and sieved to a particle size less than 250 µm to be used as a foam stabilizer.

2.2 Production of activated carbon monolith

The acid-treated tar pitch and the coal were mixed at TP:coal weight ratios of 0, 0.5, 0.8 and 1. This foaming precursor was further treated by mixing it with 50 mL aqueous solutions of KOH (KOH:precursor weight ratios of 0.25, 0.5. 0.75 and 1) at 353 K for 2 hours. The KOH-

treated TP + coal was dried in air for 12 hrs at 393 K. The dried KOH-treated TP + coal was placed in a 1-inch diameter by 1-inch tall quartz cylindrical crucible fitted with a quartz lid (see Figure 1); the weight of this lid contained the expanding foam but was the crucible was not gas tight. Foaming and activation were carried out by heating the sample under a flow of Argon in a horizontal tube furnace at 10 K·min^{-1} to 1073 K. The maximum temperature was held for 1 hour. The product obtained from the foaming and activation process was washed with 0.2 M HCl, then rinsed with water and filtered several times until the filtrate pH was close to 7. Table 1 shows the labels used to describe the activated carbon monoliths produced at various TP:coal and KOH:precursor ratios.

The yield of ACMs was calculated based on the sample weight (TP + coal) before activation, m_i; and the product weight after the activation process (after washing), m_f using the following equation:

$$Yield\,(\%) = \frac{m_f}{m_i} \times 100 \tag{1}$$

2.3 Characterization of carbon monolith structure

The morphology of the ACMs was examined by scanning electron microscopy (SEM) using a JSM-6100 (JEOL Ltd., Japan). The carbon monoliths were dried overnight at approximately 378 K under vacuum prior to SEM measurements. Proximate analysis by thermogravimetric analysis (TGA, Perkin Elmer STA 6000) according to ASTM D 7582-10 was used to determine the volatile matter, fixed carbon and ash content of the carbon monoliths.

A Micromeritics TriStar II 3020 analyser was used to measure CO_2 adsorption isotherms at (273 and 303) K and N_2 sorption isotherms at 77 K to elucidate the textural properties and adsorption capacity of the ACMs. The ACMs were degassed at 473 K at a pressure of 10^{-5}

torr for 24 hours prior to sorption measurements. The Brunauer Emmett Teller (BET) method was used to determine specific surface areas at relative pressures in the range of $P/P_0 = (0.05 - 0.30)$. Total pore volumes were estimated at $P/P_0 = 0.98$ and micropore volumes were estimated applying the Dubinin-Astakhov (D-A) equation with the 77 K N_2 isotherms and 273 K CO_2 isotherms [19-20]. Micropore surface areas were calculated from the 273 K CO_2 isotherms using the Dubinin-Radushkevich (D-R) equation. The pore size distributions (PSD) were calculated from the N_2 and CO_2 isotherms using a density functional theory model (DFT) algorithm for carbon slit pores supplied with the TriStar II 3020. Pore widths up to 60 μm were characterised by mercury porosimetry at pressures in the range (0 – 413685.44) kPa collected on a Micromeritics PoreSizer 9320.

The piece or apparent density of the monoliths was measured at room temperature using the sample weight and the geometric dimensions of the monolith [23]. True densities of ACMs were measured using helium pycnometry (Accupyc II 1340 pycnometer). Compressive strengths of the ACMs were measured in a uniaxial compression test with an INSTRON 5584 computer-controlled material testing system operated at a crosshead speed of 0.5 mm·min^{-1} [1].

2.4 Gravimetric Measurement of Adsorption Equilibrium

Adsorption isotherms of pure fluids CH_4, CO_2 and N_2 on the ACM KOH0.5TP50 were measured at (298, 313 and 323) K and pressures up to 4500 kPa using a BELSORP-BG high-pressure gas adsorption instrument (BEL, Japan). Prior to adsorption measurements the carbon monolith was degassed in-situ at 473 K for 24 hours. The BELSOP-BG is equipped with a magnetic floating balance (RUBOTHERM, Germany) to measure the weight of the sample continuously through an adsorption experiment. The balance is attached to a suspended electromagnet coupled with a permanent magnet in the measurement section. The sample basket is connected to the permanent magnet and the volume of the magnetic

coupling section is constant excluding the sample cell. The apparent weight of sample, m_s^*, measured at high pressures was corrected for the buoyancy effect of the fluid using Archimedes' Principle as in Equation 2:

$$m_s = m_s^* + \rho_f V_s \qquad (2)$$

where m_s is the true weight of solid adsorbent measured under vacuum (this mass is not influenced by buoyancy) and V_s is the volume of solid adsorbent determined by helium pycnometry. The density of the fluid ρ_f is determined at measurement conditions by a force balance on a sinker weight inside the instrument. The weight measurement resolution and reproducibility of the mass balance are 10^{-5} g and $\pm 3 \times 10^{-5}$ g (STD) and the density resolution and accuracy of the unit are 2×10^{-6} g·cm^{-3} and $\pm 2 \times 10^{-5}$ g·cm^{-3}, respectively.

3   Results and discussion

3.1 Effect of tar pitch to coal ratio on pore structure

3.1.1   Development of macrostructure in the monoliths

An objective of the synthesis experiments in this study was to produce ACMs with a mechanically stable, open cellular foam structure in the shape of the crucible mould. In experiments with KOH-treated tar pitch and no added coal particles, a porous carbon foam (KOH0.5TP100) was recovered from the tube furnace after carbonisation at 1073 K. However, it was difficult to control the foaming process of the TP because in the synthesis of KOH0.5TP100 the pitch overflowed the crucible during heat treatment and the carbon foam recovered from the tube did not retain the shape of the crucible mould (see Figure 1d). The addition of coal particles to the treated pitch was found to be an effective method to stabilise the foam composite and a typical monolith produced from a TP + coal synthesis experiment is shown in Figure 1a-c (KOH0.5TP50).

Figure 2 shows SEM images of KOH-activated coal particles that were produced to quantify any surface area generated by activation of the coal to the total porosity in the ACMs. The coal particles have some cracks and surface pits, as seen in Figure 2b, and the BET surface area of activated coal measured from the N_2 sorption analyses was 3.79 $m^2 \cdot g^{-1}$. However, the SEM images show that the coal powder alone does not contain any large open, foam-like channels or cells. In contrast, Figure 3a-c and Figure 1S (Supporting Information) show wide openings on the surface of agglomerates from the monolith and the development of a cellular structure in the tar pitch phases of KOH0.5TP50. The SEM images of the foamed tar-pitch KOH0.5TP100 (Figure 3f as well as Figure 2S) also feature large open channels. In Figure 3a-b coal particles coated with a foamed pitch can be identified. Around these coal particles two types of macropores are observed: (1) the interstitial void spaces between coal particles that have been partially filled by the pitch residue and (2) a cellular pattern of open channels with throats diameters less than about 500 nm wide. These macroporous features are consistent with the pore size distributions obtained by mercury porosimetry (Figure 4). Pyrolysis of the pitch and release of volatile components can continue to create new pores in foam walls after the foam has solidified [8, 24] and this phenomena is evidenced by the openings in the cell walls observed in Figure 3f and Figure 2S. The SEM and mercury porosimetry results, together with the physical forms of the ACMs shown in Figure 1, in our experiments with TP + coal powder are consistent with results reported by others on the effect of additives during carbon foam production [25, 26].

Based on these observations, we propose the mechanism shown in Figure 5 to describe the role of coal particles in the stabilisation of molten pitch during low pressure foaming. The first significant change in properties of the pitch occurs when the pitch begins to melt at temperatures above the mixture's softening point. In both TP and coal + TP experiments the melting of pitch leads to a volume reduction as the voids between pitch particles and pitch-

coal particles are filled. As temperatures are increased further, the first bubbles of gas form from volatiles coming out of the pitch solution and then at higher temperatures gas evolves from polymerisation and pyrolysis reactions. During this stage of foaming, the coal particles may be nucleation sites for bubbles, but the coal additives also increase the density and viscosity of the pitch mixture [25, 26] which act to restrict bubble growth (there may also be some steric effects of bubbles confined between coal particles). Gas bubbles in a less viscous mixture that doesn't contain coal particles are more mobile, thus more likely to collide and agglomerate, and bubble growth by thermal expansion of the gas is less restricted by viscous forces. However, there may be other contributing factors beyond the scope of this current study that could also affect the expansion and coalescence of bubbles in the pitch foam. For example, other factors that could affect the foaming process and should be investigated in more detail include: (a) catalysis of the pitch through polymerisation reactions at active sites on coal particles, (b) the coal particles acting as ligaments – as Inagaki et al. described the phenomena - in the cell walls [25], (c) the size distribution of coal particles, and (d the rate of heating the foam. Testing the catalytic hypothesis is beyond the scope and data presented in this paper, but in general an enhancement of the rate of polymerisation should assist in control of the foaming process.

3.1.2   *Bulk properties of the activated carbon monoliths*

Table 2 shows the apparent density, true density and mechanical strength of ACMs produced with 50 and 80 wt.% tar pitch with coal powder. The apparent density and strength of sample KOH0.5TP100 could not be measured as this carbon overflowed the crucible and consequently did not keep the desired cylindrical form. The apparent density of ACM KOH0.5TP50 was 0.42 g.cm^{-1} and this value is comparable to medium density carbon foams reported in literature [12, 27]. Note, the KOH activation method used in this study will reduce the apparent density as well as true density of the foam due to the development of

microporosity in the carbon structure. The true density of KOH0.5TP50 measured by Helium pycnometry was 2.18 g·cm^{-3} and this value is typical of other activated carbons with similar pore structure that reported in the literature [26]. Higher true density of KOH0.5TP80 compared to the true density of KOH0.5TP50 shows that after activativation and removal of volatiles, tar pitch has higher true (skeletal) density compared to coal. However the apparent density of KOH0.5TP80 is significantly lower than that the density of KOH0.5TP50 and this result is attributed to the effect of the coal particles on bubble growth in the sample with a higher ratio of coal to tar pitch (i.e. KOH0.5TP50) during foaming.

The compressive strengths of KOH0.5TP50, KOH0.5TP80 and KOH0.75TP50 are listed in Table 2. The measurements on the INSTRON 5584 confirm that the KOH0.5TP50, which was the most robust material when handled, had an adequate mechanical strength (0.964 MPa) for use in a packed adsorbent tower. This strength is similar to the strength of other carbon foams reported in the literature [20, 26]. Carbons prepared with KOH to precursor ratios greater than 0.5 were not as strong, and at a KOH ratio of 1 the carbon crumbled when washed in HCl. The effect of KOH on ACM pore structure is discussed further in Section 3.2.

Table 3 summarises the volatile matter, fixed carbon and ash concentrations of the Blackwater coal, the KOH-activated coal and the carbons produced with 50 and 100 wt.% tar pitch. The yields of carbon from the precursors are also reported in Table 3. The yield of the TP foams is significantly lower than that for the KOH-activated coal (67.6%), but this result is expected because the tar pitch loses some of the volatile hydrocarbons during the foaming and activation process at high temperatures [15].

3.1.3 Micropore development in activated carbon monoliths

N_2 sorption isotherms for ACMs prepared with a KOH to precursor ratio of 0.5 are shown in Figure 6 and a summary of pore structure properties is provided in Table 1. All the KOH0.5-carbons exhibit features of Type I isotherms with a large uptake of N_2 in micropores (narrower than 2 nm) at $P/P_0 < 0.1$ [28] and the microporosity increases with the ratio of TP to coal. In addition to micropores, each ACM shows an increase in adsorbed volume at $P/P_0 > 0.9$ and this volume can be attributed to condensation of liquid N_2 in macropores. The activated coal (KOH0.5TP0) does not show this feature of the foam macrostructure.

The BET surface area of the carbons were in the range $(725 – 1372)$ $m^2 \cdot g^{-1}$ with the KOH-activated coal having the lowest BET surface area and KOH0.5TP100 the highest surface area. The precursor Blackwater coal had a surface area of less than 5 $m^2 \cdot g^{-1}$ and the data in Table 1 confirms KOH activation can develop significant volumes of new porosity in coal. Nonetheless, the ACMs prepared with TP had surface areas more than 300 $m^2 \cdot g^{-1}$ greater than the KOH-activated coal.

The micropores in the ACMs are centred around 1 nm according to the DFT pore size distributions derived from N_2 adsorption analysis at 77 K (Figure 7). This pore width is typical of KOH ACs and the results indicate that the micropore development is mostly due to the KOH activation process. As the sorption of N_2 at 77 K in narrow micropores is kinetically limited [29], we also probed the carbon structures with CO_2 at 273 K and the CO_2 adsorption isotherms on the prepared ACMs are presented in Figure 8a. In addition, narrow micropore volume of the ACMs measured by CO_2 are included in Table 1. The CO_2 data also indicate that an increase in the tar pitch to coal ratio leads to development of both narrow and wide micropores. Micropore size distributions of ACMs resulted from equilibrium isotherms of CO_2 sorption at 273 K are included in the Supporting Information (Figure 3S).

3.2 Effect of KOH ratio on activation

The results in Section 3.1 suggest that the development of the macro-cellular structure of the monolith can be controlled by the TP:coal ratio, while the development of microporosity is mostly dependent on KOH activation. Therefore, we studied the effect of the ratio of KOH to tar pitch on ACM structure in more detail. The carbon monolith KOH0.25TP50 had a compact structure and was more difficult to break by hand than the KOH0.5 ACMs described in Section 3.1. The micropore volume and DR specific surface area of KOH0.25TP50 determined from the 273 K CO_2 sorption isotherms (Figure 8a) were $0.05\,cm^3{\cdot}g^{-1}$ and $166.4\,m^2{\cdot}g^{-1}$, respectively. We made several attempts to measure N_2 sorption isotherms on KOH0.25TP50 but equilibrium was not achieved in a practical time, which suggests that KOH0.25TP50 has a low degree of activation, a lack of pore development and that the foam cells may be well-connected [30]. Otherwise, the micropore volume developed during heat treatment increased with the ratio of KOH to carbon precursors – this is the result expected according to the literature on carbon activation (for example [31, 32]). The highest BET specific surface area of $1666\,m^2{\cdot}g^{-1}$ was obtained for KOH1TP50, but we were unable to produce a monolithic carbon with this high KOH concentration and the carbon crumbled when the sample was washed in HCl.

3.3 Adsorption equilibrium capacities of CO_2, CH_4 and N_2

Figure 8b shows the capacities for CO_2 in the measurements made with the Tristar II 3200 at pressures up to 140 kPa; these CO_2 capacities are consistent with other high surface area carbons reported in the literature (for example a summary of CO_2 capacities is provided in Rufford et al. [33]). We acknowledge that other adsorbents including amine-impregnated or treated carbons, and metal-organic frameworks (MOF) [34] have been reported with larger CO_2 capacities. However, the ACMs in our study do show higher CO_2 capacities than other reported carbon foams [14, 35].

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Although KOH1TP50 and KOH0.5TP100 had the highest measured capacities for CO_2 at 140 kPA, these samples did not retain the monolith form during the foam production process and so were not considered in the selection of an ACM for the high pressure adsorption studies. Instead we selected KOH0.5TP0.5 as this ACM had a good density and mechanical strength (Table 2); in any case at 273 K and 120 kPa the difference between CO_2 sorption capacities of KOH0.5TP50 and KOH1TP50 was less than 15 %. Low pressure adsorption measurements of CH_4 on the ACMs using the TriStar II could not be made due to flammable gas safety rules in the lab where the TriStar II is located. However, experimental and theoretical studies suggest that the optimum pore size for CH_4 adsorption is in the range of $(0.7 - 1.0)$ nm [36] and thus we considered that KOH0.5TP50 may also be a potential adsorbent for CH_4.

Absolute adsorption capacities for CH_4, CO_2 and N_2 on carbon monolith KOH0.5TP50 measured with the Belsorp apparatus at (298, 313 and 323) K and pressures in the range $(25.93 - 4500)$ kPa are reported in Table 4. These data are presented graphically in Figures 9 – 11; the shape of each of these isotherms corresponds to Type I in the IUPAC classification. The measured CO_2, CH_4 and N_2 adsorption capacities on KOH0.5TP50 are comparable to carbon adsorbents with similar pore structures reported in the literature [10, 37-40]. For example, at 298 K and a pressure of about 100 kPa Narasimman et al. reported approximately 2.5 mol.kg^{-1} CO_2 and approximately 100 kPa adsorbed on a carbon foam produced from molten sucrose [10] and we measured 3.202 mol.kg^{-1} CO_2 adsorbed on KOH0.5TP50.

Two temperature-dependent equilibrium adsorption models – the Toth model [41] and the Multisite Langmuir (MSL) model [42] - were tested to determine their ability to predict the measured adsorption capacities of CH_4, CO_2 and N_2 on KOH0.5TP50 across the range of pressure and temperature conditions measured in this study. The models were:

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Toth model

$$C_{\mu i}^{Toth} = C_{\mu si}^{Toth} \frac{b_i P}{\left[1 + (b_i P)^{t_i}\right]^{1/t_i}} \quad \text{with} \quad b_i = b_{0,i} \exp\left(\frac{-\Delta H_{Toth,i}}{RT}\right) \quad (3)$$

Multisite Langmuir model

$$C_{\mu i}^{MSL} = C_{\mu si}^{MSL} b_i P \left[1 - \left(\frac{C_{\mu i}^{MSL}}{C_{\mu mi}^{MSL}}\right)\right]^{a_i} \quad \text{with} \quad b_i = b_{0,i} \exp\left(\frac{-\Delta H_{MSL,i}}{RT}\right) \quad (4)$$

where R is the molar gas constant, P and T are the measurement pressure and temperature, and $\Delta H_{calc,i_s}$ is the isosteric heat of adsorption at zero loading. In the regression of each model, $\Delta H_{calc,i}$ was treated as an adjustable parameter together with the empirical parameters ($C_{\mu si}^{calc}$, $b_{0,i}$, t_i or a_i). The parameters t_i and a_i are used to characterise the heterogeneity of the adsorption sites in each model, but these were treated as adjustable parameters in the regression. The best fit parameters of each of Equation (3) and (4) were determined using a least-squares regression analysis to minimize the standard deviation (SD) between the measured capacities, C_μ, and the capacities $C_{\mu si}^{calc}$ calculated with each model (

$SD = ((1/N)\Sigma(C_{\mu i}^{meas} - C_{\mu i}^{calc})^2)^{1/2}$ where N is the number of data points regressed).

The optimized parameters of Equations (3) and (4) resulting from the regression of each of the models are listed in

Table 5. The pure gases adsorption capacities predicted using the best fit parameters are shown as solid lines in Figures 9a, 10a and 11a for CH_4, CO_2 and N_2, respectively. The deviation of the Toth and Multisite Langmuir model calculated capacities from the measured data $(C_\mu^{meas} - C_\mu^{calc})$ are presented in Figures 9b, 10b and 11b for CH_4, CO_2 and N_2 respectively. As can be seen in Figures 9b-11b, the Toth model provides a good fit to the adsorption data for all three components with deviations between the measured and the calculated capacities in the range of ± 0.1 mol.kg^{-1}at (298 – 323) K at pressures up to about 2000 kPa. At pressure above 2000 kPA the Toth model still gives reasonable predictions of CH_4 and N_2 adsorption capacities, but is less reliable for the CO_2 adsorption capacities. The MSL model (Eq. (4)) also provides reasonable predictions of adsorption capacities over the analysed pressure range (dotted lines in Figures 9a, 10a and 11a for CH_4, CO_2 and N_2, respectively). However the deviation between the measured and the capacities with the MSL model are larger than with the Toth model.

In addition to the absolute capacity of a potential adsorbent, in gas separation processes the selectivity for one component from the other species is an important adsorbent performance criteria. The equilibrium selectivity calculated from pure gas sorption data can be used as a screening tool to evaluate the potential of novel adsorbents such as the carbon foams reported here for application in separation processes. To evaluate the potential of the foam KOH0.5TP50 for the separation of three gas mixtures $CO_2 + N_2$, $CO_2 + CH_4$ and $CH_4 + N_2$ we calculated ideal selectivities α_{ij} at three temperatures and pressures up to 4000 kPa using the fitted Toth and Multisite Langmuir equilibrium models. The ideal equilibrium selectivity, α_{ij}, can be defined as:

$$\alpha_{ij} = \left(\frac{x_i}{x_j}\right)\left(\frac{y_j}{y_i}\right)_{if\,(y_i = y_j)} \rightarrow \alpha_{ij} = \left(\frac{C_{\mu i}}{C_{\mu j}}\right) \tag{5}$$

where y and x are the mole fraction of component i and j in the vapour and adsorbed phases, respectively. For the example here with equimolar gas mixtures $y_i = y_j = 0.5$. The selectivity of CO_2/CH_4, CH_4/N_2 and CO_2/N_2 as a function of pressure at different adsorption temperatures (298, 313 and 323) K are shown in Figure 4S (Supporting Information). As may be anticipated by the relative shapes of the different sorbate isotherms, the trends in selectivity at higher pressures suggest that the effectiveness of an adsorbent to capture CO_2 does not always increase with increased adsorption pressure. The equilibrium selectivity of KOH0.5TP50 for CO_2 from N_2 is comparable to selectivities reported for other activated carbon-based adsorbents reported in other literature including carbon beads [43], honeycomb monolith [44] and carbon foams [10], but the KOH0.5TP50 selectivity for CO_2 from N_2 is lower than that of amine-impregnated carbon materials. At pressures close to 100 KPa the selectivity of KOH0.5TP0.5 for CO_2 from N_2 was 5.94 and 298 K and increases to 7.25 at 323 K; and at 1000 kPa the selectivities reduced to 2.89 and 3.29 respectively for 298 K and 323 K.

Due to the adsorption capacity of KOH0.5TP0.5 which was $CO_2 > CH_4 > N_2$, the calculated $\alpha_{CO2/CH4}$ was lower than $\alpha_{CO2/N2}$. In addition, $\alpha_{CO2/CH4}$ was in the range 2.19 - 2.23 at 100 kPa and 1.65 - 1.70 at 1000 kPa, that shows it is not as temperature sensitive as $\alpha_{CO2/N2}$ [44, 45]. The selectivity of KOH0.5TP0.5 for CH_4 from N_2 were from 3.27 at 100 kPa and 323 K to 1.39 at 4000 kPa and 298 K. Although, the equilibrium selectivity calculated here from pure gas sorption data can be used as an initial screening tool to evaluate the separation potential of novel adsorbents, this method provides an initial screening only and a rigorous evaluation of PSA processes should consider sorption kinetics as well as equilibrium data.

Conclusions

In this study petroleum tar pitch was used as a precursor to prepare carbon monoliths with hierarchical pore structure and good gas adsorption capacities. The addition of coal particles to the treated-TP was found to be an effective method to stabilise the foam without a need for high pressure treatment as well as to increase the density of adsorption sites in the foam. The carbon foams had an open channel structure with high volumes of micro-, meso- and macroporosity, which characterize a suitable adsorbent for the gas separation or storage applications. The micropore volume created during the KOH activation process increased with the ratio of TP to coal. Increase in KOH to TP+coal ratio up to 1:1 also develops microporosity. However, at chemical to carbon precursor ratios greater than 1:1 we were unable to produce monolithic carbons as the high concentrations of KOH decreased the mechanical strength of resultant carbon monoliths. The carbon monoliths revealed high CO_2 adsorption capacities measured at low pressures (up to 140 kPa) that are comparable to adsorbents reported in literature. High pressure adsorption of CO_2 and CH_4 showed that the prepared carbons have reasonable adsorption capacity.

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Figure captions

Figure 1 Photographs of (a) the crucible used to synthesis activated carbon monoliths, (b) and (c) monolith KOH0.5TP50 and (d) the KOH0.5TP100 that overflowed the crucible.Figure 2 SEM images of KOH activated Blackwater coal (KOH0.5TP0).

Figure 3 SEM images of (a-c) KOH0.5TP50 prepared from mixture of coal and tar pitch and (d-f) KOH0.5TP100 activated carbon foam prepared from tar pitch with no added coal.

Figure 4 Macropore size distributions in KOH0.5TP50 and KOH0.5TP100 determined by mercury (Hg) porosimetry.

Figure 5 Illustration of a low pressure foaming process by bubble growth in tar pitch with and without coal particles as additives.

Figure 6 Nitrogen adsorption isotherms at 77 K on the activated carbon monoliths.

Figure 7 Micropore size distributions of ACMs calculated from 77 K N_2 sorption isotherms using non-local density functional theory algorithm.

Figure 8 Adsorption equilibrium of CO_2 on the produced AC samples measured at (a) 273 K and (b) 303 K using the Micromeritics Tristar II.

Figure 9 (a) Methane adsorption equilibrium of KOH0.5TP50 sample at 298 K, 313 K and 323 K; solid lines, Toth model; dotted lines, multisite Langmuir. (b) Deviations between the measured and the calculated capacities of Toth model, filled symbols; and multisite Langmuir, empty symbols.

Figure 10 (a) Carbon dioxide adsorption equilibrium of KOH0.5TP50 sample at 298 K, 313 K and 323 K; solid lines, Toth model; dotted lines, multisite Langmuir. (b) Deviations

between the measured and the calculated capacities of Toth model, filled symbols; and multisite Langmuir, empty symbols.

Figure 11 (a) Nitrogen adsorption equilibrium of KOH0.5TP50 sample at 298 K, 313 K and 323 K; solid lines, Toth model; dotted lines, multisite Langmuir. (b) Deviations between the measured and the calculated capacities of Toth model, filled symbols; and multisite Langmuir, empty symbols.

Table 1 Preparation conditions and summary of porous textural properties of activated carbon monoliths. BET specific surface area, total pore volume and DR micropore surface determined from N_2 sorption at 77 K. Micropore volume and narrow micropore volume determined from CO_2 sorption at 273 K.

Sample	Coal / (coal+pitch), (%)	KOH / (coal+pitch), (%)	N_2 Adsorption			CO_2 Adsorption	
			BET Surface area $(m^2 \cdot g^{-1})$	Micropore Volume $(cm^3 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	DR Micropore Surface area $(m^2 \cdot g^{-1})$	Micropore Volume $(cm^3 \cdot g^{-1})$
BW Coal	100	0	4.1	-	0.012	-	-
KOH0.5TP0	100	50	725.1	0.32	0.37	999.4	0.36
KOH0.5TP50	50	50	1044	0.46	0.5	1320.1	0.54
KOH0.5TP80	20	50	1265.4	0.52	0.65	1433.9	0.64
KOH0.5TP100	0	50	1372.2	0.63	0.67	1619.6	0.72
KOH0.25TP50	50	25	-	-	-	166.4	0.05
KOH0.75TP50	50	75	1250.9	0.54	0.61	1284.8	0.54
KOH1TP50	50	100	1665.7	0.73	0.86	1716.2	0.87

Table 2   Piece density (or apparent density) by geometric dimensions of monolith disc, skeletal density (or true density) measured by helium pycnometer, and compressive stress of the activated carbon monoliths from tar pitch + coal.

Sample	KOH0.5TP50	KOH0.5TP80	KOH0.75TP50
Piece density (g.cm^{-1})	0.42	0.13	0.24
Skeletal density (g.cm^{-1})	2.18	2.51	1.86
Compressive stress (MPa)	0.964	0.017	0.036

Table 3   Proximate analysis and production yield of raw coal and activated carbon monoliths prepared with 0, 50 and 100 wt.% tar pitch.

Sample	Content			Yield (%)
	Volatile	Fixed Carbon	Ash	
BW Coal	23.5	70.3	6.2	-
KOH0.5TP0	9.2	79.5	11.3	67.6
KOH0.5TP50	16.2	75.7	8.1	59.7
KOH0.5TP100	26.4	72.5	1.1	48.4

Table 4   Methane, carbon dioxide and nitrogen adsorption equilibrium data on KOH0.5TP50 sample at 298 K, 313 K and 308 K.

P (kPa)	C_μ (mol.kg^{-1})	P (KPa)	C_μ (mol.kg^{-1})	P (kPa)	C_μ (mol.kg^{-1})
			CH$_4$		
	298 K		313 K		323 K
28.173	0.621	28.537	0.448	28.986	0.369
59.445	1.050	60.245	0.793	60.682	0.663
100.837	1.459	101.174	1.134	101.073	0.959
200.156	2.123	200.626	1.723	200.676	1.496
399.463	2.903	399.940	2.448	399.876	2.179
699.005	3.560	699.521	3.091	699.955	2.806
999.523	3.962	999.954	3.501	1000.155	3.213
1497.884	4.376	1498.667	3.937	1498.337	3.653
1997.240	4.631	1996.701	4.213	1996.562	3.937
2496.238	4.800	2496.193	4.401	2496.485	4.133
2995.693	4.917	2998.448	4.537	2995.949	4.273
3494.691	4.995	3496.098	4.631	3494.038	4.372
3993.688	5.049	3993.749	4.701	3994.419	4.445
4000.537	5.051	4495.083	4.750	4000.840	4.447
		4500.607	4.750		
			CO$_2$		
	298 K		313 K		323 K
23.935	1.505	25.320	1.140	25.548	0.918
56.734	2.447	57.821	1.890	58.261	1.559
97.483	3.202	98.228	2.529	98.518	2.123
196.075	4.318	197.014	3.551	197.937	3.060
396.509	5.423	396.375	4.669	397.216	4.133
697.344	6.164	697.552	5.508	697.325	4.978
997.935	6.541	997.692	5.967	997.372	5.459
1496.516	6.923	1496.886	6.400	1497.065	5.908
1996.027	7.146	1997.142	6.647	1993.172	6.165
2495.311	7.278	2494.626	6.801	2493.432	6.318
2993.683	7.371	2994.396	6.901	2992.321	6.408
3492.511	7.398	3491.880	6.964	3492.581	6.456
			N$_2$		
	298 K		313 K		323 K
29.795	0.199	29.800	0.117	29.928	0.095
59.855	0.359	60.102	0.225	59.994	0.184
99.952	0.539	100.150	0.353	100.068	0.293
201.495	0.897	201.216	0.634	201.625	0.540
400.248	1.394	400.676	1.058	401.433	0.919
700.600	1.906	699.957	1.517	700.809	1.341
999.673	2.266	1000.215	1.856	999.637	1.660
1497.620	2.693	1498.284	2.269	1498.334	2.057
1997.885	2.991	1998.002	2.571	1998.556	2.351
2495.540	3.212	2496.012	2.801	2495.390	2.576
2996.410	3.382	2994.935	2.981	2995.441	2.757
3494.065	3.516	3494.313	3.127	3494.113	2.903
3993.558	3.621	3993.691	3.245	3993.704	3.024

| 4491.672 | 3.706 | 4493.525 | 3.342 | 4492.836 | 3.124 |
| 4500.854 | 3.707 | 4502.190 | 3.344 | 4500.649 | 3.126 |

Table 5 Best fit parameters of the Toth Model (Eq. 3) and Multisite Langmuir Model (Eq. 4) fitted to the absolute adsorption capacities for CH_4, CO_2 and N_2 measured on the Belsorp BG at 298 K, 313 K and 308 K.

Toth model parameters			
	CH_4	CO_2	N_2
$C_{\mu s}$ / $mol.kg^{-1}$	6.12	8.3	5.3
$b_{\infty i}.10^6$ / kPa^{-1}	0.43	0.02	0.27
$\Delta H_{calc,i}$ / $kJ.mol^{-1}$	23.3	33	21.5
t_i	0.66	0.67	0.66
SD / $mol.kg^{-1}$	0.04	0.08	0.02
Multisite Langmuir model parameters			
	CH_4	CO_2	N_2
$C_{\mu s}$ / $mol.kg^{-1}$	6	8.5	4.92
$b_{\infty i}.10^6$ / kPa^{-1}	0.19	0.012	0.14
$\Delta H_{calc,i}$ / $kJ.mol^{-1}$	25	34.7	22.2
a_i	1.7	2	1.35
SD / $mol.kg^{-1}$	0.09	0.2	0.03