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THE PREPARATION OF ACTIVATED CARBON DISCS FROM TAR PITCH AND
COAL POWDER FOR ADSORPTION OF CO$_2$, CH$_4$ AND N$_2$

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Abstract

We used a pitch foaming process to prepare high surface area activated carbon discs ACD with a relatively high mechanical strength (4.3 MPa) from mixtures of tar pitch and coal powders, with potassium hydroxide as a chemical activator. The two primary parameters investigated in this study were the amount of nitric acid used in the pitch pre-treatment and the size of the coal particles (0 – 53 µm, 150 – 250 µm, and 355 – 550 µm). The pre-treatment of the pitch was observed to be critical in the production of the carbon discs and in this study the preferred ratio of 15 M nitric acid to pitch in weight was 17/100. The coal size of 0 – 53 µm produced the activated carbon discs with the highest gas adsorption capacity, which we attribute to the stabilization of the pitch foaming process. Equilibrium adsorption capacities of CO$_2$, N$_2$, and CH$_4$ on the carbons were measured by a gravimetric sorption method at pressures up to 3500 kPa. At 298 K the adsorption capacities of carbon foam disc prepared with coal particle size of 0 - 53 µm and pitch pre-treated with 18 ml HNO$_3$ per 100 g pitch were 3.08 mol/kg N$_2$, 5.48 mol/kg CH$_4$ and 8.88 mol/kg CO$_2$ at about 3500 kPa.

Key words: activated carbon, chemical activation, coal particle size, pitch, carbon foam
1 Introduction

Carbon monoliths with foam-like hierarchical pore structures and connected macropores have potential applications in high temperature insulation, electrodes for electric energy storage devices, thermal energy storage systems, and as structured catalyst supports and adsorbents [1]. In packed reactors and adsorbent towers some of the potential advantages of structured foam and honey-comb type monoliths over random packings (e.g. beads, extruded pellets, and granules) include lower bed pressure drops and higher packing densities of the catalytic or adsorption sites in a vessel [2-4]. Foam-like carbon monoliths with open cellular structures may also provide better radial mixing of fluids in packed beds than the typical linear macro channels in honeycomb monolith, and any enhanced heat and mass transfer in carbon foams could be utilized to reduce contact times in reactors or pressure swing adsorption systems. The current limitations to development of carbon foams for industrial catalyst-support, electrochemical and adsorption applications include mechanical strength, and the optimization of macropore structure and micropore surface area (to balance fast macroscale fluid transport and density of active catalytic or adsorption sites).

In a recent review paper Inagaki et al.[1] describe five classifications of the state-of-the-art methods to produce carbon foams including blowing of carbon precursors followed by carbonization, template carbonization, compression of exfoliated graphite, assembly of graphene nanosheets and assembly of carbon-foam precursors from oil-water emulsions. Blowing of carbon precursors either by pyrolysis under pressure or the use of chemical additives are the most commonly applied methods to produce carbon foams. A wide range of precursors have been reported for carbon foam synthesis including coal [5-7], coke [8, 9], pitch [6, 10-15], polymer [16-19] and biomass [20-23]. Of these materials, bituminous tar pitch and coal tar pitch are some of the most commonly used carbon precursors because pitch is already used in more-conventional activated carbon production processes, low cost pitch is widely available from the petrochemicals industry, and pitch has a high carbon content [24]. However, foams produced directly from tar pitch by pyrolysis at low pressure (close to atmospheric pressure) typically have a low bulk density and poor mechanical strength. Carbon foams with improved mechanical strength have been achieved by (1) blowing the precursor at high pressures (e.g.
30 – 100 bar) or (2) incorporating filler particles such as clay [25], coal [26], graphite [27], carbon nanofibers [28] or carbon nanotubes [29] with the carbon foam. Both approaches have been used together: for example, Zhu et al. [27] reported that the addition of graphite particles to mesophase pitch blown at a pressure 8 MPa and carbonized at 1200 °C increased the compressive strength of the carbon foam from 3.7 MPa to 12.5 Mpa. However, foaming processes at high pressures introduces extra complexity, costs and risks to an industrial scale carbon production process. In this paper, we focus on the second approach to incorporate coal filler particles in carbon foams to produce activated carbon discs (ACD).

Carbon filler particles may serve multiple functions in composite foams as filler particles can (i) provide additional surface areas, (ii) modify the density of the produced foam, and (iii) act to stabilize the pith in low pressure foam preparation processes. In this context, the term of stabilization 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 stabilization in reference to maximizing bubble size). We selected coal particles as a low cost filler particle (relative to the cost of carbon nanotubes or graphite) and investigated the effect of the coal particle size on the foaming process. The coal particles affect the development of the mesopore and macropore structure during foaming and carbonization. As the pitch viscosity and reactivity are the other key parameters affecting the stability of the pitch + coal mixture during pyrolysis and carbonization we also investigated the effect of treating the pitch with nitric acid prior to the foaming procedures on the carbon foam monolith properties. A chemical activation agent, KOH, was used to enhance the microporosity of the ACDs for increased adsorption of CO₂, CH₄ and N₂.
2 Experimental

2.1 Materials and pitch pretreatment

BP Bitumen Class 170 pitch with a softening point of 320 K and density of softening $1.03 \text{ g/cm}^3$ was used as the carbon foam precursor in this study. The pitch was pretreated using nitric acid (HNO$_3$) and a thermal treatment step; this process increased the softening point of the pitch which improves the foaming properties and allows better physical mixing of the pitch with the coal powder. We investigated the effect of pitch pretreatment conditions on the final carbon foam properties by treating the Class 170 pitch with three ratios of HNO$_3$ to pitch: 12 mL, 18 mL and 24 mL of 15 M HNO$_3$ to 100 g of pitch. The pitch was heated to 393 K using an oil bath, and stirred with an impellor at 150 rpm, before the HNO$_3$ was added dropwise and the temperature of the oil bath increased to 433 K. The acid pretreatment step was allowed to continue until the impellor could no longer stir the pitch at 433 K. Then the acid-treated pitch was transferred to a tube furnace and thermally treated at 623 K for 2 hours in Argon (heating rate 5 K/min).

Coal from the Blackwater coal mine in Queensland’s Bowen Basin (Australia) was ground and screened into three size fractions: 0 - 53 µm, 150 - 250 µm and 355 - 550 µm.

2.2 Carbon foam preparation

The pretreated pitch was ground by hand in a mortar and pestle, then mixed with the selected size of coal powder and potassium hydroxide at a pitch: coal: KOH mass ratio of 1:1:1. To improve the dispersion of the KOH through the solids, the pitch + coal + KOH mixture was sonicated for 5 minutes in 50 mL of distilled water. This free water was subsequently evaporated at 353 K for 2 hours over a hot plate with the mixture continuously stirred at 350 rpm. Discs (20 mm diameter) were formed from about 1 g of the pitch + coal + KOH blend in a hydraulic press and these discs were dried overnight in oven at 353 K.

The foaming of the discs was performed under Argon in a horizontal tube furnace at 1073 K (heating rate 10 K/min) with a soaking time 1 h. Foamed discs were washed with 0.2 M HCl in a vacuum vessel for one day, dried overnight in oven at 353 K, rinsed with distilled water several times to remove KOH until a filtrate pH of 7 was achieved, and finally dried in the
oven at 353 K overnight. Activated carbon discs (ACD) obtained from the different synthesis conditions are labeled (see Table 1) with the HNO$_3$ pretreatment volume (in mL) and the coal particle size fraction added to the pitch (in micron). For example, the sample labeled ACD18-053 was prepared with 18 ml of 15 M HNO$_3$ added to 100 g pitch in the pretreatment and with the 0 – 53 µm coal fraction. Photographs of ACD18-150250 are shown in Figure 1a-b.

In addition to the ACDs produced from the method described above we also (1) activated 0 - 53 µm coal particles with KOH to estimate the contribution of the coal to the porosity of the ACDs, and (2) attempted to foam the pre-treated pitch in the tube furnace without any coal particles. In the experiment performed with pitch without any coal particles led to the pitch overflowing the furnace crucible (Figure 1c) and did not produce a stable carbon disc.

The carbon yield of the ACDs was calculated from the treated-pitch weight ($m_p$), coal weight ($m_c$), and the weight of the washed ACD end product ($m_f$) according to:

$$Yield\ (%)=\frac{m_f}{m_p+m_c}\times 100\%$$

The carbon yield increased from 45.08% to 48.17 % with increasing HNO$_3$ to pitch ratio from 12 ml to 24 ml/100g pitch. This result is attributed to a greater removal of volatiles, for example by polymerization of shorter chain carbon molecules, at higher concentrations of HNO$_3$ during the pitch pretreatment. Subsequently, during the foaming there is a smaller mass of volatiles to be evolved from the pitch treated with 24 mL HNO$_3$/100 pitch than pitch treated with 12 mL HNO$_3$/100 g pitch.

2.3 Characterization

Scanning electron microscope (SEM) images were collected on a JSM-7100F instrument (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) was performed on a PHI-560 ESCA (Perkin Elmer) at 15 kV. The C1s peak position was set to 284.8 eV and taken as an internal standard. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were performed with a Perkin Elmer STA 6000 instrument at heating rates of 10 K/min and a nitrogen flow of 20 mL/min. Compressive strength was measured by a uniaxial compression test with an Instron 5584 computer controlled material testing system. The bulk or apparent density ($\rho_{Hg}$) of the carbon discs was measured by mercury porosimetry.
(Micromeritics PoreSizer 9320) and the skeletal density \( (\rho_{\text{He}}) \) by helium pycnometer (Micromeritics AccuPyc II 1340). The disc porosity \( (\phi) \) was calculated with Equation 2:

\[
\phi(\%) = \frac{\rho_{\text{He}} - \rho_{\text{Hg}}}{\rho_{\text{He}}} \times 100
\] (2)

Sorption isotherms of \( N_2 \) at 77 K and \( CO_2 \) at 273 K were measured with a TriStar II 3020 apparatus (Micromeritics, USA) after degassing the activated carbon discs at 473 K and a pressure of \( 10^{-5} \) torr for 24 h. The \( N_2 \) isotherms were used to determine the Brunauer Emmett Teller (BET) specific surface area at a relative pressure in the range of the \( P/P_0 = (0.05 - 0.35) \); total pore volumes at \( P/P_0 = 0.99 \); micropore volumes using the t-plot method and mesopore volumes from the Barrett Joyner Halenda (BJH) method. The pore size distributions (PSD) were also calculated from the \( N_2 \) adsorption on TriStar II 3020. Limiting micropore volumes were also calculated from the \( CO_2 \) isotherms measured at 273 K with the Dubinin-Astakhov (DA) equation [31]. We also measured, with the TriStar II 3020 apparatus, adsorption isotherms on ACD18-053 for \( CO_2 \) at 283 K and 303 K, \( N_2 \) at 273 K, 283 K and 303 K and \( CH_4 \) at 273 K and 303 K. These low pressure isotherms were used to determine isosteric heats of adsorption (\( q^{st} \)).

Adsorption equilibrium capacities of \( CH_4 \), \( CO_2 \) and \( N_2 \) on ACD18-053 were measured at 298 K with pressure up to 3500 kPa on a Belsorp-BG instrument (BEL, Japan) equipped with a magnetic floating balance (Rubotherm, Germany). The activated carbon discs were degassed at 423 K for 24 hour prior to high pressure adsorption measurements.

3 Results and discussion

3.1 Bulk properties of the activated carbon discs

A summary of the bulk properties of the activated carbon discs is provided in Table 1. No density or yield results are reported in Table 1 for the foamed tar pitch prepared without coal powder (shown in Figure 1c) as this sample overflowed the crucible and a monolithic disc was not produced. In addition, we were not able to measure the bulk density of ACD12-150250 by mercury intrusion porosimetry because after washing in HCl this disc broke apart.
Instead, the ACD12-150250 bulk density of 0.39 g/cm$^3$ was estimated from the dimensions of the cylindrical disc before washing and the weight of the carbon obtained after washing. The low strength of ACD12-150250, which was prepared from pitch treated only with a low HNO$_3$ to pitch ratio, is consistent with results reported in the literature [6].

The bulk densities of the other four ACDs measured by mercury intrusion porosimetry were in the range of (0.48 to 0.56) g/cm$^3$, which is within the typical range of densities reported for activated carbon foams prepared by other researchers [32]. Chemical activation of the carbon foams with KOH develops microporosity in the carbon walls, and as a result our ACDs can be expected to have a lower bulk density than carbon foams that have not been chemically activated. The bulk density of ACD24-150250 was greater than that of ACD18-150250 and ACD12-150250, which shows in general the bulk density increased with the ratio of HNO$_3$ used in the pitch pretreatment. When more acid was used, the molecular weight of pitch and softening point increase as well as the viscosity of precursor. In such case, the total bubbling volume decreases and leads to the increment of bulk density. The ratio of HNO$_3$ to pitch was not observed to have a large effect on the skeletal density of the ACDs. In contrast, the particle size of coal powder had a significant effect on skeletal density; we will discuss this result in the following section.

Table 2 compares the mechanical strength of ACD18-053 and the strength of three carbon foams reported in the literature [33-35]. The compressive strength of ACD18-053 measured by an Instron instrument was 4.3 MPa. This is comparable with low density carbon foams produced by Narasimman et al. [33], but less than some high density foams that have been reported. The aim of our current study was not to maximize compressive strength. Instead, our aim is to produce a high surface area carbon monolith with sufficient strength to be used in a pressure swing adsorption process, and for this purpose a crushing strength of 4.3 MPa may be sufficient. Detailed investigations of the stresses induced by pressure swings in an adsorbent bed are recommended but such investigations are beyond the scope of this paper.

The relative concentrations of oxygen functional groups on the surface of activated carbon disc ACD18-053 were examined by deconvolution of the XPS C1s spectra (Figure 2). Curves fitted to the C1s spectra was for (1) C–C bonds of graphite at 284.6 eV, (2) phenol and ether
groups (C–O) at 285.3 eV, (3) carbonyls, quinone and aldehydes (C=O) at 286.9 eV, (4) carboxyls, carboxylic anhydrides and esters (O=C–O) at 289.1 eV, and (5) the characteristic shake-up line of aromatic carbon (\(\pi=\pi^*\)) at 290.5 eV [36]. The results of the deconvolution analyses are summarized in Table 3. This result showed that C-O bond is the most dominant oxygen functionality on the surface of ACD18-053. The surface chemistry of ACD18-053 is consistent with that of other carbon materials prepared from pitch and coal and carbon materials prepared at temperatures up to 1073 K [37-39].

3.2 Effect of coal filler particles on the morphology of carbon discs

Figure 3 shows SEM images of the KOH activated coal produced from the 0 to 53 µm coal particle size fraction without tar pitch, and the activated carbon discs ACD18-053 produced from coal and pitch mixtures. The activated coal particles (Figure 3 a and b) feature large cracks and interparticle void spaces, but there are no open macropore cells observed in the surfaces of the coal particles. In Figure 3c-d the shape of coal particles is still identified in the ACDs, but the texture of the ACDs is clearly different to that of the coal particles. In the SEM images of ACD18-053 the coal particles are coated in a foam derived from the pitch and this foam forms bridges between coal particles. Two types of pore structures between the coal particles are observed: (1) Irregular shaped pores approximately 50 µm in diameter, which result from partial filling of the voids between the coal particles, and (2) open cells and channels of 100 – 200 nm width with bubble-like shapes (for example in Figure 3d). The bimodal distribution of macropores in ACD18-053 is confirmed with the pore size distributions determined by mercury intrusion porosimetry (Figure 4).

The 100 – 200 nm macropore structures developed in the pitch component of the ACDs during the foam blowing process, and these pores are created in the pitch by the evolution and expansion of volatile hydrocarbons in the pitch as the furnace temperature is increased. As the temperature is increased further during foaming and carbonization reactions occur, the remaining pitch components begin to solidify and form solid carbon walls around the bubbles [6, 40, 41]. The pore macropore structures observed in the ACDs are consistent with structures of foams derived from pitch and other precursors that have been reported [20, 25, 34]. We propose that the coal filler particles have two main mechanistic roles during the low-
pressure pitch foaming process: (1) the particles act to stabilize bubble growth in the pitch
during the heating and volatilization, and (2) at temperature greater than about 800 K the coal
particles provide a skeleton to the foam structure during carbonization.

The TGA curves in Figure 5 show the weight loss from a mixture of pitch (pretreated in
HNO₃) and coal particles in an experiment that replicated the conditions used for foaming and
carbonization in the tube furnace to produce ACD18-053. There are four distinct stages in the
thermal treatment of the pitch + coal mixture. (i) In the first stage of the heat treatment the
temperature is increased from room temperature to the pitch softening point of approximately
623 K, and only a small mass of moisture and any dissolved light hydrocarbon gases (that
remained after pitch pretreatment) is lost from the pitch + coal mixture. A weight loss of
moisture and adsorbed volatiles is also observed from the coal in the TGA curves. (ii) In the
second stage at temperatures above 623 K, the pitch starts to soften and then melt, which
allows the pitch to fill the interparticle voids between coal particles. This phenomenon is not
observed directly in our TGA measurements, but can be assumed to lead to a reduction in the
total volume of the composite as the molten pitch fills void spaces between coal particles.
Since the pitch has been pre-treated at 623K before foaming, no bubbling occurred at this step
due to the absence of volatile in pitch. (iii) In the third stage, bubbles and pitch
polymerization begin to occur at temperatures above the pitch pre-treatment temperature of
623 K, and an increase in the rate of weight loss from pitch + coal is observed. During this
stage, the coal particles act as bubble nucleation sites, increase the density and viscosity of the
mixture and reducing the bubbling expansion rate [25, 34]: the combined effects are that a
larger number of small bubbles are formed than in a pitch that is foamed without any coal
filler particles, the latter tends to form large bubbles that overflow the foaming crucible
(Figure 1c). The derivative thermogravimetric analysis (DTG) curve in Figure 5 shows the
maximum rate of weight loss from pitch + coal occurred at approximately 760 K, which is
nearly the same as the temperature (763 K) at which Wang et al. observed a maximum rate of
weight loss from mesophase pitch [15]. The significance of the temperature of maximum
weight loss in the foaming process is that this temperature corresponds to the point at which
the pitch has maximum fluidity and expansion [40]. (iv) The fourth and final stage in the
carbon foam process is observed above 800 K as a steady weight loss due to pyrolysis and carbonization reactions.

3.3 Adsorption of N\textsubscript{2}, CO\textsubscript{2} and CH\textsubscript{4} on the activated carbon discs

The N\textsubscript{2} sorption measurements at 77 K show that all the ACDs exhibited Type I isotherms (Figure 6a). The ACDs adsorbed large volumes of N\textsubscript{2} at P < 10 kPa, which is attributed to adsorption in the micropores that were predominantly created by KOH activation of the ACDs. Table 4 summarizes the pore textural properties of the ACDs and the Blackwater coal samples. The BET surface areas of the ACDs were all greater than 1000 m\textsuperscript{2}/g. The as-received Blackwater coal has a BET surface area of 3.1 m\textsuperscript{2}/g but this specific area was increased to 1182 m\textsuperscript{2}/g after KOH activation. This suggests that the KOH activated coal filler particles provide significant contributions of micropores to the total surface area of the composite ACDs and the BET surface area associated with the micropore volume in coal filler particles is larger for ACDs prepared with smaller size fractions of coal particles. Due to the kinetic limitations associated with the sorption of N\textsubscript{2} in narrow micropores at 77 K [42], we also probed the ACD structures with CO\textsubscript{2} at 273 K and results from CO\textsubscript{2} sorption analysis are included in Table 4.

Activated carbon disc ACD18-053 had the highest CO\textsubscript{2} and N\textsubscript{2} adsorption capacities at a pressure of 100 kPa; so we selected this ACD for further adsorption studies at high pressure including measurements of CH\textsubscript{4} uptake. Absolute equilibrium adsorption capacities for CH\textsubscript{4}, CO\textsubscript{2} and N\textsubscript{2} on ACD18-053 measured with the Belsorp-BG at 298 K and pressure up to 3500 KPa are reported in Table 5 and Figure 7. As expected for an activated carbon the adsorption capacities on ACD18-053 were in the order CO\textsubscript{2} > CH\textsubscript{4} > N\textsubscript{2}. The CO\textsubscript{2} adsorption capacity of ACD18-053 is comparable to the CO\textsubscript{2} uptakes reported for activated carbons at high pressures [43, 44]. There are few reports of high pressure adsorption measurements on carbon foams, but at 100 kPa the adsorption of 3.51 mol/kg CO\textsubscript{2} on ACD18-053 is comparable to the 2.5 mol/kg CO\textsubscript{2} reported for carbon foams prepared by Narasimman, Vijayan and Prabhakaran [23]. Table 6 presents further comparisons of adsorption capacities of ACD18-053 with other carbon foams and commercial activated carbons.
To provide additional data to readers that may be useful for the evaluation of gas adsorption processes based on ACD18-053 we calculated isosteric heats of adsorption \( (q^s) \) at different CO\(_2\), CH\(_4\) and N\(_2\) loadings by the direct method [45] of applying the Clausius-Clapeyron equation (Equation 3). For this part of the study adsorption isotherms were measured at (273.15, 283.15 and 303.15) K and pressures up to 120 kPa on the Tristar II instrument. These equilibrium adsorption isotherms are included in the Supplementary Information.

\[
q^s = -R \left[ \frac{\partial \ln p}{\partial \frac{1}{T}} \right]_Q
\]

where \( p \) is the pressure, \( T \) is the temperature, \( Q \) is the amount adsorbed, and \( R \) is the universal gas constant. Integrating Equation (3) gives:

\[
(\ln p)_Q = - \left( \frac{q^s}{R} \right) \left( \frac{1}{T} \right) + C
\]

where \( C \) is a constant. To determine \( q^s \) values we fitted a high-order polynomial equation to each isotherms to obtain an expression for \( Q \) as a function of \( p \), and used these fitted isotherm equations to interpolate for values of \( p \) at a given \( Q \) for each temperature so that \( \ln(p)^Q \) could be plotted against \( 1/T \). Then with these plots, \( q^s \) was obtained by linear regression of Equation 4. Figure 8 summaries the isosteric heat of adsorption results. The heats of adsorption were in the ranges 22 – 26 kJ/mol for CO\(_2\) at loadings of 2 – 3 mmol/g, 21 – 22.7 kJ/mol for N\(_2\) at loadings of 0.1 – 0.6 mmol/g, and 6 – 8 kJ/mol for CH\(_4\) at loadings of 0.2 – 1.2 mmol/g. The values of CO\(_2\) isosteric heat of adsorption on ACD18-053 in this study similar to the range of reported values for other activated carbons [46] and isosteric heats of adsorption for N\(_2\) are also similar to other reported ranges for similar pressures and coverages [47]. However, our calculated isosteric heat of adsorption for CH\(_4\) is at a lower range than some other reports for activated carbons [47, 48]. To reduce the uncertainty in these results for CH\(_4\), and confirm the enthalpies of adsorption for the other two adsorbates, additional adsorption measurements at the range of temperatures and a wider pressure range may be required. Those additional measurements are beyond the scope of this current paper and will feature in our continued efforts to develop carbon foam materials for gas separation and storage applications.
4 Conclusions

Petroleum tar pitch and coal filler particles were used as precursors to prepare activated carbon discs with high surface area, hierarchical pore structures, and relatively strong mechanical strength. The coal particles act to stabilize bubble growth during the pitch foaming and carbonization, with smaller coal particles providing more bubble nucleation sites and KOH-activated surface areas than larger coal particles. We found that a $\text{HNO}_3$ to pitch ratio of 17/100 in weight for pretreatment of the pitch produced the ACDs with the best mechanical strength and highest bulk density. The ACD18-053 with a surface area of 1401 m$^2$/g adsorbed 3.51 mol/kg of CO$_2$ at 100 kPa and 298 K, which is comparable to other activated carbons in the literature. The high selectivity of CO$_2$ over N$_2$ and CH$_4$ shows that the ACDs prepared in this work have a good potential for pressure swing adsorption.

Acknowledgments

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Figure 1 Photographs of (a, b) the carbon foam disc ACD18-053 and (c) the overflow of pitch from the crucible observed when attempting to foam the pitch without any coal powder.

Figure 2 Curve fitting of C1s XPS spectra of ACD18-053053 prepared from mixture of coal and tar pitch.
Figure 3 SEM images of (a, b) KOH activated coal without adding pitch and (c, d) ACD18-053 prepared from mixture of coal and tar pitch.
Figure 4: Pore size distribution in activated carbon disc ACD18-053 determined by (a) main figure showing the distribution determined by mercury injection porosimetry (Hg) and (b) inset the size distribution of micropores and mesopores determined by NLDFT from the N$_2$ sorption isotherm measured at 77 K.
Figure 5 Weight loss (TGA) and derivate weight loss (DTG) curves measured for Pitch + coal 1:1:1 weight mixture of pitch (pretreated with 18 mL 15 M HNO₃ to 100 g pitch), 0 – 53 µm coal particles and KOH; and KOH activated coal. Heating rate 10 K/min. Nitrogen flow rate 20 mL/min.
Figure 6 Adsorption of (a) $N_2$ at 77 K and (b) $CO_2$ at 273 K on activated carbon discs prepared from BP Class 170 pitch and Blackwater coal powders of different size fractions 0 - 53 µm, 150 - 250 µm and 355 - 550 µm.

Figure 7 Adsorption equilibrium of ACD18-053 sample at 298K.
Figure 8 Isosteric heat of adsorption of CO₂, CH₄ and N₂ on ACD18-053 calculated via the Clausius-Clapeyron equation.
Table 1 The bulk density, skeletal density, porosity and carbon yield of the coal and activated carbon discs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HNO₃/Pitch ml/100g</th>
<th>Coal particle size µm</th>
<th>Bulk density g/cm³</th>
<th>Skeletal density g/cm³</th>
<th>Porosity %</th>
<th>Carbon yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Water Coal</td>
<td>-</td>
<td>-</td>
<td>1.30</td>
<td>1.38±0.009</td>
<td>6.01±0.62</td>
<td>-</td>
</tr>
<tr>
<td>KOH Activated Coal</td>
<td>-</td>
<td>0-53</td>
<td>0.79</td>
<td>1.92±0.24</td>
<td>58.92±5.88</td>
<td>46.99</td>
</tr>
<tr>
<td>ACD12-150250</td>
<td>12</td>
<td>150-250</td>
<td>0.39</td>
<td>2.07±0.16</td>
<td>81.03±1.58</td>
<td>45.08</td>
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<tr>
<td>ACD18-053</td>
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<td>0-53</td>
<td>0.48</td>
<td>1.85±0.07</td>
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<td>150-250</td>
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<td>2.05±0.09</td>
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<tr>
<td>ACD18-355550</td>
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<td>355-550</td>
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<td>1.59±0.13</td>
<td>64.61±3.14</td>
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<tr>
<td>ACD24-150250</td>
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<td>150-250</td>
<td>0.49</td>
<td>2.05±0.10</td>
<td>75.96±1.23</td>
<td>48.17</td>
</tr>
</tbody>
</table>
Table 2 Bulk properties of the carbon foam disc ACD18-053 and representative carbon foams in literature (GF₀ [27] was made from graphitized carbon black particles and mesophase pitch, CFS carbon foam made by Narasimman and Prabhakaran [33] was prepared from activated carbon powder and aqueous sucrose resin and CTP3 [35] was prepared using coal tar pitches modified with cinnamaldehyde (CMA) and boric acid).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ACD18-053</th>
<th>GF₀ [34]</th>
<th>CFS [33]</th>
<th>CTP3 [35]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive  strength/MPa</td>
<td>4.3</td>
<td>5.39</td>
<td>3.4</td>
<td>21.27</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.48</td>
<td>0.76</td>
<td>0.22</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 3 Relative concentration (at. %) of oxygen functional groups on ACD18-053. Calculated from deconvolution of high resolution XPS C1s spectra.

<table>
<thead>
<tr>
<th>Group</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>O=C-O</th>
<th>π-π*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>284.8</td>
<td>286.1</td>
<td>287.4</td>
<td>288.8</td>
<td>290.1</td>
</tr>
<tr>
<td>ACD18-053</td>
<td>71.0</td>
<td>15.0</td>
<td>6.2</td>
<td>2.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 4 Main textural parameters of the obtained activated carbon discs (BET surface area was evaluated at p/p₀ ~ 0.99, micropore volume was evaluated by the t-plot method applied to N₂ adsorption isotherms and mesopore volume was evaluated by the BJH method applied to N₂ adsorption isotherms at 77K. DA Micropore surface area and narrow micropore volume determined from CO₂ adsorption at 273K).

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂ Adsorption</th>
<th>CO₂ Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S_BET (m²·g⁻¹)</td>
<td>V_total (cm³·g⁻¹)</td>
</tr>
<tr>
<td>Blackwater coal</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>KOH activated coal</td>
<td>1182</td>
<td>0.505</td>
</tr>
<tr>
<td>ACD12-150250</td>
<td>1221</td>
<td>0.515</td>
</tr>
<tr>
<td>ACD18-053</td>
<td>1401</td>
<td>0.600</td>
</tr>
<tr>
<td>ACD18-150250</td>
<td>1302</td>
<td>0.534</td>
</tr>
<tr>
<td>ACD18-355550</td>
<td>1055</td>
<td>0.436</td>
</tr>
<tr>
<td>ACD24-150250</td>
<td>1269</td>
<td>0.542</td>
</tr>
</tbody>
</table>
Table 5 Methane, carbon dioxide, nitrogen adsorption equilibrium data on ACD18-053 sample at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th></th>
<th></th>
<th>CO$_2$</th>
<th></th>
<th></th>
<th>N$_2$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P(kPa)</td>
<td>Q$_{ads}$(mol/kg)</td>
<td>P(kPa)</td>
<td>Q$_{ads}$(mol/kg)</td>
<td>P(kPa)</td>
<td>Q$_{ads}$(mol/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.22</td>
<td>0.19</td>
<td>5.74</td>
<td>0.52</td>
<td>8.64</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.65</td>
<td>0.52</td>
<td>28.41</td>
<td>1.68</td>
<td>28.12</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71.60</td>
<td>1.00</td>
<td>68.56</td>
<td>2.87</td>
<td>70.99</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102.88</td>
<td>1.22</td>
<td>99.13</td>
<td>3.51</td>
<td>101.77</td>
<td>0.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303.96</td>
<td>1.72</td>
<td>297.51</td>
<td>5.74</td>
<td>302.47</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>701.54</td>
<td>2.57</td>
<td>698.30</td>
<td>7.31</td>
<td>701.18</td>
<td>1.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1001.06</td>
<td>2.89</td>
<td>998.61</td>
<td>7.87</td>
<td>1000.63</td>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500.87</td>
<td>3.24</td>
<td>1497.94</td>
<td>8.35</td>
<td>1499.77</td>
<td>1.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2500.35</td>
<td>4.70</td>
<td>2495.47</td>
<td>8.76</td>
<td>2497.84</td>
<td>2.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2999.30</td>
<td>5.11</td>
<td>2994.94</td>
<td>8.84</td>
<td>2997.72</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3500.07</td>
<td>5.43</td>
<td>3493.96</td>
<td>8.87</td>
<td>3495.76</td>
<td>3.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6: Equilibrium capacity of adsorbents in literature and ACD for $N_2$, $CO_2$, and $CH_4$ at 100 and 1000 kPa and ambient temperature.

<table>
<thead>
<tr>
<th>Adsorbent Type</th>
<th>CO$_2$ capacity (mol/kg)</th>
<th>CH$_4$ capacity (mol/kg)</th>
<th>N$_2$ capacity (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100kPa</td>
<td>1000kPa</td>
<td>100kPa</td>
</tr>
<tr>
<td>ACD18-053 ACD</td>
<td>3.51</td>
<td>7.87</td>
<td>1.22</td>
</tr>
<tr>
<td>Norit RB1 extra[49]</td>
<td>2.20</td>
<td>7.60</td>
<td>1.22</td>
</tr>
<tr>
<td>13X [50, 51] Zeolite</td>
<td>3.3</td>
<td>6.40</td>
<td>0.59</td>
</tr>
<tr>
<td>MOF-177 [52] MOF</td>
<td>1.59</td>
<td>-</td>
<td>0.63</td>
</tr>
<tr>
<td>ACHM [53] Monolith</td>
<td>3.0</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>CA300[54] Foam</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
</tbody>
</table>
THE PREPARATION OF ACTIVATED CARBON DISCS FROM TAR PITCH AND COAL
POWDER FOR ADSORPTION OF CO$_2$, CH$_4$ AND N$_2$

Shuai Gao, Lei Ge, Thomas E. Rufford* and Zhonghua Zhu*

Highlights

- Carbon discs with hierarchical pore structures prepared from pitch and coal powder.
- Nitric acid pretreatment of pitch improved foaming properties.
- Smaller coal particles produce carbon discs with better mechanical strength.