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Synthesis and characterisation of porous carbons with optimised properties for targeted sustainable energy applications

Ibtisam Khalil Alali

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Abstract

Porous carbons are increasingly receiving attention as energy materials for many ongoing attempts to find new methods of generating and storing energy. This thesis describes the synthesis and characterisation of porous carbons with tuneable properties that are directly targeted at energy-related applications. Particularly, the thesis explores the effects of the preparation parameters on the textural properties of the carbons and their performance towards CO₂ and CH₄ storage. The thesis also explores various carbonisation methods for generating carbonaceous matter that may be activated.

Chapter 1: Gives a general background to the key themes of porous materials that have been investigated in this thesis. This chapter presents the fundamental properties of porous carbons and their classification based on structure, pore size and pore types. The energy storage applications of porous carbons are also emphasised.

Chapter 2: Describes experimental techniques and instrumentation that have been used to investigate and characterise the porous materials generated within this thesis. The chapter also presents gas storage techniques used to examine CO_2 and CH_4 storage.

Chapter 3: Explores the one-step synthesis of porous carbons from two organic metal salts. Potassium hydrogen phthalate (KHP) and potassium phthalimide (PPI) as carbon precursors were carbonised to highly porous carbons via a simple one-step strategy. This chapter investigates the simplicity of the synthesis process, the effects of particle size, carbonisation temperature, and the impact of the nature of the precursor, KHP or PPI. The resulting porous carbons were found to have excellent CO₂ and CH₄ storage capacity.

Ι

Chapter 4: Presents the preparation of cost-effective porous carbon from plastic waste by two different activation methods; conventional activation via hydrothermal carbonisation (HTC) and the direct chemical activation with potassium hydroxide. A single plastic waste component (Polyethylene terephthalate, PET) has been used to produce porous carbons. The physical characteristics and properties of the waste PET-derived carbons were analysed, and the gas sorption performance was also studied. Depending on the washing step post activation, this chapter provides a promising material for energy storage applications.

Chapter 5: Presents the targeted and predictable synthesis of biomass-derived activated carbons that achieve high porosity and specific properties suitable for CO_2 and CH_4 storage. Highly microporous activated carbons have been successfully generated via two carbonisation methods from an environment-friendly and abundantly available biomass precursor, cloves (*Syzygium aromaticum*). This chapter demonstrates that careful carbonisation of biomass can dramatically improve the characteristics of both the activatable carbonaceous matter and the final carbon products. In addition, this chapter shows that the cloves can be used to generate activated carbons with appropriate porosity, high packing density and record levels of CO_2 and CH_4 storage capacities.

Chapter 6: Investigates the efficiency of direct nitrogen doping with urea as a nitrogen source and clove as a carbon precursor. It also explores the effects of using a less corrosive and less toxic activating agent, i.e., potassium oxalate (PO). A high porosity of > $3000 \text{ m}^2 \text{ g}^{-1}$ was achieved, and the generated carbons display excellent CO₂ adsorption behaviour in both low pressure (post-combustion) and medium-to-high pressure (pre-combustion) conditions.

Π

Chapter 7: Provides a brief overall conclusion to this research work, as well as recommendations for future research.

Publications and Conferences

Publications

- I. Alali and R. Mokaya, Generalised predictability in the synthesis of biocarbons as clean energy materials: targeted high performance CO₂ and CH₄ storage, *Energy Environ. Sci.*, 2022, **15**, 4710.
- I. Alali and R. Mokaya, Porous carbon composites as clean energy materials with extraordinary methane storage capacity, *Submitted*

Conferences

- Ibtisam Alali and Robert Mokaya, Women in Chemistry Conference, The University of Nottingham, 6th March 2020, 'Organic salt carbonisation to carbons for methane storage' Poster.
- EMDoc Sustainability Conference; East Midlands Doctoral Network by United Nations University, UK, 9-10th September 2020, Attendance.
- International Virtual Conference on Advanced Materials for Energy and Environmental Applications (ICAMEEA-2020), **3-4th December 2020**, Attendance.
- Ibtisam Alali and Robert Mokaya, ¹⁵th International conference on materials chemistry (MC15), **12-15th July 2021**, 'One-step synthesis of porous nitrogen doped carbon from organic salt' Poster.
- Ibtisam Alali and Robert Mokaya, International Conference on Recent Advances in Carbon Capture and Storage (ICRACCS), **15-16th March 2022**, London, 'Biomass-derived nitrogen-doped porous carbon with excellent physical properties for efficient gas storage' Poster.

Presentations

- Ibtisam Alali and Robert Mokaya, Chemistry Research Seminar 2020, The University of Nottingham, 24th February 2020, 'Organic salt carbonisation to carbons for methane storage.' Presentation.
- Ibtisam Alali and Robert Mokaya, Department of Inorganic and Materials Chemistry 3rd Year PhD Talks, **13-14th September 2021**, 'A benchmark for CO₂ uptake from biomass- derived highly microporous activated carbons'.

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List of Abbreviations and Definitions

- AC Activated Carbon
- ANG Adsorbed Natural Gas
- BDDT Brunauer, Deming, Deming and Teller
- BET Brunauer, and Emmett and Teller
- BJH Barrett-Joyner-Halenda
- BSE Backscattered Electrons
- CCS Carbon Dioxide Capture and Storage
- CH₄ Methane
- CNG Compressed Natural Gas
- CO₂ Carbon Dioxide
- CO2-EOR Carbon Dioxide-Enhanced Oil Recovery
- DFT Density Functional Theory
- DOE Department of Energy
- DTG Derivative Weight Loss Curve
- GHGs Greenhouse Gases
- HTC Hydrothermal Carbonisation
- IGA Intelligent Gravimetric Analyser
- IPPC Intergovernmental Panel on Climate Change
- IUPAC International Union of Pure and Applied Chemistry
- KHP Potassium Hydrogen Phthalate
- KOH Potassium Hydroxide
- LNG Liquefied Natural Gas
- MOFs Metal Organic Frameworks
- NDC Nitrogen Doped Carbon
- NG Natural Gas

- NGVs Natural Gas Vehicles
- NL-DFT Non-Local Density Functional Theory
- PET Polyethylene Terephthalate
- PPI Potassium Phthalimide
- PSD Pore Size Distribution
- RON Research Octane Number
- SAD Surface Area Density
- SE Secondary Electrons
- SEM Scanning Electron Microscopy
- STP Standard Temperature and Pressure
- TGA Thermal Gravimetric Analysis
- VED Volumetric Energy Density
- XRD X-Ray Diffraction
- ZTCs Zeolite-Templated Carbons

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1.1 Climate Change

Rapid economic growth has led to the ever-growing demand for energy today. Since the industrial revolution, fossil fuels such as coal, oil and natural gas have become the main energy sources.¹ However, the high consumption of fossil fuels and associated emissions of greenhouse gases (GHGs), such as carbon dioxide (CO₂) and methane (CH₄), has become an area of concern due to environmental and socio-economic adverse effects.¹ According to the Global Atmospheric Research Emission Database,² the global CO₂ emissions were 33.4 billion tonnes in 2011, up 48% from two decades earlier. CO₂ levels in the atmosphere have risen by more than 39% over the past century, reaching a record high of 400 ppm in 2013 from 280 ppm in pre-industrial times.³ Therefore, reducing anthropogenic CO₂ emissions is of utmost importance because CO₂ emissions are directly linked to climate change. Without climate change mitigation policies, global emissions of GHGs, with correspondingly high CO₂ levels in the atmosphere, are expected to rise by between 25 and 90% by 2030 with the potential of reaching 600-1550 ppm.² The unparalleled rise in the concentration of CO₂ in the atmosphere within such a short timescale can be ascribed to the increase in anthropogenic CO_2 sources due to developments in science and technology since the industrial revolution.⁴⁻⁶ Today, fossil-fuel-based power production, transport, manufacturing processes and chemical production are the major contributors to anthropogenic CO_2 emissions.⁷ In 2017, the emissions of CO_2 from the energy sector reached a historic high of 32.5 Gt with 65% of the world anthropogenic emissions and ca. 78% of world GHG emissions resulting from fossil fuel use and industrial processes.^{8,9} In order to tackle climate change,

the amount of anthropogenic CO₂ emitted into the environment, essentially through the fossil fuels' combustion, needs to be significantly reduced. Several countries, therefore, have set long-term carbon emission reduction goals. For example, the United States has committed to decreasing carbon emissions by 17% and 83% by 2020 and 2050, respectively. The United Kingdom's goal is to decrease carbon emissions by at least 80% by 2050.¹⁰

An essential part of solutions to climate change depends on finding renewable energy sources, mostly solar, wind, hydro, and biomass-based processes. Nevertheless, although imperative, this enormous move towards stabilising atmospheric CO₂ levels is expected to take decades to achieve. The Intergovernmental Panel on Climate Change (IPCC) published a report in October 2018 stating that in order to avoid highly damaging climate changes; drastic action should be taken to decrease CO₂ emissions; the most ambitious studies estimate that complete dependence on renewable energy can be achieved by 2050.¹¹⁻¹³

Regrettably, many obstacles must be overcome to achieve complete reliance on renewable energy. At present, many manufacturing processes have no feasible 'green' alternatives. For instance, the chemical and cement industries currently account for over 5.5% and 5% of global anthropogenic CO_2 emissions, respectively.^{14,15} The scale of the new infrastructure and investment needed to build a renewable energy network is currently challenging for most nations; therefore, the simple 'turning off' of fossil fuelbased power supplies is unlikely. Thus, different alternatives, such as energy efficiency improvements, the substitution of low-carbon fuels or CO_2 capture, and the production of sustainable and clean energy sources, may be used for reducing CO_2 emissions in the short to medium term.¹ Carbon capture and

storage (CCS) is currently thought to be the most realistic solution to reduce CO_2 emissions because fossil fuels will continue to be a substantial energy source in the foreseeable future.

1.2 Carbon Capture and Storage

Carbon capture and storage (CCS) is characterised by separation of CO_2 from industrial and energy sources and transfer to storage for long-term sequestration. It is an attainable solution to climate change and could allow fossil fuels to be burned and industrial processes to continue but without the release of CO_2 emissions into the atmosphere.¹⁶ CCS can, therefore, be used as a 'green' addition to the burning of fossil fuels, as well as for controlling emissions from carbon dependent industries, such as the chemical, cement and petroleum refining industries, which account for approximately 60% of the global CO_2 emissions, and which as of yet have no viable alternative 'clean' processes.¹⁶

With widespread utilisation, it has been predicted that CCS technology could account for up to 12% of CO₂ emission reduction by 2050. In many cases, CCS technology can be retrofitted to existing plants, a lower and easier investment for the medium term compared to constructing new networks of renewable energy sources. Different carbon capture technologies are being researched and developed worldwide, with a few making it into the trialling and commercial stages. The Global CCS Institute currently identifies 18 'large-scale' CCS facilities across the globe, where CO₂ is being captured in various ways across a range of industries and many projects in planning and development. Currently, the largest operating CCS system is the Petra Nova Carbon Capture facility at WA Parish power station in Texas, U.S.A.^{8,17} An

amine scrubbing process is used to capture 90% of the plant's CO₂ emissions (5000 t per day), pumped through an 80 mile pipeline for CO₂-enhanced oil recovery (CO₂-EOR). CO₂-EOR is the process that involves injecting CO₂ and storing it in oil reservoirs, simultaneously increasing the amount of oil that is extracted from the reservoir and providing a long-term storage solution for captured CO₂.^{18,19} The Petra Nova Carbon Capture system's contribution to CO₂-EOR increased local oil recovery by 1300%, providing both environmental and economic benefits.²⁰ In 2014, the Boundary Dam Carbon Capture Project in Saskatchewan, Canada, was the first power station to implement retrofitted CCS technology successfully²¹, and it is one of the most significant geological CO₂ storage projects in the world.^{22,23} Despite several functional and financial problems, the project acts as one of the first and largest demonstrations of commercial CCS technology.



Figure 1.1: Carbon dioxide capture, storage and enhanced oil recovery.²³

1.3 Current Status of CO₂ Capture Technologies

The fundamental purpose of CO_2 capture and storage is to decrease CO_2 emissions from fossil fuel use. There are two basic approaches to CCS.²⁴ One approach involves capturing CO_2 directly from industrial sources, concentrating it into an almost pure form, and then pumping it deep underground for long-term storage. CO_2 storage in the ocean has also been proposed as an alternative to storage in underground geological formations.²⁵ This might be accomplished by dissolving CO_2 in the mid-depth ocean (1–3 km) or by producing CO_2 pools on the sea bottom where the ocean is deeper than 3 km and, hence, CO_2 is denser than seawater.

The second approach of capturing CO₂ directly from the atmosphere involves boosting natural biological processes that impound CO₂ in plants, soils, and marine sediments.²⁵ Over the previous decade, these CCS options have been studied and their potential to reduce CO₂ emissions has been assessed. CCS has a significant probability of considerably contributing to lowering CO₂ emissions. Over 60% of global CO₂ emissions come from point sources potentially suitable to CO₂ capture, and there is a minimum of 2000 Gt of storage capacity in deep geological formations. According to technical and economic evaluations, CCS might contribute up to 20% of the required reductions of CO₂ emission over the next century, on par with predicted contributions from efficiency improvements and extensive use of renewable energy resources.¹³



Figure 1.2: Schematic presenting carbon dioxide capture and storage.²⁵

Three technological systems can be used for capturing CO₂ directly from industrial sources, including pre-post and oxy-fuel combustion.^{2,25,26} In an oxy-fuel combustion system, pure oxygen is used instead of air for combustion. This removes a significant proportion of NOx from the flue gas stream and produces a flue stream rich in CO₂ (80-98%). However, this process is energy-intensive, along with the high cost of purifying oxygen and high concentration of SO₂ in the flue gas may lead to corrosion issues within the system.^{26,27} In a pre-combustion system, the fuel is first gasified to syngas, a mixture of CO and H₂. This is followed by further reaction with steam, converting CO into CO₂ and yielding streams of concentrated CO₂ (suitable for storage) and hydrogen for electricity generation or other purposes. CO₂ can be removed, usually by a separation process from the gas

mixture.¹ Although the pre-combustion technology can produce hydrogen, reduce compression requirements, and use less energy in the separation process, gasification technology is immature for power production, and large capital investment is needed for repowering.^{26,28} In a post-combustion system, CO₂ is separated from a flue gas stream after fuel combustion, using chemical solvents. Both pre and post-combustion capture technologies separate and capture CO₂ from a mixed gas stream. However, post-combustion capture is the preferred method applied to both fossil-fuel based power stations and a range of industrial processes such as cement or chemical production due to its position as the final step in the processing chain.^{24,26,28} Presently, capturing CO₂ using amine solutions for practical applications is an advanced technology.²⁹ However, it is constrained by inherent constraints such as chemical instability, corrosion of process equipment, high energy needs and limited impurity tolerance.^{30,31}



Figure 1.3: Principles of the main technological systems for capturing CO₂ from industrial sources.²

Therefore, the use of porous materials as CO₂ capture sorbents is a promising alternative to the amine liquid-phase absorption technique due to the former's high sorption capacity, low energy requirements for regeneration, improved selectivity, and easy handling.³²⁻³⁴ Porous materials are solids that mainly have voids within their framework. These internal spaces permeate the material and are constrained by defined boundaries resulting in pore systems with a random character or ordered pore systems with, in some cases, high regularity.³⁵ Various porous materials have been widely studied for pre-combustion and post-combustion CO₂ capture and storage, including zeolites, mesoporous silicas, microporous polymers, activated carbons and metal organic frameworks. Carbons are particularly attractive as one of the

most promising candidates for carbon dioxid capture owing to their abundance, low cost, excellent thermal and chemical stability, high surface area and large pore volume, easy preparation and regeneration and their structural flexibility.³⁶⁻³⁸ Most investigations that are pointed into postcombustion CO₂ capture normally emphasise the uptake at 1 bar, where CO₂ capture from fossil fuel power stations occurs at atmospheric pressure (or lower) depending on partial pressure of CO₂ in flue gases.³⁹ Given that postcombustion flue gas streams from power plants contain approximately 70-75% N₂, 15% CO₂ and water (5-7%), the CO₂ uptake at 0.15 bar must be considered.^{37,39} Therefore, it is important to target materials with enhanced CO₂ uptake capacity at low pressure (\leq 1 bar). For instance, Mokaya's group has previously reported an unprecedented CO₂ storage capacity of up to 2.0 mmol g⁻¹ at 0.15 bar, and 5.8 mmol g⁻¹ at 1 bar, which is the highest reported for carbonaceous materials.³⁹

The use of cleaner and renewable fuels with low or no carbon content is alternative strategy towards lowering atmospheric CO_2 . The ultimate solution is hydrogen technology, but it is still not adequately developed and deliverable. Consequently, natural gas can be used as an alternative clean fuel to reduce CO_2 emissions.⁴⁰⁻⁴²

1.4 Methane Storage

Natural gas (NG), consisting mainly of methane (CH_4) , has been regarded as a promising candidate as fuel source due to its attractive properties. Since the beginning of the 1980s,⁴³ natural gas has attracted a lot of research interest as a possible vehicle fuel alternative to conventional petroleum-based fuels due to its abundant reserves, lower cost, and lower negative environmental impact compared to conventional liquid hydrocarbon fuels. It also has a higher hydrogen to carbon ratio, resulting in a higher research octane number (RON = 107) that allows for more energy per fuel mass, higher combustion efficiency, and cleaner-burning because it has less carbon per unit of energy of any fossil fuel.⁴³⁻⁴⁸ In addition, due to the high price of gasoline, natural gas will play an essential part in shaping the energy industry in the coming years and decades.⁴⁹ It could also be a transition fuel between crude oil and future clean/renewable energy sources.49 Nevertheless, methane has a relatively low volumetric energy density (VED) at standard conditions; only 0.11% that of gasoline (34.8 MJ L^{-1}), which severely limits its vehicular on-board applications.43-48

Three strategies have been proposed to increase natural gas storage density; compressed natural gas (CNG), liquefied natural gas (LNG) and adsorbed natural gas (ANG). CNG is stored in a steel cylinder as a supercritical fluid at 200–300 bar and room temperature. The key drawbacks of this strategy are the requirement for costly and heavy high-pressure storage vessels, expensive multistage compression facilities and potential safety concerns. LNG is produced using cryogenic techniques and stored at 112 K and 100 kPa as a boiling liquid. Although LNG has a high energy density, it requires specific Dewar containers and should be stored at a low temperature. Furthermore,

periodic venting is essential due to pressure build-up in a cryogenic fuel tank. Adsorbed natural gas (ANG) has been recently regarded as a promising strategy to overcome these problems, as porous adsorbents appear to be safer, simpler, and more cost-effective for storing NG at developed densities at room temperature and relatively mild pressure conditions (30-60 bar).⁴³⁻ ⁴⁸ Upon using ANG under the aforementioned conditions, the ultimate requirement is to get the maximum gas storage density to store and deliver the required volume of gas per volume of a storage container (v/v). Appropriate adsorbents may reduce the storage pressure of the gas in tanks by up to 20% of the value needed in CNG; alternatively, the use of low-cost fuel containers and single-stage compressors may significantly increase the stored quantity at the same pressure. Lower storage pressures can also make home gas refuelling easier, reducing the cost of constructing a new infrastructure because NG distribution systems are already connected to many homes worldwide.⁴⁷ Furthermore, ANG systems allow the use of lightweight, compatible fuel tanks that can be more efficiently merged into the available limited space inside the vehicle.⁴⁷

It has been frequently reported that there are several requirements for an ANG adsorbent, namely, (i) high adsorption/desorption rates, (ii) high adsorption capacity, (iii) low heat of adsorption with high capacity to decrease modifications in the container's temperature throughout the adsorption and desorption processes, (iv) microporous, with pore diameters of ca. 0.8 nm, to maximise the deliverability at ambient pressure, (v) cheap to the end-user, (vi) highly hydrophobic, (vii) has good mass transfer properties, (viii) has a high packing density, to guarantee that both energy density and storage volume on a volumetric basis are high.^{43,47,50,51} Accordingly, the volumetric

storage capacity and delivery, and the volumetric energy density are determined by the adsorbent's characteristics.⁴³

To completely apply NG fuel systems for passenger vehicles, it is necessary to obtain porous materials capable of storing and transporting enormous quantities of methane under a specific storage pressure (usually 35 or 65 bar).⁵⁰ It should be noted that 35 bar has commonly been used as a typical pressure to evaluate the adsorbents for ANG storage.⁵⁰ Moreover, for direct study of methane storage systems based on adsorbents, the US Department of Energy (DOE) has stated a methane storage target of volumetric storage capacity of 263 cm³ STP cm⁻³, based on gas volume under STP conditions; T = 298 K, P = 35 to 65 bar), corresponding to the energy density of 9.2 MJ L⁻¹ and gravimetric storage capacity of 0.5 g (CH₄) g⁻¹ (700 cm³ g⁻¹) at room temperature.⁴³⁻⁴⁸ Considering the loss of about 25% in volumetric energy density of some porous materials through the packing process, an adsorbed natural gas (ANG) system requires a volumetric capacity of 350 cm³ STP cm⁻³.⁴³⁻⁴⁸ The ideal adsorbent must also be resistant to contaminations commonly found in natural gas sources.⁴⁵

It is critical to develop safe and effective methods for obtaining low-cost volumetric energy density for large-scale usage. One possible approach is to store methane at extremely high pressures, as currently done by many existing natural gas-powered vehicles. However, due to technological requirements, this approach is better suited to large vehicles such as buses and trucks rather than private cars.⁵² As an alternative, porous materials can store methane with a similar high density but at considerably lower pressure.⁵² Notably, current advances in NG-adsorbing and high surface area materials, such as zeolite, metal-organic frameworks and activated carbons,

have revealed the potential for enhancing the density of NG in the form of ANG under moderate conditions, providing an opportunity to improve small, light-weight, and high-capacity tanks for vehicular applications.⁴⁵

1.5 Fundamental Concept of Methane Storage 1.5.1 Definition of of Excess, Absolute and Total Adsorption

The definitions of excess, absolute, and total adsorption have frequently been used to identify gas adsorption capabilities in porous solids. Excess adsorption (n_{ex}) is defined as the amount of adsorption of gas particles that interact with the pore surface. Absolute adsorption is the sum of gas molecules that interact with surface pores and others remaining in the adsorption region with no gas-solid interactions.⁵³ Consequently, experimentally defining the adsorbed region is challenging because the experimental techniques applied cannot detect the borderline between the adsorbed and bulk gas phase.⁵⁰ As a result, absolute adsorption cannot be directly measured but can be calculated using high-pressure adsorption measurements. The majority of the recorded experimental adsorption measurements give excess adsorption isotherms.⁵⁰ In this case, the total adsorption (n_{tot}) is often used as an approximation for absolute adsorption. Total adsorption refers to the total amount of gas molecules within the pores of an adsorbent. As shown in equation (1), total adsorption can be calculated from the excess adsorption and the total pore volume, Vp, where the Vp is typically calculated from an N_2 adsorption isotherm at 77 K by presuming that all pores have been fully filled with condensed N₂ at a sufficiently partial P/Po.^{44,50}

$$\mathbf{n}_{\text{tot}} = \mathbf{n}_{\text{ex}} + \boldsymbol{P}_{\text{bulk}} (\mathbf{P}, \mathbf{T}) \times \mathbf{V} \mathbf{p} \qquad (1)$$

Total adsorption is used in gas storage applications to compare the capacities of various adsorbents, and it is the fundamental properties of a material that determines the total gas that can be stored inside the pores of an adsorbent.⁴⁴ However, as the gas density in the bulk phase at high pressures is significant, there is typically a big difference between the excess and total amount adsorbed at natural gas storage conditions. Consequently, the inconsistent usage of the terms excess, absolute, and total creates challenges when comparing the methane storage capacity of various materials. Therefore, it is always necessary to identify the type of adsorption capacity reported.⁴⁴

Precise measurements at high pressures are inherently more complicated than gas-sorption measurements at low pressures. Significant measurement errors can occur due to mistakes made when collecting isotherm data, in explaining the results, and erroneous volume calibrations and pressure readings.^{44,50} For instance, when describing high-pressure adsorption capacities, the terms excess, total, and absolute are frequently used inconsistently, leading to unnecessary doubt when comparing the uptakes of different materials.⁴⁴ To effectively decrease these errors, background methane adsorption isotherms should be measured with an empty sample cell and then subtract the effect of the background in an actual experiment.⁴⁴ Additionally, the methane used should be pure and free of contaminants, as negligible amounts of heavier hydrocarbons or water cause significant errors in the measured statistics due to their powerfully adsorbing properties.⁵⁰



Figure 1.4: Schematic showing excess, total, and absolute adsorption.⁴⁴

1.5.2 Gravimetric and Volumetric Uptake

Gravimetric uptake and volumetric uptake are the important indicators of the adsorption performance of porous materials. Gravimetric uptake is defined as the mass of gas adsorbed per unit mass of adsorbent, whereas the volumetric uptake is the volume of gas adsorbed per unit volume under standard conditions divided by the volume of adsorbent.^{44,50} Gas adsorption measurements are commonly given as gravimetric readings. However, given the limited size of automobile fuel tanks, volumetric uptake seems to be the most suitable method for quantifying the storage capacity of the adsorbents for vehicular applications.⁵⁰ A variety of material densities, including crystal density, packing density, bulk density, and pellet density, have been used to calculate volumetric uptake and volumetric storage capacity.⁵⁰ Basically, a

high packing density for the adsorbent and suitable textural properties are critical to reaching a high volumetric CH₄ storage capacity.^{43,47,54}

1.5.3 Deliverable or Working Capacity

The working capacity is determined by selecting the upper adsorption and a lower limiting working pressure.⁵⁰ The pressure of 35 and 65 bar are commonly used as the adsorption pressure because they are the maximum achievable pressures of low-cost single-stage and two-stage compressors.⁵⁰ Even though the methane storage capacity at 35 or 65 bar is beneficial for evaluating an adsorbent's storage performance, not all of this capacity is utilised for delivering natural gas to an engine, since the lowest inlet pressure is necessary to push a methane flow from the adsorbent to the engine.⁵⁰ Accordingly, the material used for methane storage should have a high deliverable capacity in addition to a high maximum adsorption capacity.⁴⁷ The deliverable capacity (working capacity) is the volume of gas delivered per volume of the storage vessel and is represented volume/volume (v/v). Given that the deliverable capacity can be the amount of gas released from the adsorbent when the adsorption pressure is reduced to atmospheric, heat and/or vacuum can increase the amount of gas delivered.⁴⁷

In practical applications, the volumetric working capacity is critical as it determines the driving range of natural gas vehicles (NGVs).⁵⁵ As NGVs require inlet pressures of 5–10 bar to enable an adequate methane flow from the adsorbent to the engine, a pressure of 5 or 5.8 bar is commonly quoted as the minimum desorption pressure.^{45,56} To improve the working capacity of possible adsorbents, it is essential to maximise the storage capacity at 35 or 65 bar while also minimising methane adsorption at low pressures of 5 or 5.8

bar.⁵⁰ In vehicular applications, the working capacity is also mainly correlated to basic thermal effects in the ANG storage system and the adsorbents themselves since adsorption is exothermic and desorption is endothermic.⁴⁴ For instance, if the heat emitted through refuelling is not sufficiently dissipated or replaced, the adsorbent bed heats up, reducing methane storage at the adsorption pressure. Likewise, if the heat absorbed through discharge is not replenished, the temperature of the adsorbent bed rapidly drops, and more CH₄ is trapped in the tank at a low pressure.⁵⁰

All of the previously mentioned factors can considerably decrease the working capacity. Working under possible temperature-management approaches in ANG storage systems is critical for reducing losses in a working capacity. Additionally, increasing the final release temperature for methane or adsorption at a lower temperature are other suggested strategies to improve the working capacity.⁵⁰ Moreover, the ideal materials for methane storage purposes must have a high deliverable quantity of methane gas and high methane uptake capacities.⁵⁷ This implies that it is necessary to maximise the working capacity of methane at 35 bar (or the selected storage pressure) while simultaneously decreasing the methane uptakes at a low pressure of 5 bar. To meet the DOE target for deliverable methane storage capacity, the total methane uptake at 35 bar must be significantly higher than the target.⁵⁷

1.6 Background of Gas Adsorption

Gas adsorption is an area that is of great interest and technological importance. Gas adsorption on a solid surface has been used in many applications such as heterogeneous catalysis⁵⁸, adsorption chillers⁵⁹, air purification⁶⁰, gas separation⁶¹ and hydrogen storage.^{62–64} The first

documented systematic investigation into the phenomenon of adsorption was conducted by Scheele in 1773.⁶⁵⁻⁶⁷ In 1836, Berzelius found that highly porous materials were the best adsorbents.⁶⁷ In 1881, Chappuis and Kayser discovered that increasing the surface area of a sorbent material increased its adsorption capacity.⁶⁷ Kayser presented the term adsorption and decided that it was a surface phenomenon. Chappuis and Kayser were also among the first researchers to measure adsorption isotherms.^{65–68} The term adsorption isotherm describes adsorption measurements at a constant temperature. Equations derived from these isotherms give beneficial information about the characteristics of adsorbents. These include but are not limited to the surface area, pore volume and pore size distribution. Several studies on adsorption measurement were done in the early 20th century. In 1918, the first isotherm was provided by Langmuir, who devised a model for monolayer adsorption that became the basis for modern-day adsorption theory.^{69,70} During the 1930s, Brunauer, Emmett and Teller (BET) developed Langmuir's ideal localised monolayer model to include multilayer adsorption.⁷¹ The BET theory assumes that the Langmuir model applies to each adsorption layer on an energetically homogenous surface.67-71 Later, Brunauer, Demming, Demming and Teller further extended BET theory to include capillary condensation, the phenomenon of a gas adsorptive condensing to a liquid-like phase within a pore structure at a pressure lower than the saturation pressure.⁷² Classifications of 8 different types of adsorption isotherm were laid out, which were later adapted into the classifications defined by the International Union of Pure and Applied Chemistry (IUPAC) today.72

Nowadays, the BET method is accepted as a typical procedure for determining the surface area of many porous materials. BET can describe the entire course of the isotherm, including monomolecular adsorption, polymolecular adsorption and capillary condensation. However, BET theory has some limitations, which cannot sufficiently describe capillary condensation in a material with various capillary widths and cannot account for adsorption taking place above the critical temperature of the adsorptive.^{68,72}

1.6.1 Physisorption

In a gas/solid system, adsorption is known as the enrichment of molecules, atoms, or ions close the solid surface and beyond the solid structure.⁷² Although the concept of the adsorption of gases onto solid materials has been studied for centuries, a comprehensive understanding of the adsorption process has only developed in the last few decades. In a solid porous material, adsorption takes place within the internal pore structure and on the outer particle surface.⁷² Adsorption differs from absorption; adsorption describes the interaction when a molecule comes into contact with a surface, whereas absorption defines an absorptive infiltrating the material surface and entering the bulk material.

Adsorption can occur either chemically (chemisorption) or physically (physisorption). Chemisorption refers to adsorption onto a surface by forming new chemical bonds. The adsorptive and the adsorbent are chemically changed through the process. Physisorption refers to adsorption onto a surface that takes place through intermolecular forces. Both the adsorptive and the adsorbent remain unchanged, and the process is easily reversed.⁷²

Adsorption is always a spontaneous thermodynamic process. This statement can be explained in two ways: (i) During adsorption, there is a decrease in surface energy, which appears as heat, so it is an exothermic process. (ii) Δ H of the adsorption is always negative (Δ H < 0). At a point, when gas is adsorbed on a solid surface, a freedom of movement of the adsorbate molecules becomes restricted, causing a reduction in the entropy of the gas (Δ S is negative). For a process to be spontaneous, Δ G must be negative (Δ G <0). As $\Delta G = \Delta H - T\Delta S$, since Δ S is negative, ΔH has to be negative to make Δ G negative. This means that the adsorption is permanently an exothermic process, and the extent of gas adsorption increases as temperature decreases.⁷³ This indicates that it is necessary to maintain low storage temperatures to ensure the molecules are stably adsorbed.

1.6.2 Pore Classifications

Porous materials contain interconnected pore systems, whereby the pores within the material matrix that contain a fluid. Pores are generally classified according to their shape and size.^{72,74} According to their geometry, shape classification has been proposed by Kaneko, who groups these pore types into cylindrical, funnel, slit-shaped and ink-bottle shapes (Fig. 1.5).⁷⁵ The geometry of the pores can be estimated using adsorption isotherms and electron microscopy techniques.^{35,75,76}



Figure 1.5: Pore shape classifications.^{35,75}

Pore modelled systems are usually described in geometric bodies like cylinders (for alumina) and slits (for activated carbons).³⁵ The pore shapes of porous materials are typically based on these model systems for simplicity.

Various categories of pore size classifications have been described.⁷⁷⁻⁷⁹ The classification was done according to pore diameter by Dubinin in the early 1950s and are now part of IUPAC recommendations, which are widely used and accepted in the size classification of pores.^{72,77} The IUPAC pore size classifications are as follows:

- Micropores: pores of width < 20 Å (e.g. Zeolites)
- Mesopores: pores of width 20 500 Å (e.g. Aerogels)
- Macropores: pores of width > 500 Å (e.g. Glasses)

The category of micropores can be further divided into:⁷²

- Supermicropores: micropores > 7 Å
- Ultramicropores: micropores < 7 Å

Pore size determination is based on various mechanisms that occur in the pores during nitrogen adsorption at -196 °C and 1 bar. Multilayer adsorption correlates to macropores, capillary condensation correlates to mesopores and micropore filling relates to micropores.⁷²

Pore size and pores size distribution play significant roles in porous material applications. However, given the irregularities and complexities of the pore system of porous materials, there is yet to be a unified agreement on which pore classification criteria is better. Nevertheless, the size classification proposed by IUPAC is a universally accepted method for classifying pores.^{72,77}

Pore type classification considers the pores accessibility to its surrounding. Figure 1.6 shows five types of pores based on the accessibility to an external fluid. There are open pores that are accessible from the external particle surface. An open pore that is opened at one end is labelled as a 'blind' pore, while an open pores that is opened at both ends are 'through' pores.³⁵ Open pores are of more interest in functional applications such as catalysis, filtration and adsorption as they are necessary for substrates to penetrate and exit pores. Pores that are not accessible from the external particle surface are closed pores, and they are not connected with a molecule's adsorption or permeability. Closed pores, on the other hand, have an effect on the mechanical properties of materials and are useful in lightweight structural applications and insulation.^{35,79}
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Figure 1.6: Schematic of pore type classifications.^{35,76}

Porous materials can have either uniform porosity, where all the pores are the same size and shape or hierarchical porosity where pores are arranged in a hierarchy and comprised of pores of differing dimensions. In addition, different materials characteristically show particular porous structures, which might vary based on the synthesis conditions used. For example, MOFs, which are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules, and zeolites, which are any member of a family of hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals, both can have uniform porosity, where the material's framework structure determines the pore size and shape.^{80,81} In contrast, the pore structure of activated carbons is often non-uniform and hierarchical, but can be controlled by the synthesis conditions.^{82–86}

The wide variety of porous materials available - each with their unique porous properties and structures results in porous materials playing a significant role in adsorption and fields such as purification, electrode synthesis, catalysis medicine and superconductors.^{80,82,87,88}

1.6.3 Pore Filling Mechanisms

It is critical to understand the mechanism of how porous structures fill with an adsorbing gas, particularly when analysing and developing porous materials. The process of pore filling can be described by four main phenomena: micropore filling, monolayer adsorption, multilayer adsorption and capillary condensation. Physisorption can be illustrated in stages, as shown in Figure 1.7, based on a linear increase in the proportion of surface coverage by adsorbed molecules with increased pressure.

Micropore filling occurs initially as an adsorptive is introduced. Adsorbentadsorbate interaction is strongest in micropores, as adsorbing molecules are surrounded by stabilising intermolecular forces from all pore walls. The adsorbent diffuses through the network of pores, and the adsorbed molecules will spend the most time in the smallest and most energetic open pore of the porosity at low pressures.^{72,89–91}

As gas pressure increases, mesopores begin to fill when all accessible micropores are completed, and the coverage of adsorbed molecules rises to form a monolayer. With further increase in gas pressure, multilayer coverage begins in mesopores. Here, the adsorption layer contains more than one layer of adsorbed molecules, and not all adsorbed molecules are in contact with the adsorbent surface. Adsorption interaction energies for the additional layers are low as adsorbing molecules are further away from the adsorbent

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surface; therefore, multilayer adsorption only occurs at higher relative pressure.^{72,89} Co-operative adsorption aids multilayer adsorption, and some open pores are capable of holding two or three molecules, and the presence of one molecule in a pore capable of holding two causes the pore to behave like a smaller pore, providing a more stabilising environment for incoming molecules, therefore encouraging further adsorption.⁹²



Figure 1.7: Schematic illustrating the pore filling process.⁹³

Capillary condensation occures at a higher relative pressure (P/Po > \sim 0.2), and it involves residual pore spaces being filled with condensed liquid from the adsorbate vapour within the mesopores at a pressure (P) below the saturation pressure of the bulk liquid (Po). The condensed fluid fills residual space within the mesopores once multilayer adsorption has been completed due to increased van der Waals forces in the confined pore.⁷²

In general, the isosteric heat of adsorption decreases as gas uptake increases. Adsorption sites with intense binding energies (small micropores)

fill at very low pressures, with less favourable sites not filling until the system is at higher relative pressure.⁸⁹⁻⁹¹ In hierarchical pore structures, which possess a multimodal pore size distribution of micro-, meso-, and/or macropores, gas adsorption occurs efficiently due to better diffusion. Micropores allow for high uptake at low pressures, whereas mesopores have good channel connectivity and allow for rapid gas diffusion through the pore structure. Macropores allow adsorptive molecules from outside the particle to diffuse into the internal pore structure quickly.⁹²

1.7 Porous Materials

Porous materials have received extensive attention as because of their unique properties, including their hydrophobicity, chemical inertness, good thermal and mechanical stability and high surface area, giving good physisorption capacity.⁹⁴⁻⁹⁶ Porous materials have been extensively investigated to understand the nature of their framework and enhance usability and functionalisation. A variety of porous materials are presently being developed for gas storage. Each has advantages and disadvantages, with research focusing on improving the performance and commercial applicability of the materials.

1.8 Types of Porous Materials

1.8.1 Metal Organic Frameworks

Metal-organic frameworks have gained considerable attention as a promising adsorbent for their possible uses in energy carrier gas storage (e.g., hydrogen, methane and acetylene) and carbon dioxide capture, due to their unique properties such as exceptional surface areas, well-defined and

chemically tunable pore sizes and functionalizable/modifiable pore walls.^{44,52,57,97}

MOFs consist of metal ions or metal-containing clusters connected by organic ligands through metal coordination bonds. The metals and linker molecules can be varied to create a seemingly infinite number of different MOFs.⁵⁷ This enables the creation of MOFs for various applications, including drug delivery, purification, catalysis and gas separation and storage.^{98,99}

In 2018, Hönicke *et al.*¹⁰⁰ synthesised a MOF, DUT-60, that have the highest recorded surface area and pore volume of any material of up to 7839 m² g⁻¹ and 5.02 cm³ g⁻¹, respectively.¹⁰⁰ In addition, many studies on metal-organic frameworks have reported CH₄ uptake capacity; for example, in 1997, Kitagawa¹⁰¹ and co-workers were the first researchers to work on the porous MOF material for methane storage purposes. Subsequently, many researchers have attempted to create MOF materials with higher methane storage capacities. Enhancement in CH₄ adsorption has been achieved with several MOFs. Examples include HKUST-1⁵², MAF-38⁵², and Ni-MOF-74⁹⁷, which display high methane uptakes (267 cm³ cm⁻³, 263 cm³ cm⁻³, and 251 cm³ cm⁻³), respectively, at 65 bar, which are close to the DOE target.

Despite the impressive potential of MOFs in gas storage, they have significant challenges that must be overcome for widespread commercial use. Considerably higher usable methane volumetric capacity is needed to improve the driving range to levels closer to gasoline vehicles.⁴⁴ Therefore, it is essential to discuss and treat systems-level factors that will seriously affect the actual MOF performance, such as heat capacity, compaction, thermal conductivity and resistance to impurities.⁴⁵ The price of MOFs, which is

relatively high, is also be an essential factor in determining their competitiveness as a methane storage material.⁴⁴

1.8.2 Zeolites

Zeolites are a class of crystalline microporous aluminosilicates formed naturally by pre-historic volcanic eruptions and, more recently, synthetically, for various applications such as molecular sieves, catalysis and gas adsorption.^{46,55,97} Zeolites were the first materials used as adsorbents for ANG technologies owing to their high surface area and flexibility when tailoring pore volumes and particle shapes.¹⁰² Traditional zeolites usually show methane uptake below 110 cm³ cm⁻³ at room temperature and 35 bar.⁵⁰ However, studies of methane adsorption in zeolites have continued to aid the understanding and design of novel adsorbent materials. For instance, zeolite-template carbons (ZTCs) have been developed for methane storage.¹⁰³ The ZTCs, which possess small micropores of size ~1.3 nm, presented volumetric CH₄ storage capacity and working capacity of up to 210 cm³ cm⁻³ and 175 cm³ cm⁻³ at 5-65 bar, respectively. The ideal microporous structures and uniform particle morphology of ZTCs contributed to efficient packing of particles.⁵⁵

Although zeolites have good methane uptake, their use as NG sorbents in ANG storage systems is limited by several factors. Zeolites are highly hydrophilic, which favours interactions with water instead of methane, consequently decreasing their storage capacity for natural gas.¹¹ Furthermore, methane storage is exclusively limited to micropores and some mesopores, whereas macroporosity is an unavoidable product during the bulk

packing of crystals. Consequently, macroporosity must be avoided as it is not valuable for methane storage in ANG systems.⁴⁵

1.8.3 Porous Carbons

The IUPAC defines activated or porous carbons as carbon materials produced by subjecting a char to various physical or chemical reactions before, during, or after carbonisation to improve their adsorptive properties. Adsorptive properties are improved by increasing surface area and volume via creating or developing small pores within the structure.¹⁰⁴ Porous carbons have an amorphous, graphitic-like laminar structure that varies depending on the preparation conditions.^{82,96,105} Carbon atoms preferentially form graphitic-like sheets of sp2 hybridised carbon during high-temperature activation, which are likely to contain defects. Graphite sheet stacking is disrupted and disordered, resulting in slit-shaped voids or pores throughout the structure.¹⁰⁵ The graphite stacking becomes increasingly disordered as the degree of activation increases, resulting in a porous and amorphous structure. The pore structure is generally hierarchical to varying degrees; pores can range in diameter from ~ 0.5 nm to large macropores.⁸² Owing to the nature of graphite stacking, such carbons are commonly assumed to have slit-like pores. Curvature in the sheets can be caused by defects in the graphite structure, such as holes or non-hexagonal rings. Overall, porous carbons do not show long-range order but do show a variety of short-range orders.^{82,96,105}

Porous carbons have a long history as a multipurpose adsorbent with many applications, including water purification, recovery and removal of impurities from gaseous, aqueous and non-aqueous streams, and many energy-related applications.^{82,85} The considerable usage is due to their abundance, thermal

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and chemical stability, the possibility and "processability" of tuning their structural and textural properties to fulfil specific application requirements.⁸² Activated carbon, the most researched class of porous carbons, has been conventionally used as an adsorbent for removing impurities and pollutants from gases and liquids.⁸² Early in the 20th century, the first industrial manufacture procedures of defined-property activated carbons were developed with powder forms, and later, the development of granular activated carbon was promoted. Currently, to meet advancing industrial and technological needs, activated carbons are available in other different physical forms such as fibres, pellets, cloths, and felts.⁸² In addition, many advances have been made in controlling the textural properties of activated carbons and their various physical forms. For example, unlike traditional activated carbons, which have a wide pore size distribution (PSD) ranging from the micropore to the macropore region, recent advances in activation procedures and precursors allow for greater control over the pore size distribution.⁸² These properties have expanded the range of uses for activated carbons to include energy storage in catalysis/electrocatalysis, supercapacitors and Li-ion batteries and CO₂ capture or H₂ storage.⁸²

In synthesising activated carbons, a wide range of organic products can be employed as feedstock. Agricultural produce and biomass such as peat, rice husk, sawdust, wood, coconut shells or fruit bones are preferred as uncarbonised feedstocks.¹⁰⁶⁻¹¹² Using these materials is very attractive because they are available as low-cost wastes that may be turned into highvalue-added products. In addition, carbonised feedstocks, including coal, lowtemperature lignite coke, charcoal, and biochar, can be used in activated

carbon production. The type of feedstock used has a significant impact on the characteristics of activated carbons.^{113,114}

The activation of carbon materials can be performed either physically, chemically, or a combination of both.⁸² Physical activation can be done in two steps wherein the first step is pyrolysis of the carbon precursor at 400–900 °C in an inert atmosphere to remove volatiles, followed by partial gasification as the second step in the presence of mildly reactive oxidising gases, such as CO₂, steam or air, either singly or in combination at 350–1000 °C.^{82,85,115} The activating gas penetrates the internal structure of the precursor and undergoes oxidative reactions, which results in the removal of carbon atoms leading to subsequent opening and widening of pores. The physical nature and chemical charachterisations of activated carbons depend on the precursor, the oxidising agent, the activation temperature and the activation time.^{82,85,115}

Chemical activation, on the other hand, is a one-step process in which a carbon precursor is mixed with a chemical activating agent (commonly a strong acid or base such as ZnCl₂, H₃PO₄, KOH and NaOH) before pyrolysis within a temperature range of 450–900 °C under an inert atmosphere.^{82,85,115} The common feature of the activating agents is their ability to act as dehydrating agents (ZnCl₂ and H₃PO₄) or oxidising agents (KOH and NaOH), thereby influencing pyrolytic decomposition and inhibiting tar formation.^{82,85,115} In particular, activated carbons with highly developed microstructure and high surface area can be generated by chemical activation with KOH. This KOH-carbon reaction, along with the decomposition of the carbonates at high temperature, releases H₂, CO and CO₂, which develop the pore network as they escape to the particle surface.^{82,83} Mineral, organic and

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lignocellulosic raw materials have been processed with KOH to generate highly porous carbons. These include but are not limited to coal¹¹⁶, petroleum coke¹¹⁷, walnut shells¹¹⁸, corncob¹¹⁹, dates stones¹¹² and sawdust.¹¹⁰

Pore structure formation is influenced by several parameters, including the nature of precursor, the type of activating agent and the ratio of both, as well as activation temperature and duration. Generally, porosity development increases with the activating agent's ratio, activation temperature and duration.^{82,85,115} This is often accompanied by broadening the pore size distribution (PSD); as a greater volume of gas is created and escapes to the particle surface, small pores collapse into larger pores.^{82,85} Chemical activation has several advantages over physical activation, including the use of lower temperatures in a typically single step and shorter heat treatment periods. Materials with high carbon yield, high surface area and large pore volume can therefore be generated via chemical activation. Microporosity can be well developed, with narrow and more controllable PSD. Controllable PSD is critical for the use of activated carbons in supercapacitor energy storage and gas storage applications.^{82,115} On the downside, the chemical activating agents are usually corrosive, which can have adverse effects on ease of handling and waste removal.¹²⁰

As stated above, KOH activation has gained growing attention since it has proven to be a powerful technique for producing carbons with high surface area and pore volume from different carbon sources.^{115,117,121} Activation with KOH consistently produces carbons with comparatively narrow PSDs with a higher proportion of microporosity.¹¹⁵ Despite the fact that KOH activation is a well-known approach for generating the pore network in carbons, the activation mechanism is complex due to the numerous variables in both the

experimental parameters and the reactivity of various precursors.¹¹⁵ Generally, the reaction of KOH and carbon starts with solid-solid reactions and then progresses through solid-liquid reactions, which include the reduction of potassium (K) to metallic K, carbon oxidation to carbon oxide and other carbonate, and reactions among various active intermediates.^{115,117,121} Several reaction products have been identified in multiple attempts to understand the reaction mechanism of KOH-C systems. Otowa *et al.*¹¹⁷ proposed that the KOH activation process consists of several consecutive/simultaneous reactions, some of which are presented below. The activation starts with the reaction below.

$$6KOH + 2C \quad \rightarrow \quad 2K + 3H_2 + 2K_2CO_3$$

At 400 °C, KOH dehydrates to form K_2O . The carbon is then consumed by the reaction of carbon and H_2O , which results in the emission of H_2 . The reaction of K_2O and CO_2 gives K_2CO_3 .

$$2KOH \rightarrow K_2O + H_2O$$

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO_2 + K_2O \rightarrow K_2CO_3$$

The formation of carbonate, as elemental C is consumed, and the intercalation of K and its compounds generates pores. Micropores are also formed via gasification as volatile molecules are released. At higher temperatures above 700 °C, K_2CO_3 , decomposes into CO_2 and K_2O , the latter reacts with the carbon skeleton, releasing CO_2 , as shown below.¹¹⁵

$$\begin{array}{c} \mathsf{K_2CO_3} \rightarrow \mathsf{K_2O} + \mathsf{CO_2} \\ \\ \mathsf{CO_2} + \mathsf{C} \rightarrow \mathsf{2CO} \\ \\ \\ \mathsf{K_2CO_3} + \mathsf{2C} \rightarrow \mathsf{2K} + \mathsf{3CO} \\ \\ \\ \\ \mathsf{C} + \mathsf{K_2O} \rightarrow \mathsf{2K} + \mathsf{CO} \end{array}$$

The intercalation of metallic potassium into the carbon matrix causes the development of the porosity and the surface area of activated carbons, where several carbon atomic layers have widened and pores are formed.¹¹⁵ Nevertheless, the activation mechanisms and the reaction processes vary depending on the reactivity of various carbon sources and the activation parameters. As a result, it is impossible to predict which activation procedure will produce activated carbons with the desired structure and properties and which reactions and activation mechanisms will be involved for each carbon precursor. Activation parameters have a substantial impact on the surface chemistry and pore microstructure, which affects the performance of KOH-activated carbons in a variety of applications. Despite these limitations, KOH activation remains an effective and successful method for developing porous networks in carbon materials.¹¹⁵

As previously mentioned, a wide range of precursors can be used to produce porous carbons. Different precursors need different preparation conditions and this can affect the pore structure of resulting porous carbons. Regardless of the precursor used, the preparation of porous carbons offers a wide range of tailoring opportunities to create carbons with specific properties. The choice of preparation and activation conditions and the activating agent, the changes in the ratio of activating agent to precursor, as well as the activation temperature and duration have varying effects on the development of the pore structure. Variation is these variables can lead to porosity development,

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often with increased surface area and pore volume, with smaller pores collapsing into larger ones and broadening the PSD.^{82,85,115,122}

These tailorable factors have stimulated extensive research into the preparation of carbon materials, providing promising results. Activated carbons have been broadly used as CH₄ storage adsorbents. Activated carbons can display high volumetric CH₄ uptakes in the range of 120 - 200 cm³ cm⁻³ at pressures of 5 - 35 bar, and high volumetric CH₄ uptake higher than 200 cm³ cm⁻³ at pressures greater than 65 bar. For instance, Casco et al.¹²³ reported on carbon materials (LMA series) with high surface area that achieved promising methane storage capacity with the best sample (LMA-738) having storage capacity of 220 cm³ cm⁻³, and a high working capacity of 174 cm³ cm⁻³ at 100 bar. Recently, Altwala et al.¹¹² reported excess methane uptake up to 196 cm³ cm⁻³ and total uptake of up to 222 cm³ cm⁻³, at 35 bar, which is superior to any previously published carbon and comparable to the best metal-organic framework. Generally, activated carbons have higher mechanical strength than MOFs, allowing them to avoid packing-related damage to their efficiency, which further enhances their performance.112

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Chapter 2: Characterisation techniques

It crucial to to investigate the material properties in order to design a porous material for any application. In this respect, pore structure, the nature of the materials, and the level of porosity are important features to study. This chapter describes the experimental techniques and instrumentation that have been used to investigate and characterise the generated porous materials, such as the elemental analysis, thermogravimetric analysis (TGA), porosity analysis using the Brunauer, Emmett and Teller (BET) theory, powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). This chapter also presents gas storage techniques used to examine carbon dioxide and methane storage uptake.

With respect to the accuracy of the results, the most important thing to note here is that in our cases, we have not looked at one sample or a limited number of samples. We look at many samples and the trend. As a result, the trend is far more important than any individual, which tends to reduce any problems or errors made by workers. Secondly, because we're looking at a large number of samples and a trend, reproducibility is less of a concern. For example, if you make one sample and get it wrong, you really get it wrong. But if you prepare six samples and you observe a trend within those samples and it is a consistent trend, that trend is real, which therefore means that the samples and the values that you're getting for each of the samples are correct.

2.1 Elemental Analysis

Elemental CHN analysis is a technique for determining a sample's composition and provides the proportion (as a percentage) of carbon, hydrogen, and nitrogen in the sample. The technique involves combustion analysis, where a sample is burned (or combusted) and the resulting products are analysed.¹ The analysis typically uses a small amount (typically 2 mg) of sample that is burnt in a furnace at high-temperature (975 °C) under a flow of pure oxygen. The use of high purity oxygen is essential to avoid any contaminants particularly with respect to the presence of carbon dioxide. This problem can, however, be mitigated by performing oxygen calibration tests before analysis. The analysis of the burnt products is carried out using helium gas as carrier gas and passed through appropriate reagents to remove by-products such as sulphur, phosphorus, and halogen gases. Nitrogen oxides are transformed to molecular nitrogen, and any remaining oxygen is removed. Subsequently, the sample gas flows into a mixing volume, where it is homogenised to an accurate volume, temperature, and pressure and then passed through three thermal conductivity detector pairs. The first pair eliminates water from the sample gas, and the signal measured before and after this operation indicates the concentration of water in the sample; hence, the quantity of hydrogen present. The carbon content is calculated from carbon dioxide extracted by the second pair of thermal conductivity cells. The third thermal conductivity cell is used for N determination from the remaining N₂/helium flow. The resulting signal is compared to a reference cell through which pure helium flows, giving the original sample's nitrogen content.¹

Method: The carbon samples were analysed using a CE-440 Elemental Analyser (Exeter Analytical). Samples were typical submitted to Analytical Services within the School of Chemistry for analysis.

2.2 Thermal Gravimetric Analysis (TGA)

TGA is used to ascertain carbon purity and thermal stability by heating at increasing temperature and monitoring any mass or phase changes. Other characteristics of materials that may be probed by TGA include determination of (i) degradation temperature, (ii) amount of absorbed moisture content, (iii) organic and inorganic components in composite materials, and (iv) decomposition points of explosive and solvent residues. TGA measures changes of a sample weight as a function of temperature in a controlled environment. Materials that display weight loss or gain weight because of the disintegration, oxidation or dehydration can be characterised thus providing information on thermal stability, oxidative stability, moisture content, and

volatile content. For instance, at a final heating temperature higher than the carbon combustion point, the residual weight is nil for a fully carbonaceous sample. In contrast, the presence of residual weight indicates the presence of other inorganic or other refractory materials. A TGA analyser typically consists of a high precision microbalance with a pan upon which the sample loader is placed. The pan is set in a heated furnace with a thermocouple to observe the mass changes and measure the temperature accurately. The thermal analysis is typically carried out using an atmosphere of inert or oxidising gas with controlled flow rate, and an appropriate computer program gathers data from the analysis.^{2,3} Thermal stability and degradation temperature can be determined from a plot of sample mass as a function of temperature. A derivative weight loss curve (DTG) can also be derived from the data, and which is useful in determining the weight loss percentage per unit temperature and the point at which weight loss is most accelerated. The simultaneous use of TGA and DTG enables distinction between exothermic and endothermic events that are not related to weight loss (e.g. melting and crystallisation) and those that include weight loss (e.g. degradation).^{2,3}

Method: Thermogravimetric analysis was performed using a TA Instruments SDT Q600 analyser under appropriate atmospheric conditions. The analysis was typically carried out by measuring the weight change with an increase in temperature at ramp rate of 10 °C min⁻¹ up to 1000 °C under a static air atmosphere.

2.3 Porosity Analysis - Brunauer, Emmett and Teller (BET) Theory

The BET theory is the most common formalism used for characterising the porosity of porous materials. It uses the principle of gas adsorption at solid surfaces to determine the surface area, pore volume and pore size distribution. Stephen Brunauer, P.H. Emmet and Edward Teller developed this method in 1938⁴ as an extension to the Langmuir theory of adsorption developed by Irvin Langmuir.⁵ The Langmuir theory relates the number of molecules adsorbed at a surface to the pressure of the overlaying gas. Data is collected by exposing the surface of a clean sample in a controlled environment to the probing gas (typically nitrogen) at -196 °C and recording the amount adsorbed/desorbed as a function of applied pressure. Adsorption is measured by gradually increasing the pressure from relative pressure $(P/P_0) = 0$ up to saturation, $P/P_0 = 1$ and desorption then follows by decreasing the pressure back to $P/P_0 = 0$. These series of measurements give rise to adsorption/desorption isotherms used to characterise the adsorbent.⁵ The adsorption isotherm consists of a sequence of measurements of the adsorbed quantity as a function of the equilibrium gas pressure at a constant temperature.⁶ The adsorption isotherm is plotted based on the amount adsorbed expressed as a molar quantity in mmol/g versus relative pressure (P/Po). The shape of the adsorption isotherm suggests the nature of the sample, particularly the type of porosity and the nature of adsorption taking place. The isotherm can also display hysteresis loops that yield further information about the nature of the sample.⁷

In 1940, Brunauer, Deming, Deming and Teller (BDDT) introduced the first systematic attempt to describe and classify adsorption isotherms for the

solid-gas interphase.⁸ Over the following years, further research into pore structures led by IUPAC redefined the classification into 8 isotherm types (Fig. 2.1).^{9,10} The shape and classification of an isotherm can be used to inform on the characteristics of a porous material.

- **Type I** isotherms indicate a microporous structure and particles with a relatively small external surfaces area, with the primary adsorption taking place below a relative pressure of 0.1. The limiting uptake is defined by the accessibility of the micropore volume as opposed to the internal surface area. In type I isotherms, high uptake at very low P/Po indicates enhanced favourable adsorbate-adsorbent interactions in small micropores. However, whilst the sharp knee of type I(a) isotherms suggests the presence of micropores, the broader knee of type I(b) indicates a wider pore size distribution, including larger micropores and small mesopores.
- Type II isotherms are observed for non-porous or macroporous materials. The point of inflexion (B) represents the completion of monolayer adsorption and the start of multilayer adsorption at higher relative pressure. A wider knee indicates more overlap between the completion of the monolayer and the commencement of multilayer adsorption. The second convex knee indicates that multilayer adsorption onto the particle surface is continuing with increasing pressure, but without reaching saturation at P/Po= 1.
- **Type III** isotherms correspond to a non-porous or macroporous material. It is convex to the relative pressure, which implies adsorbate-adsorbent interactions are weak with no definable monolayer.

- Type IV isotherms are characterised by a hysteresis loop, indicating capillary condensation taking place in mesoporous adsorbents. Type IV(a) isotherms show a hysteresis in mesopores when the pore size exceeds a certain width. Type IV(b) isotherms correspond to structures with narrower mesopores with cylindrical or conical-shaped pores with a closed, tapered end.
- **Type V** isotherms are uncommon and exhibit weak adsorbateadsorbent interactions, with pore filling at higher relative pressures.
- Type VI isotherms are stepwise adsorption, indicating a non-porous material. The steps show multilayer adsorption taking place as relative pressure increases. The sharpness of the steps relies on the system type and temperature. The height of each step corresponds to the monolayer capacity for each adsorbed layer.¹⁰





Figure 2.1: The IUPAC classification of sorption isotherms.^{9,10}

Three stages can define the adsorption of gas molecules into pore surfaces. Firstly, micropore filling occurs, where adsorbate molecules cover all pore and cavity walls, and all adsorbed molecules are contacted with the adsorbent surface. Secondly, mono-multilayer coverage occurs, where the adsorbent surface is covered in more than one layer of the adsorbate, and not all adsorbate molecules are in contact with the adsorbent surface. Finally, capillary condensation occurs; this is where pore space remaining in larger pores once complete multilayer coverage is filled by condensate separated

Chapter 2: Characterisation techniques

from the gas phase by a meniscus. Therefore, capillary condensation only occurs in mesopores and usually causes a hysteresis loop to appear in the sorption isotherm.^{10,11}

Hysteresis loops appear when adsorption and desorption of the adsorbate occur at different relative pressures due to capillary condensation.¹¹ Hysteresis loops are typically linked with the condensation of the adsorbing gas in mesoporous materials; they occur in the multilayer region of the physical adsorption isotherm. In addition, hysteresis is related to thermodynamic effects, i.e. the stability of the adsorption and desorption branches or network effects, for example, if larger pores can access the surroundings only via smaller pores, the pressure needs to be low enough to evacuate the smaller pores first before the adsorbate can be evacuated from the larger pores. Hysteresis loops can be classified into different types as shown in Figure 2.2.⁹





Figure 2.2: Types of hysteresis loops of adsorption isotherms.⁹

- Type H1 hysteresis loops appear to be vertical and parallel to the two branches (adsorption and desorption) over a reasonable range of gas uptake. They are given by mesoporous structures with a narrow pore size distribution of approximately uniform and spherical geometries in a regular array hence having narrow pore size distribution. The narrow loop at high relative pressure indicates that capillary condensation occurs late during adsorption.
- Type H2 hysteresis loops are associated with porous adsorbents with undefined shape and pore size distribution. H2 (a) loops occur in

porous materials that do not have well-defined shapes which present pores with a narrow neck and a wide body. H2 (b) loops have a gentler desorption curve due to pore blocking occurring in pore necks of broader size distribution.

- Type H3 loops are shown by plate-like particles, giving rise to slitshaped pores. It does not show limiting adsorption at high pressures.
- Type H4 loops are related to narrow slit-like pores and are similar in appearance to H3 loops but show horizontal and parallel branches of adsorption and desorption over a reasonable range of pressures. H4 loops are indicative of materials possessing a mix of mesopores and micropores.
- Type H5 hysteresis loops are uncommon and indicative of mesoporous structures that contain open and partially blocked pores.^{10,11}
- Type H3, H4 and H5 hysteresis loops have a clear closure point where the desorption curve re-joins the adsorption branch. The closure point is characteristic of certain adsorptive at particular temperatures.^{10,12}

The Langmuir theory describes monolayer adsorption as observed in type I isotherms. The heat of adsorption influences the initial steep rise in the isotherm; the stronger the interaction between the adsorbent and the adsorbate, the more intense the initial increase. The isotherm reaches a plateau that corresponds to complete monolayer coverage.¹³

The BET model extends the Langmuir theory to account for multilayer adsorption. Type II, IV and VI isotherms can be evaluated using this method. The following assumptions are made by the BET method for the determination of specific surface area:

- The surface is flat and homogenous.
- There is no lateral interaction between adsorbed molecules.
- The uppermost layer is in equilibrium with the vapour phase, and at saturation pressure, the number of layers becomes infinite.
- The first layer adsorbed on the surface involves the heat of adsorption, while subsequent layers involve the liquefaction energy of the adsorbent.

Taking into account these assumptions, the BET equation for multilayer adsorption is expressed as:¹⁴

$$\frac{P}{V(Po - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left(\frac{P}{Po}\right)$$

Where P = relative pressure of adsorbed gas, P_o = saturation pressure, V = the molar volume of the adsorbate gas at STP, V_m = monolayer volume and C = dimensionless constant related to the enthalpy of adsorption.

The BET equation assumes a straight line in the specified relative pressure range, P/Po = 0.05 - 0.30, and the BET surface area is calculated from the isotherm data within this range. This linear section should be shifted to a lower relative pressure for highly microporous materials.

The BET surface area (S_{BET}) can then be calculated:¹⁴

$$S_{BET} = \frac{V_m N_A \sigma_A}{V}$$

Where V_m = the amount of gas adsorbed in the monolayer, N_A = Avogadro's number (6.02 x 10²³), and σ_A = the cross-sectional area occupied by each

adsorbed nitrogen molecule (0.162 nm²) and V = the molar volume (22414 mL).^{10-12,14,15}

The material's pore volume is determined from the amount of adsorbed gas at saturation vapour pressure (P/Po = 0.99) when the pores are fully filled with the adsorbed gas. This can be done by converting the quantity of gas adsorbed to the corresponding volume of liquid at the adsorption temperature. Data is taken from this pressure point to ensure that the monolayer, multilayer and capillary condensation stages have been completed. At standard temperature and pressure and using liquid nitrogen, the conversion factor will be 0.0015468 (cm³/g, STP).

The micropore volume and micropore surface area can be estimated using the thickness-plot (t-plot) method. The volume of gas adsorbed is plotted against the thickness of the adsorbate molecular film. The thickness can be calculated using either the Halsey¹⁶ or the Harkins and Jura equations.¹⁷

$$t = \left[\frac{13.99}{\log\frac{Po}{Ps} + 0.034}\right]^{1/2}$$

$$t = 3.54 \times \left[\frac{5}{2.303 \times \log \frac{Po}{Ps}}\right]^{1/3}$$

The value of the y-intercept is calculated from the t-plot, which gives the micropore volume when the amount of adsorbed gas is converted to a liquid volume. According to the equations below,¹⁰ the slope of the linear section is
used to calculate the external surface area, then the micropore surface area can be determined.

 $V_{\text{micropore}} = (0.001547) \times (t - \text{plot intercept})$

 $S_{mesopore} = 1.547 \times (t - plot slope)$

 $S_{micropore} = S_{BET} - S_{mesopore}$

Gas adsorption can also be used to evaluate the pore size distribution, which is based on the fact that gas condenses to liquid within narrow pores at pressures less than that the saturated vapour pressure of the adsorbate gas. The Kelvin equation presents the relationship between the lowering of vapour pressure above a cylindrical column of liquid contained in a capillary and the radius (r) of the capillary.^{10,18} It is given as:

$$In \ \frac{P}{Po} = \ \frac{2\gamma Vm}{rRT}$$

Where P is the vapour pressure, P_0 is the saturated pressure, γ is the surface tension, V_M is the molar volume, R is the universal gas constant (8.3145 J/K/ mol), T is temperature and r is the radius of droplet/meniscus.¹⁸

The Kelvin equation is limited in some cases because adsorption on mesoporous solids is accomplished through multilayer adsorption followed by capillary condensation. As a result, the BJH (Barrett, Joyner, and Halenda) model, based on the Kelvin equation, is commonly used to calculate pore size distribution in mesoporous materials.¹⁹ The BJH model involves the following

assumptions: (1) the pores are cylindrical, (2) the equilibrium between the adsorbed phase and the gas phase during the desorption is determined by two possible mechanisms, physical adsorption on the pore wall and capillary condensation in the inner capillary volume.^{10,18,19}

The BJH method is not readily applicable for determining micropore sizes because the multilayer thickness correction on the Kelvin equation relies on the pore width, pressure, and temperature.⁷ It is generally accepted that the BJH method only gives a rough but still useful assessment of the mesopore size distribution.

Unlike the BJH method, which is limited to pores within the mesopore range, the density functional theory (DFT) is independent of capillary condensation and can be applied to micro and mesoporous adsorbents. DFT is based on classical and statistical thermodynamic principles, and it is assumed that the adsorbate is in thermodynamic equilibrium with the adsorptive in the gas phase under specific controlled conditions. The DFT shows a satisfactory characterization of adsorption and phase transitions in slit-shaped and cylindrical mesopores. The DFT can be used to interpret different types of adsorption isotherm, and the PSD is evaluated from the adsorption isotherm data that is introduced as follows:^{10,18}

Nexp
$$\frac{P}{Po} = \int_{Wmin}^{Wmax} Ntheo\left(\frac{P}{Po}, w\right) f(w)dw$$

Where N_{exp} is the experimental isotherm, W_{max} and W_{min} are the maximum and minimum pore, N_{theo} ($\frac{P}{Po}$, w) is the theoretical isotherms in model pores and f(w) is the PDS over a finite range of pore size.

Method: Nitrogen sorption isotherms and textural properties were determined using a Micromeritics 3Flex sorptometer. The surface area was calculated using the BET method based on adsorption data at a relative pressure (P/Po) range of 0.02 - 0.30, total pore volume from the amount of nitrogen adsorbed at P/Po of 0.99. The micropore surface area and micropore volume were determined via t-plot analysis. The pore size distribution was determined using non-local density functional theory (NLDFT) applied to nitrogen adsorption data. In a typical experiment, the samples were first heated at 200 °C and degassed for 16 h under vacuum. The samples were then weighed before analysis to obtain the precise weight of the sample. The sample is then moved to the analysis channel purged with nitrogen gas before analysis at -196 °C.

2.4 Powder X-Ray Diffraction Analysis (XRD)

Powder XRD is a valuable analytical technique for analysing the crystal structure of materials. It can be used to identify and characterise unknown crystalline materials and confirm known structures. Furthermore, "nonstructural" information thermal such as motion analysis, pressure/temperature dependency, charge density/high-resolution investigations, phase behaviour, and particle size analysis can be obtained. The principle behind this technique is that any radiation aimed towards materials will be scattered or absorbed. The scattered radiation can be used to identify materials based on the diffraction pattern of crystalline or ordered structure. X-rays are electromagnetic radiation with wavelengths between about 0.02 Å and 100 Å ($1\text{\AA} = 10^{-10}$ meters), and have been widely used to examine crystalline structures at the atomic scale. X-rays for analysis are

generated by bombarding high-energy electrons from a filament onto a metal target, often copper. The electrons have high energy to ionise some of the Cu 1s electrons. An electron in an outer shell then fills the unoccupied 1s level, and the energy released in the transition appears as X-radiation. As a result of the transition from 2p to 1s, Cuk α radiation with a characteristic wavelength of 1.5418 Å and energy of 8.04 keV is emitted. The generated X-ray beams are then directed towards a sample. The interaction with the sample leads to diffraction of the X-ray at a certain angle where a portion of the beam interacts with the atoms on the sample's surface, which are diffracted. The remaining amount penetrates the sample and is diffracted by the atoms in the second layer and so on. The diffracted beam is detected and can be used to produce a three-dimensional picture of the electron density within the sample and thus the crystalline structure.²¹

The fundamental equation for XRD studies is the Bragg equation, which is used to relate the X-ray wavelength to the diffraction angle and the lattice spacing of the structure:

$n\lambda = 2dsin\theta$

Where n is an integer representing the diffraction order: 1, 2, 3..., λ is the X-ray wavelength, θ is the diffraction angle, and d is the interlayer spacing distance. Strong diffraction can occur when the angle of incidence and diffraction are equal (Fig. 2.3). When the incident X-rays satisfy the Bragg equation, constructive interference occurs, resulting in a peak in intensity.

The powdered sample is scanned across various 2θ angles to get all potential diffraction directions of the lattice due to its random orientation.





Figure 2.3: Schematic diagram showing the diffraction of X-rays.²¹

X-ray analysis produces a diffractogram consisting of a plot of the angle of incidence against the diffracted beam's intensity at a range of angles characteristic of the sample's structure. The more crystalline a sample is, the better the diffraction and, therefore, a more defined diffractogram with sharper peaks. The peaks' position allows the pattern to be indexed, and the crystallographic structure can be determined. The d spacing and the size of the unit cell can also be determined.²¹ Additionally, comparing the XRD patterns of a material to the database of well-known structures can help to identify the materials under study.

Method: The XRD analysis was performed using a PANalytical X'Pert Pro diffractometer with CuK α radiation ($\lambda = 1.5406$ Å). The standard operating power of the X-ray tube was set at 40 kV and 40 mA, with a 0.02° step size and 2s step time in the 2 θ range of 2° to 80°. A zero-background single-crystal silicon sample holder was used.

2.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is one of the essential techniques used to examine the morphology of materials. It can also be used to obtain information about the chemical composition of a specimen, as well as the topography, and crystalline structure. A scanning electron microscope (Fig 2.4) uses a concentrated beam of high-energy electrons to probe the specimen surface. An electron gun generates a beam of electrons at the top of the microscope. The electron beam travels vertically over the microscope and becomes focused on the sample through electromagnetic fields and lenses. When the incident electrons, with high kinetic energy, are decelerated on the sample, signals are generated, including secondary electrons, backscattered electrons, diffracted backscattered electrons, X-rays and heat. Detectors collect these signals to produce SEM images.²²

The secondary electrons (SE - 10 eV to 50 eV) have low energy and exist only near the specimen's surface. They are used for displaying the topography and morphology of the sample.²³ Backscattered electrons (BSE) are fewer in number than secondary electrons but have higher energies and can, therefore, penetrate the surface and give information mainly about the interior surface of the sample. Heavy elements (those with a high atomic number) backscatter electrons more strongly than light elements, making them appear brighter in images. Thus, backscattered electrons are used to depict compositional contrasts in multiphase samples by displaying the spatial distribution of elements or compounds within the sample.²³ SEM can also generate very high-resolution images of a sample surface at various magnifications.²⁴ The obtained image is three-dimensional because of a significant depth of scanning field with a resolution approximately 1-5 nm.





Figure 2.4: Schematic diagram of a typical SEM.²⁵

Method: SEM images were recorded using a JEOL 7100F microscope operating with a 5-kV accelerating voltage. Samples were installed using a conductive carbon double-sided sticky tape prior to analysis.

2.6 Gas Uptake Measurements

CO₂ uptake of carbon samples was determined using an Intelligent Gravimetric Analyser (IGA). The IGA system precisely measures weight changes, pressure, gas flow, temperature and composition using a precise computer-control system. Thus, the amount of CO₂ adsorbed at changing pressure over the stated range is calculated, and the corresponding isotherm is generated. In a typical experiment, the dried sample (typically between 20 to 50 mg) was placed in a sample holder and loaded in the analyser. Prior analysis, the sample was outgassed at a high temperature of up to 240 °C and at a ramp rate of 5 °C min⁻¹ for several hours to eliminate adsorbed gaseous molecules, including water. The uptake measurements were carried out in the adsorption range of 0 - 20 bar, followed by a decrease in pressure from 20 bar for desorption.

Methane uptake was conducted with high purity methane (99.999%) and determined using a Hiden Isochema XEMIS Analyser. The sample is first degassed at 240 °C for \sim 3 h under vacuum. The isotherms of methane uptake were obtained at a temperature of 25 °C and pressures between 35 and 100 bar. During adsorption, the pressure is varied and then held constant at the set point pressure until equilibrium is reached. The weight will change accurately as the gas is adsorbed and desorbed at different pressures. The adsorption equilibrium points that have been collected from each single equilibrium (at each pressure point) are plotted as an isotherm between the uptake (mmol/g) and pressure (bar). The sorption isotherm can be considered as a series of equilibrium points. The measured weight changes are used to calculate the sorption uptake, and the resulting gas sorption isotherm (as shown in Figure 2.5) can be used to calculate the molar adsorption of the gas.^{26,27} The measurements by the XEMIS directly determine the excess methane uptake. Therefore, by considering the total pore volume of the carbon and the methane density at any given conditions, the excess values can be used to calculate the total methane storage capacity.

This can be accomplished by using the equation:

$$\theta_{\rm T} = \theta_{\rm Exc} + d_{\rm CH4} \times V_{\rm T}$$

Where θ_T is total methane uptake, θ_{Exc} is excess methane uptake, d_{CH4} is the density (g cm⁻³) of methane gas under the prevailing pressure and temperature, and V_T is total pore volume (cm³ g⁻¹) of the activated carbon.²⁸ The methane density was obtained from the National Institute of Standards and Technology (NIST) website (<u>https://www.nist.gov/)</u>.²⁹



Figure 2.5: Gas measurement isotherm.

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3.1 Abstract

The synthesis of porous carbons via an appropriate novel one-step method has been investigated. The heating of rich-carbon metal salts produces carbons having a porosity tailored to the targeted energy storage applications. Potassium hydrogen phthalate (KHP) and potassium phthalimide (PPI) were used to generate porous carbons with advantageous textural properties. All carbons showed the irregular, non-graphitic structure expected for porous carbons. TGA analysis showed that the carbons have high thermal stability, corresponding to their amorphous structures. The PPI-derived carbons exhibited high surface area of up to 2889 m² g⁻¹ and pore volume of up to 1.36 cm³ g⁻¹ after carbonisation at 900 °C, whilst those obtained using KHP as a carbon precursor have the surface area and pore volume varied between 488–1851 m² g⁻¹ and 0.20–1.03 cm³ g⁻¹, respectively. The carbon porosity can be readily tailored by adjusting the carbonisation temperature and, to a smaller extent, carbonisation time to optimise the textural properties. The PPI-derived carbons showed an ideal porosity for CO₂ uptake to the extent that the carbons captured up to 5.2 mmol g⁻¹ at 1 bar and 25 °C, which is amongst the highest ever reported for any porous carbons. Under CO₂ post-combustion capture conditions (0.15 bar at 25 °C), the PPI carbons stored 1.7 mmol g⁻¹ of CO₂, which is also among the highest so far reported for porous carbons. Methane storage capacities were also investigated at room temperatures (25 °C) and up to 35 bar. Both KHP and PPI carbons

displayed high adsorption behaviour in gravimetric methane storage capacity at 35 bar and 25 °C. A significant finding is that the carbons may be easily compacted to a high packing density of up to 1.15 g cm⁻³ with retention of their textural properties. The consequence of the compaction is that the high packing density of the PPI-derived carbons, coupled with their high gravimetric CH₄ uptake, gives high volumetric uptake and high working capacity of up to 227 cm³ (STP) cm⁻³ and 138 cm³ (STP) cm⁻³, respectively, at 35 bar and 25 °C, which are significantly higher than any previous value for porous carbons and comparable to the best metal-organic framework (MOF). According to the findings of this study, KHP and PPI are very competitive precursors for the simple synthesis of porous carbons with an attractive and unrivalled mix of properties for CO₂ and CH₄ storage applications.

3.2 Introduction

The demand for crude oil has steadily increased with growth in the world economy, raising concerns over the sustainability of oil reserves and on the associated environmental consequences of continued use of fossil fuels. The anthropogenic emissions of CO₂ from the combustion of fossil fuels are a key global environmental concern. Significant ongoing research efforts are currently focused on developing alternative cleaner fuels to relieve the environmental pressures and minimise the considerable dependence on crude oil.¹ Attention has been paid to hydrogen as a cleaner energy source as no greenhouse emissions or additional environmentally hazardous chemicals are emitted through the combustion of H₂. However, the so-called Hydrogen Economy is still far away from being commercialised.¹ In the interim, natural gas or biogas have been touted as ecologically friendly alternative fuels because they are naturally available and reasonably environmentally benign compared to oil-based fuels. Despite the fact that natural gas and biogas still produce CO₂, they burn more cleanly than conventional liquid or solid hydrocarbon fuels. However, methane, which is the main ingredient of natural gas and biogas, suffers from a low volumetric energy density.² Therefore, the use of methane in a variety of applications, particularly for vehicular on-board scenarios, is severely limited.² As a result, in order to achieve a competitive volumetric energy density on a broad scale, it is essential to design a safe and efficient techniques that yield reasonable driving ranges from a full fuel tank. Compression (compressed natural gas, CNG) or liquefaction (liquefied natural gas, LNG) can enhance the volumetric energy density of natural gas, but both of these techniques are expensive and unsuitable for light-duty passenger cars.³ The promising alternative to LNG and CNG is storing

methane as an adsorbed phase (adsorbed natural gas, ANG) in porous materials at room temperature and moderate pressure. Reduction in the working pressure would make tanks lighter, smaller and minimise the price and space requirements.^{3–5}

The effectiveness or viability of ANG technology depends mainly on improvements in methane storage. Many porous materials have been extensively examined and assessed for methane storage. Early efforts mainly concentrated on zeolites; however, their low surface area, which is typically < 1000 m² g⁻¹, limits the CH₄ uptake capacity.³ Metal-organic frameworks (MOFs) have been identified as excellent candidates to meet methane storage needs as they have promising characterisations such as high surface area and adjustable pore sizes. However, MOFs suffer from an inability to be compacted without loss of form and porosity meaning that they have low packing density and low volumetric uptake.^{6,7}

Activated carbons are one of the most extensively investigated class of materials for ANG technology due to their attractive properties in terms of cost, availability, thermal and chemical stability, high surface area and pore volume, readily designed pore structure, and the fact that their characteristics can be easily tailored for particular applications. The variety of methods for the preparation of porous carbons and the ability to tailor their textural properties have resulted in a various porous carbon types, each with unique properties.^{8,9}

The main parameters determining the suitability of porous carbons for gas storage applications are the surface area, pore volume and pore size.⁹ The most common method for generating highly porous carbons is chemical

activation, which involves heat treatment of carbon precursors impregnated with a chemical activating agent, usually KOH, under an inert atmosphere. Although porous carbons with highly improved textural properties can be obtained, several drawbacks pose concerns when using this method.¹⁰ Firstly, activating agents are corrosive, and large excesses (usually at least twice the mass of the carbon precursor) are required for chemical activation. Special equipment and handling conditions are therefore required, especially for large-scale use. Secondly, a strict acid washing of the resulting porous carbon is needed to leach out inorganic salts and residual products of activation to release the carbon's porosity.¹⁰ This adds an unwanted extra step to the activation procedure. As a result, a move to simple methods for preparing highly porous carbons is desirable.

Searching for simpler synthesis methods to activated carbons with suitable properties is a significant research theme in developing porous carbons for gas storage.¹¹ Recent reports have proposed using organic salts as templates for porous carbons production. For instance, the one-step preparation of porous carbons by carbonising solid organic salts such as phthalate,¹¹ potassium hydrogen sodium chloroacetate, lithium dichloroacetate and potassium dichlorate amongst others, have been reported with high surface areas.¹² A very simple method for forming carbon aerogels using a metal salt as a template, in which subcritical drying is used, and no activation is needed to achieve high surface area has also been published.¹³ The metal salt acts as a porogen, generating porosity upon elimination by dissolving. In such a case, the metal salt could also act as an activating agent, allowing porous carbons to be produced directly from organic salts, provided the metal salt is chosen appropriately.¹⁴ However, the

optimal conversion of an organic salt into porous carbon needs careful selection of the salt to obtain an appropriate carbon source and a suitable metal species that can operate as an activating agent once formed during thermal treatment. By careful selection, it is possible to create a scenario that simulates the activation process of the carbon except that the activating agent and carbon precursor are both provided by the organic metal salt, resulting in improved solid-solid contact.¹¹

This chapter reports on using a simple method for preparing porous carbons and on the carbon's physical proprieties and gas storage capacity. Porous carbons have been prepared by heating carbon-rich metal salts at various temperatures. The chosen metal salts in this work are potassium hydrogen phthalate (KHP) and potassium phthalimide (PPI). KHP is attractive in analytical chemistry because (i) it is readily available as a pure substance with no water of crystallisation, (ii) it has a well-characterised reactivity near ambient temperature and pressure, (iii) it is solid and air-stable, thus it is easy to weigh accurately, and (iv) it is unreactive in the air.¹⁵⁻¹⁸ The structure of KHP is given below:¹⁹



The organic moiety of KHP is carbon, which will carbonise at high temperatures to generate elemental carbon. Potassium can cause activating species in carbon, oxygen, hydrogen, and heat, as observed during chemical

activation with KOH. As a result, it is proposed that KHP can carbonise in a nitrogen atmosphere to produce porous carbon once all impurities are removed.

Potassium phthalimide (PPI) was also used as a carbon precursor. It has been broadly used in producing different organic compounds because it is commercially available, stable, and cheap.^{20,21} The structure of PPI is given below:



PPI contains 7.6% of nitrogen content, making it a possible precursor for nitrogen-doped carbon (NDC), in which doping with heteroatoms such as N/P/S is also a successful approach for carbon modification. Nitrogen-containing or nitrogen-free precursors can be used to make NDC with high porosity.^{22,23} One of the most widely utilised methods is the carbonisation-activation of nitrogen-containing precursors.²⁴ NDCs synthesised using activation from polyacrylonitrile,²⁵ polypyrrole,²⁶ polyurethane,²⁷ and gelatin²⁸ have been thoroughly documented. The templating method, as an alternative, has also been extensively researched. For example, Xia *et al.*,²⁹ prepared NDCs using acetonitrile as the carbon precursor and zeolite as the hard template. The resulting carbon showed a significant surface area of up to 3000 m² g⁻¹.²⁹ NDCs could be synthesised from nitrogen-free precursors using high-temperature reactions between nitrogen-containing chemicals and

carbon. These chemicals, such as NH₃³⁰ and urea, ³¹ serve as nitrogen sources. Moreover, using a nitrogen-containing activation agent is a simple way to make NDCs since it combines activation and nitrogen doping in a single step. Carbons activated by HNO₃, ³² LiNO₃, ³³ and NaNH₂³⁴ have been used to make NDCs. The above procedures require a multi-step synthesis process, regardless of the precursors used. The primary objective of the research in this chapter is to find inexpensive and straightforward synthesis methodologies that produce carbons with tuneable properties targeted at gas storage applications. In this work, the chosen organic salts are carbon-rich precursors with an oxidising activation agent (K) in one starting material. KHP and PPI undergo 'self-activation'; KOH forms upon heating, so the generated carbon is activated directly, thus eliminating the need to add a separate activating agent.

Both KHP and PPI have previously been utilised as precursors for porous carbons.^{11,24} Adeniran *et al.* found that KHP-derived carbons are highly microporous with moderate surface area, which translated to excellent CO₂ uptake at low pressure.¹¹ However, there appeared to be a limit to the porosity achievable by KHP-derived carbons that topped off at 2100 m² g⁻¹ and 1.1 cm³ g⁻¹ for surface area and pore volume, respectively.¹¹ Thus, the porosity of the KHP-derived carbons was suitable for CO₂ uptake at low pressure, but not for CH₄ uptake, which requires higher porosity. PPI-derived carbons, which achieved similar levels of porosity (maximum surface area and pore volume of 2053 m² g⁻¹ and 1.14 cm³ g⁻¹, respectively) to that of KHP-derived carbons, have recently been reported.²⁴ However, their preparation²⁴ included washing of the carbons in acid post carbonisation as opposed to simpler use of water as demonstrated for KHP-derived carbons.¹¹

These previous studies on KHP and PPI-derived carbons present two unanswered questions, namely, (i) is it possible to prepare carbons with higher porosity (i.e., surface area > 2100 m² g⁻¹, and pore volume > 1.1 cm³ q^{-1}) that may be more suited for CH₄ storage, and (ii) can the preparation of PPI-derived carbons be simplified to just need carbonisation and washing with water rather than acid. In the quest to answer these questions, it is essential to note that the presence of N in a precursor has been shown to increase susceptibility to activation and thus the ready generation of higher porosity.³⁵⁻ ³⁹ In this regard, polypyrrole (PPY) is known to generate activated carbons with very high porosity.³⁵⁻³⁹ Indeed, the porosity of KOH activated carbons can be modulated by judicious addition of PPY to other precursors, wherein the level of porosity trends with the amount of PPY added.^{40,41} This suggests that the presence of N in precursors can act as an in-situ porogen. The expectation, therefore, is that the presence of N in PPI means that it should be possible, given the right synthesis procedure, to generate porous carbons with higher porosity than is possible for KHP-derived carbons. In this chapter, we therefore prepared PPI-derived carbons using a simpler method, and compared their porosity and performance for CO₂ and CH₄ storage to KHPderived carbons.

3.3 Expermental section

3.3.1 Porous carbon synthesis

2 g of the organic salt (potassium hydrogen phthalate (KHP) or potassium phthalimide (PPI)) were placed in a tubular furnace and heated at a ramp rate of 10 °C min⁻¹ to temperatures ranging from 600 to 1000 °C under nitrogen flow, and held at the final temperature for 2 h. Another series of PPI-

derived carbons were also similarly prepared, but they were held at the target temperature for 1, 3 or 4 h. The resulting samples were washed with deionised water and dried at 100 °C for 24 h. The KHP-derived carbons were denoted as CKHP-X, and the resulting PPI-derived carbons were represented as PPI-X-Y, where X is the carbonisation temperature (°C), and Y is the time (h).

3.3.2 Material characterisation

CHN elemental analysis was performed using an Exeter Analytical CE-440 Elemental Analyser. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 analyser under flowing air conditions (100 mL min⁻¹). Powder XRD analysis was performed using a PANalytical X'Pert PRO diffractometer with Cu-K α light source (40 kV, 40 mA) with step size of 0.02° and 50 s time step. Analysis of porosity and determination of textural properties was performed via nitrogen sorption analysis (at -196 °C) using a Micromeritics 3FLEX sorptometer. Prior to analysis, the carbon samples were degassed under vacuum at 200 °C for 16 h. Surface area was calculated using the Brunauer-Emmett-Teller (BET) method applied to adsorption data in the relative pressure (P/P_o) range of 0.02 – 0.22, and pore volume was estimated from the total nitrogen uptake at close to saturation pressure ($P/P_o \approx 0.99$). The micropore surface area and micropore volume were determined via t-plot analysis. The pore size distribution was determined using Non-local density functional theory (NL-DFT) applied to nitrogen adsorption data. Scanning electron microscopy (SEM) images were recorded using an FEI Quanta200 microscope, operating at a 5 kV accelerating voltage. The packing density of the carbons was calculated by pressing a given mass of activated carbons,

and the compaction was carried out in a 1.3 cm diameter die for 5 minutes at ambient temperature, corresponding to a compaction pressure of 370 MPa. The volume occupied by the pellet was evaluated using a cylinder volume, $V = \pi r^2 h$, where r and h are the radius and height of the pellet, respectively. Packing density values can also be calculated by the general equation; d_{carbon} $= (1/Ps + V_T)$, where Ps is the skeletal density that is determined from helium pycnometry, and V_T is the total pore volume from the nitrogen sorption analysis.

3.3.3 Gas uptake measurements

CO₂ uptake was measured in the pressure range 0–20 bar at room temperature (25 °C) using a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003). The carbons were degassed at 240 °C and at a ramp rate of 5 °C/min for several hours prior to performing the CO₂ uptake measurements.

Methane uptake was determined using a Hiden Isochema XEMIS Analyser. Before the uptake measurements, the carbon samples were outgassed at a high temperature of up to 240 °C under vacuum for several hours. Methane uptake isotherms were obtained at 25 °C, over the pressure range of 0–35 bar.

3.4 Results and Discussion

3.4.1 The Yield and elemental composition of activated carbons

The yield of CKHP and PPI-derived carbons is summarised in Tables 3.1 and 3.2, respectively. The yield of CKHP-activated samples ranges from 35% to 14%, while for PPI activated samples, it is between 40% and 20%. According

to the data in Tables 3.1 and 3.2, the yields of samples activated at the highest temperature (1000 °C) are much lower than those of samples activated at the lowest temperature (600 °C), indicating that it is only the activation temperature that determines the carbon yield. In general, the yield of PPI-derived carbons at any given temperature, is higher than what is obtained from CKHP-derived carbons. This high yield appears to be a general advantage of using PPI as a carbon source.

The elemental composition of CKHP and PPI-derived carbons is shown in Tables 3.1 and 3.2, respectively. In general, the carbon content of CKHP carbons increases compared to KHP, while the H, N and O content decreases, which is as expected for activated carbons. The carbon content increases from 47 wt% for KHP to between 57 and 88 wt% for CKHP samples, whereas it rises from 51% for PPI to between 73 and 93 wt% for PPI samples with the increase being more significant at higher temperatures (1000 °C). However, the H content reduces, with lower content at higher activation levels. As the level of activation rises, the amount of O and N also gradually decreases. As a result, the O/C atomic ratio of CKHP carbons was reduced from 0.797 to 0.103. However, as activation temperature rises, the C/H atomic ratio of CKHP-derived carbons significantly increases, owing to higher C content and a reduction in H content.⁴³ The elemental composition of PPI-derived carbons shows that they have a low relative O/C atomic ratio of 0.574, and it is the lowest ratio that has been observed from many sources, including KHP and activated carbon precursors that usually have O/C ratios ranging from 0.75 to 1.0.44-46

Sample	Yield [%]	C [%]	H [%]	N [%]	O [%]	O/C ^a
KHP	-	47.0	2.3	0.8	49.9	0.80
CKHP-600	35	56.8	2.2	0.5	40.5	0.53
CKHP-700	29	70.6	2.1	0.0	27.3	0.29
CKHP-800	25	71.8	2.1	0.1	26.0	0.27
CKHP-900	18	79.4	1.6	0.0	19.0	0.18
CKHP-1000	14	87.8	0.1	0.0	12.1	0.10

Table 3.1: The yield and elemental composition of potassium hydrogenphthalate (KHP) and KHP-derived carbon samples.

^aAtomic ratio

Table 3.2: The yield and elemental composition of potassium phthalimide
(PPI) and PPI-derived carbon.

Sample	Yield [%]	C [%]	H [%]	N [%]	O [%]	O/C ^a
PPI	-	51.3	2.0	7.4	39.3	0.57
PPI-600-2	40	73.2	1.0	5.3	20.6	0.21
PPI-700-2	36	76.3	0.8	2.6	20.4	0.20
PPI-800-2	30	87.6	0.2	1.8	10.4	0.09
PPI-900-2	24	90.5	0.1	1.3	8.1	0.07
PPI-1000-2	20	93.0	0.1	0.8	6.1	0.05

^aAtomic ratio

3.4.2 Nature and thermal stability of carbons

TGA was used to assess the thermal stability and the purity of the carbons to ensure the samples were fully carbonaceous and not a mix of carbon and metal oxides. Fig. 3.1 shows TGA curves of CKHP-derived carbons carbonised at temperatures range of 600 - 1000 °C. The first mass loss below 100 °C can be attributed to the evaporation of water, followed by a further mass loss at temperatures ranging from 330 to 620 °C due to carbon combustion.⁴³ The carbon burn off temperature ranges between 330 and 550 °C for the CKHP-600, 360 and 600 °C for the CKHP-700, 400 and 605 °C for the CKHP-800, 440 and 610 °C for the CKHP-900, and 617 °C for the CKHP-1000. These temperatures are in the expected range for carbons, which are amorphous and non-graphitic.¹¹ Moreover, the amount of water retained is not necessarily related to the porosity, but is related to the carbonisation temperature. A sample carbonised at 600 °C is the lowest, and that seems to have the highest amount of water, which decreases as the carbonisation temperature goes up to 1000 °C. That simply implies that there is a change in the nature of the carbon because it is carbonised at much higher temperature and is much more hydrophilic. As noticed in the elemental composition, samples exposed to higher temperatures showed a high carbon content and a decrease in the oxygen and hydrogen content, and any hydrophobic and hydrophilic properties will be related to the presence of oxygen and hydrogen. Therefore, those decreases at high temperatures, and so the amount of water that samples can hold is reduced.



Figure 3.1: Thermal gravimetric analysis (TGA) curves of CKHP-derived carbon.

All samples show residual mass below 1 wt.% at 100 °C, suggesting that they are essentially fully carbonaceous. This means that any inorganic residues generated during the self-activation process are efficiently washed away by water.^{10,47} In addition, carbons prepared at a higher level of activation exhibit greater combustion resistance due to their high thermal stability. The increase in thermal stability at higher temperatures may be related to the rise in the graphitisation level as a result of samples being exposed to higher temperatures during carbonisation.⁴⁶

3.4.3 Structure ordering of carbons

XRD analysis was performed to assess the structure of the porous carbon samples. The XRD patterns of KHP and PPI-derived carbons carbonised at various temperatures are shown in Fig. 3.2 and Fig. 3.3. Generally, all samples of both KHP and PPI sets show broad and low-intensity peaks at 20 = 22° and 44°, which is typical for such porous carbons.¹¹ These values are indexed as (002); the diffraction plane of graphitic carbon of the interlayer spacing between adjacent graphite layers and (100); in-plane orderings of graphite, respectively.^{42,48} The broadness of the peaks and the low intensity of the (002) diffraction indicate that the carbons are amorphous with a high level of irregularity.¹¹ The peaks are relatively prominent at a carbonisation temperature of 600 °C. As carbonisation temperature increases, the $2\theta = 22^{\circ}$ peak reduces in intensity and flattens out, demonstrating the effect of carbonisation temperature on the level of graphene stacking. At higher temperatures, there is more intercalation of potassium ions and compounds into the carbon structure, disrupting the order and stacking of the graphene layers. Higher levels of gasification are also expected during activation, as K₂CO₃ thermally decomposes, and K₂O reacts with the carbon skeleton, both releasing CO₂.^{10,47} This results in a further developed porosity, resulting in a less ordered and more amorphous structure with fewer graphitic features, as shown by the gradual disappearance of the $2\theta = 22^{\circ} \text{ peak}^{.48}$



Figure 3.2: Powder XRD patterns of CKHP-derived carbon samples carbonised at various temperatures for 2 h.



Figure 3.3: Powder XRD patterns of PPI-derived carbon samples carbonised at various temperatures for 2 h.

A critical method to study the extent of graphitic features is to measure the empirical parameter value (R) of the $2\theta = 22^{\circ}$ peak in the XRD pattern. As shown in Fig. 3.4, the R-value expresses the ratio of the peak height to the average intensity of the background.⁴⁹ The value indicates the number of graphene sheets layered parallel within the structure. The background (A) is created by drawing a line connecting the data of either side of the peak, and the height (B) is deduced by drawing a line that is a tangent to the linear background estimate and that intersects the (002) peak at a single point. The R-value is then calculated as B/A. As R decreases, fewer layers are arranged together, and the structure becomes more disordered.^{49,50} In this work, the R-values for each sample are difficult to measure because there are no clear peaks at $2\theta = 22^{\circ}$. However, it can be assumed to be R = 1, which describes all graphene sheets as being randomly distributed and the material as being very disordered. It is also expected to show a decrease as the carbonisation temperature increases. Again, this is due to higher levels of potassium intercalation and gasification at higher temperatures. This disrupts the arrangement of graphene sheets during activation, resulting in their disordered distribution.¹¹



Figure 3.4: Schematic diagram of calculating the R-value from XRD patterns.³²

3.4.4 Porosity and textural properties Effect of carbonisation temperature

The nitrogen sorption isotherms and pore size distribution (PSD) curves of KHP-derived carbons are shown in Fig. 3.5, and the corresponding textural properties are summarised in Table 3.3. As seen in Figure 3.5A, all CKHP samples display predominantly type I isotherms, indicating a microporous structure.⁴³ A large volume of nitrogen is adsorbed at $P/P_o < 0.05$, which is further evidence of high levels of microporosity.¹¹ The widening of the adsorption knee of the isotherm as carbonisation temperature increases indicates the presence of larger micropores.¹¹ Sample CKHP-900 shows a slight hysteresis loop, while CKHP-1000 shows a clear type H4 hysteresis loop, suggesting the existence of larger pores. Overall, the isotherms show that all CKHP samples have a highly microporous structure with little, if any, mesoporosity. As the carbonisation temperature increases, so does the nitrogen quantity adsorbed at P/P_o < 0.05. This demonstrates that a high

carbonisation temperature leads to a more developed pore structure with a larger surface area and pore volume.⁵¹ Notably, the large jump in the quantity of nitrogen adsorbed between samples CKHP-700 and CKHP-800 indicates a large increase in uptake ability due to the increase in activation temperature.¹¹



Figure 3.5: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of KHP-derived carbons.

Sample	Surface area ^a	Pore volume	e ^b Pore size	Packing density
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(Å)	(g cm ⁻³)
CKHP-600	488 (471)	0.20 (0.18)	5.8/7.2/10	1.15
CKHP-700	857 (823)	0.35 (0.33)	6/7.4	0.98
CKHP-800	1609 (1551)	0.70 (0.62)	6/8/12	0.73
CKHP-900	1851 (1446)	1.03 (0.63)	5/8.2/9.7/12/21	0.66
CKHP-1000	1654 (979)	0.92 (0.43)	5.3/8.5/10/12/21	0.58

Table 3.3: Textural properties and packing density of KHP-derivedcarbons.

^aThe values in the parenthesis refer to micropore surface area. ^bThe values in the parenthesis refer to micropore volume.

According to Table 3.3, the surface area and pore volume of CKHP carbons are, in the context of all porous carbons, moderate to high, with textural values increasing to a maximum and then reducing at higher carbonisation temperatures. A carbonisation temperature of 900 °C (sample CKHP-900) shows the maximum surface area and pore volume of 1851 m² g⁻¹ and 1.03 cm³ g⁻¹, respectively. An increase in surface area at a higher carbonisation temperature is expected due to the previously mentioned higher levels of activation arising from the greater extent of reactions between KOH and the carbon structure, releasing more gas and developing more pores. However, a slight decrease is observed for sample CKHP-1000, which can be attributed to the fact that the weaker intermolecular forces, such as Van der Waals, holding open the pore structure begin to break down at higher temperatures. This might lead to the partial collapse of the pore structure, causing a lower surface area.⁵¹

The micropore surface area of CKHP samples (Table 3.3.) are medium to high, with up to 97% micropore surface area for CKHP-600. Samples prepared at higher temperatures have a lower proportion of micropore surface area, at 78% and 59% for CKHP-900 and CKHP-1000, respectively. This can also be attributed to the higher levels of activation seen at higher temperatures, which leads to larger pores, including via small pores collapsing into larger ones.⁵¹

Table 3.3 also shows the pore volume and micropore volume of CKHP carbons. The sample carbonised at 900 °C shows the highest pore volume of 1.03 cm³ g⁻¹. Again, this is expected due to higher levels of activation taking place at higher activation temperatures. The proportion of micropore volume increases from CKHP-600 (90%) to CKHP-700 (94%) due to more potassium intercalation and the release of volatiles creating micropores during activation.^{48,51} However, the subsequent reduction in proportion of micropore volume above 700 °C is attributed to the collapse of smaller pores into larger ones in the harsher conditions of higher carbonisation temperature.⁴⁵ The reduction in proportion of micropore volume above 700 °C is further evidence of increased gasification resulting in a widened PSD.⁵¹ Overall, the level of microporosity for the CKHP carbons is high when compared to other carbons including zeolite template carbons, activated carbons or carbide-derived carbons.^{13,26,51-54}

The pore size distribution (PSD) of CKHP carbons is shown in Figure 3.5B. Samples carbonised at lower temperatures (600 °C) show a completely microporous structure with pore diameters of 6-12 Å, and do not possess pores larger than 10 Å. However, samples carbonised at higher temperatures

> 800 °C show a broader pore size distribution, but are still dominated by micropores. This is confirmed by the surface area data and the change in the isotherm shape for the samples carbonised at higher temperatures, as presented in Figure 3.5A. The broadening of the adsorption knee points to the presence of micropores along with wider micropores. Overall, the porosity of the present KHP-derived carbons, both in terms of the magnitude, microporosity and trends with respect to carbonisation temperature, is similar to that previously published by Adeniran and Mokaya.¹¹

The nitrogen sorption isotherms and pore size distribution curves of PPIderived carbons are shown in Fig. 3.6, and the corresponding textural properties are given in Table 3.4. All the isotherms in Fig 3.6A are type I, indicating a microporous structure, which is desirable for small gas (CO₂ and CH₄) storage applications. The isotherms all show high nitrogen adsorption at $P/P_0 < 0.03$, which points to high levels of microporosity. At high carbonisation temperatures, the increase in the amount of N₂ adsorbed signals increase in overall porosity. As the carbonisation temperature rises, the slope of the knee region increases slightly in the pressure range (P/P_{o}) of 0.01-0.3, indicating that more large micropores are formed, consistent with previous reports.²⁴ However, the shapes of the isotherms remain comparable and representative of high microporosity even at high carbonisation temperature. This means that whilst carbonisation temperature increases the overall porosity, it has hardly any effect on the level of microporosity. This contrasts with a previous report,²⁴ where higher carbonisation temperature generated porous carbons with lower levels of microporosity, which was also evident from the isotherm shapes.²⁴ It is likely that the use of water, rather than acid as previously reported, to wash the present carbons after carbonisation is milder and allows

for better retention of microporosity, which should also contribute to the achievement of higher total surface area. The similarity in the shapes of the isotherms also suggests that the samples all have a similar pore structure; however, the expanding of the hysteresis loop size in the pressure range of $P/P_o \sim 0.45$ -0.99 may reflect the development of microporous structures at higher temperatures.⁵⁵ The large jump in the quantity of nitrogen adsorbed between samples carbonised at 700, 800 and 900 °C indicates a large increase in uptake ability, corresponding with increased carbonisation temperatures.¹¹



Figure 3.6: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of PPI-derived carbons carbonised for 2 h.

Sample	Surface area ^a	Pore volume ^b	Pore size	Packing density
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(Å)	(g cm ⁻³)
PPI-600-2	1227 (1000)	0.64 (0.42)	5/8	1.10
PPI-700-2	1517 (1295)	0.77 (0.53)	5/8	1.04
PPI-800-2	2106 (1803)	1.04 (0.74)	5/8/11	0.92
PPI-900-2	2889 (2576)	1.36 (1.05)	5/8/9/12	0.87
PPI-1000-2	2744 (2410)	1.29 (0.95)	5/8/9/12	0.83

Table 3.4: Textural properties and packing density of PPI-derived carbonscarbonised for 2 h.

^aThe values in the parenthesis refer micropore surface area. ^bThe values in the parenthesis refer to micropore volume.

As expected, increasing carbonisation temperature increases the surface area and pore volume due to higher levels of activation and pore development at higher temperatures. As a result, PPI-900-2 has a very high surface area and pore volume of 2889 m² g⁻¹ and 1.36 cm³ g⁻¹, respectively. However, sample PPI-1000-2 exhibits a slightly lower surface area and pore volume due to the collapse of the structure. All the samples show a high level of microporosity with micropore surface area and micropore volume of up to 81 – 89% and 66 – 77%, respectively. As the carbonisation temperature increases up to 900 °C, the magnitude and proportion of microporous surface area and pore volume rise with increase in total values. The present PPI-derived carbons achieve much higher surface area and pore volume compared to that reported by Shi *et al.*²⁴ In particular, the surface area and pore volume of sample PPI-900-2 at close to 2900 m² g⁻¹ and 1.4 cm³ g⁻¹, respectively, are higher by 40% (surface area) and 20% (pore volume). Furthermore, the level of microporosity is high regardless of carbonisation temperature, and greater
than for previous reports.²⁴ Thus the proportion of micropore surface area for the present PPI-derived carbons (81 – 89%) is higher than that (35 – 72%) reported by Shi *et al.*²⁴ There is a particularly large difference at 700, 800 and 900 °C, where the present PPI carbons have, respectively, 85, 86 and 89% of surface area arising from micropores, compared to 62, 47 and 35%, respectively, as reported by Shi *et al.*²⁴ A similar picture is observed for the proportion of pore volume from micropores; 69, 71 and 77% of pore volume arising from micropores for the present samples carbonised at 700, 800 and 900 °C, respectively, compared to 53, 39 and 28%, respectively, as reported by Shi *et al.*²⁴ It is likely that this greater overall porosity and higher levels of microporosity are due to the use of water, rather than acid,²⁴ to wash the PPI-derived carbons after carbonisation. The use of water is not only simpler, cheaper and milder, but appears to be advantageous in achieving higher porosity with retained high levels of microporosity.

The pore size distribution (PSD) curves of PPI-X-2 samples are displayed in Fig. 3.6B, and the maxima of pore size from the curves are summarised in Table 3.4. At lower carbonisation temperature, samples PPI-600-2 and PPI-700-2 show narrow pore size distribution with pore diameter between 5-8 Å; no other pores are observed. A broader micropore size distribution is observed at a temperature above 700 °C but is still dominated by micropores. Increasing gasification at higher temperatures leads to more uncontrolled pore formation, forming a broader micropore size range.¹⁰

Effect of carbonisation time

Carbons were prepared at 700 and 800 °C for carbonisation durations of 1, 3 or 4 h to assess the effect of carbonisation time. The sorption isotherms of samples carbonised at 800 °C are shown in Fig. 3.7, and the corresponding textural properties are presented in Table 3.5. As shown in Fig. 3.7A, the isotherms of the PPI samples carbonised for 1, 2, or 4 h are similar with respect to the shape, and are consistent with a high level of microporosity. As summarised in Table 3.5, the surface area and pore volume are slightly affected by altering the carbonisation time at 800 °C, but remain at 1928–2106 m² g⁻¹ and 0.86–1.04 cm³ g⁻¹, respectively. The PPI-800-2 sample has the highest surface area and pore volume of 2106 m² g⁻¹ and 1.04 cm³ g⁻¹, respectively. All PPI-800-Y samples have a high proportion of micropore surface area of 93%, while the proportion of micropore pore volume is in the range of 71–85%.



Figure 3.7: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of PPI-derived carbons carbonised at 800 °C and various periods of time.

Sample	Surface area ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size (Å)	
PPI-800-1	1976 (1804)	0.87 (0.73)	5,8,9,11,15	
PPI-800-2	2106 (1803)	1.04 (0.74)	5,8,11,15	
PPI-800-3	1928 (1768)	0.86 (0.71)	5,8,11,15	
PPI-800-4	1981 (1844)	0.87 (0.74)	5,5,11,15	

Table 3.5: Textural properties of PPI-derived carbons carbonised at 800 °Cand various periods of time.

^aThe values in the parenthesis refer to micropore surface area. ^bThe values in the parenthesis refer to micropore volume.

The pore size distribution curves in Fig. 3.7B show that the pore size has not been significantly affected by altering the carbonisation time at 800 °C, and the maxima of pore size summarised in Table 3.5 are considerably similar. Generally, carbonisation time 800 °C appears to have a negligible effect on the textural properties of the carbons. Hence, to generate porous carbons with attractive physical characterisation and reduce the energy consumed, it is possible to carbonise PPI precursor for 1 hour while maintaining the required textural properties.

PPI-derived carbons were also prepared at 700 °C for 1, 3 or 4 h to clarify the role played by carbonisation temperature in determining the effects of carbonisation time. The nitrogen sorption isotherms and pore size distribution curves of PPI samples carbonised at 700 °C are shown in Fig. 3.8, and the corresponding textural properties are summarised in Table 3.6. The isotherms of PPI-700-Y samples are similar and show a microporous structure. Compared to the series of PPI-800-Y samples, these samples

exhibit a narrower pore size distribution. This confirms that a lower carbonisation temperature generates carbons with a narrow micropore size distribution but at lower surface area, ranging from 1502 to 1922 m² g⁻¹, whereas the pore volume varied between 0.67 and 0.85 cm³ g⁻¹. PPI-700-Y carbons show a high level of microporosity with micropore surface area and micropore volume of 92% and 84%, respectively, regardless of the carbonisation duration.



Figure 3.8: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of PPI-derived carbon samples carbonised at 700 °C and various periods of time.

Sample	Surface area ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size (Å)
PPI-700-1	1502 (1367)	0.67 (0.55)	5,8,11
PPI-700-2	1517 (1295)	0.77 (0.53)	5,8,11
PPI-700-3	1790 (1612)	0.81 (0.65)	5,8,11
PPI-700-4	1922 (1773)	0.85 (0.71)	5,8,11

Table 3.6: Textural properties of PPI-derived carbon samples carbonised at700 °C and various periods of time.

^aThe values in the parenthesis refer to micropore surface area. ^bThe values in the parenthesis refer to micropore volume.

3.4.5 Morphology of activated carbons

SEM analysis was used to study the morphology of the CKHP and PPI carbons. The SEM images (Figure 3.9A&B) show that the CKHP carbons have a sheetlike morphology with irregular forms and rough topography. Micro-sized cracks and carbon flakes can be seen on the surface, indicating that carbon may have swelled and then shrunk through the carbonisation and the following the washing process. The morphology appears to be unaffected by the carbonisation temperature, excluding an increase in the extent of connection in the sheet-like particles at higher temperatures. The relative similarity of the carbon's morphology indicates that any textural changes are likely to take place at considerably smaller nanoscales. For PPI-derived samples, SEM images (Figure 3.10A&B) show morphology of particles that are irregularly shaped and sized, with large holes randomly distributed across the carbon surface. Many small particles in the carbon framework can be seen in the higher magnification images. The white spots in some images may reflect the formation of the developed porous structure. Graphene layers were

not observed, indicating the amorphous nature of the carbon, in agreement with the XRD pattern in Fig 3.3.



Figure 3.9A: SEM images of KHP-derived carbon samples.



Figure 3.9B: SEM images of KHP-derived carbon samples.



Figure 3.10A: SEM images of PPI-derived carbon samples.



Figure 3.10B: SEM images of PPI-derived carbon samples.

3.5 Gas uptake measurements

3.5.1 Carbon dioxide uptake

The CO₂ uptake of KHP-derived carbons has previously been extensively reported¹¹ and so was not performed in this work. The CO₂ uptake of PPI-derived carbons was measured at pressures between 0-20 bar and 25 °C. The CO₂ uptake isotherms of PPI-X-2 samples carbonised for 2 h are shown in Fig. 3.11, and the uptake capacity at various pressures (0.15, 1 and 20 bar) is summarised in Table 3.7. The attractive properties (i.e., high surface area and well-developed microporosity) can draw a lot of attention to PPI carbon samples as solid-state storage materials for energy storage applications. The CO₂ uptake at 0.15 bar is important as it is the relevant pressure for post-combustion CO₂ capture because the flue gas streams contain ca. 15% CO₂, with the rest being mainly N₂ (70–75%), and water (5–

7%). PPI-600-2 and PPI-700-2 exhibit a high uptake of 1.6 and 1.5 mmol g⁻¹, respectively, at 0.15 bar, despite showing a low surface area and pore volume. This is most likely due to the abundance of micropores and their optimum pore size of ca. 8 Å (Fig. 3.6 B). The CO₂ uptake of these samples at 0.15 bar is comparable to some published values.^{48,50,51} However, the samples with a high surface area and broader pore size exhibit lower CO₂ uptake at 0.15, and the reduction in CO₂ uptake performance may be ascribed to the widening of pore size. It is noteworthy that the CO₂ uptake of the present PPI-derived carbons at 0.15 bar (1.2 – 1.6 mmol g⁻¹) is higher than that previously reported as being 0.1 – 1.1 mmol g⁻¹.²⁴ We attribute the higher uptake of the present carbons to greater levels of microporosity arising from a gentler and milder preparation route as discussed above.



Figure 3.11: CO₂ uptake isotherms of PPI-derived carbons carbonised at various temperatures for 2 h.

Sample	CO ₂ uptake (mmol g ⁻¹)					
	0.15 bar	1 bar	20 bar			
PPI-600-2	1.6	4.1	10.1			
PPI-700-2	1.5	4.7	13.7			
PPI-800-2	1.2	4.2	15.7			
PPI-900-2	1.4	4.2	16.3			
PPI-1000-2	1.2	4	16.8			

Table 3.7: CO₂ uptake of PPI-derived carbons carbonised at various temperatures for 2 h.

The CO₂ uptake of PPI carbons at a pressure of 1 bar is between 4.0 and 4.7 mmol g⁻¹, with the highest adsorption capacity being for sample PPI-700-2. The CO₂ uptake at 1 bar rises from 4.1 mmol g⁻¹ to 4.7 mmol g⁻¹ for the samples carbonised at 600 °C and 700 °C, respectively, and then drops to 4.0 mmol g⁻¹ for samples carbonised at higher temperatures. The CO₂ uptake at 1 bar reduces even though the samples have a high surface area, indicating that carbons must contain optimised pores rather than just a high surface area to possess high CO₂ uptake at low pressure. This is in line with previous findings that narrow pores determine the CO₂ uptake at low pressure.^{13,45,56-59} It is worth noting that the CO₂ uptake of 4.7 mmol g⁻¹ at 1 bar and 25 °C is among the highest ever reported for carbons,^{25,51,54,60-64} and comparable to the best N-doped activated carbons (4.8–5.14 mmol g⁻¹).^{25,65} Moreover, the current PPI carbons have the advantage of being easy and simple to synthesise, as they only require the carbonisation process and no other

chemical compounds than the precursor (organic metal salt). This simple preparation process yields better CO_2 uptake at 1 bar (4.1 mmol g⁻¹ to 4.7 mmol g⁻¹) compared to that (3.1 mmol g⁻¹ to 3.4 mmol g⁻¹) of equivalent PPIderived carbons wherein acid was used during the washing step post carbonisation.²⁴

Although the CO₂ uptake at 1 bar for sample PPI-700-2 (4.7 mmol g⁻¹) is considerably higher than that of PPI-1000-2 (4.0 mmol g⁻¹), the trend is reversed at 20 bar, where the former captures 16.8 mmol g⁻¹ compared to 13.7 mmol g⁻¹ for PPI-700-2. This shows that the CO₂ uptake at 20 bar relies more on the total surface area than the pore size. Notably, the CO₂ uptake isotherms of narrowly distributed samples (PPI-600-2 and PPI-700-2) at 20 bar approach saturation. However, samples with a slightly wider pore size (PPI-800-2, PPI-900-2 and PPI-1000-2) are far from saturation, suggesting that more CO₂ can be stored at higher pressures. It is worth noting that the change in the carbonisation temperature can cause significantly attractive performance in CO₂ uptake capacity for post-combustion at low pressure and pre-combustion at high pressure.⁴³

As previously discussed, the textural properties of PPI carbons are not significantly affected by changing the carbonisation time (between 1 and 4 h) at 800 °C. As presented in Figure 3.12 and Table 3.8, the comparable CO_2 uptake at various pressures for PPI-800-Y samples is consistent with their relatively similar textural properties. PPI-800-3 has the highest CO_2 uptake (4.8 mmol g⁻¹) at 1 bar and 25 °C. The uptake of 4.8 mmol g⁻¹ is comparable to the best-published values, particularly carbons derived from sawdust (4.8 mmol g⁻¹), ⁵¹ petroleum pitch (4.7 mmol g⁻¹), ⁶⁶ and N-doped activated carbons

(4.8–5.14 mmol g⁻¹).^{25,65} On the other hand, a slightly lower CO₂ uptake of 4.2 mmol g⁻¹ has been shown by the sample carbonised for 2 h, despite having the highest surface area. This observation indicates that the main determinant of CO₂ uptake at low pressure is the pore size, not the total surface area.¹¹ However, CO₂ uptake at high pressure (20 bar) is determined by the total surface area, where all the PPI-800-Y series have a comparable surface area and show CO₂ uptake in the range of 15.3 and 16.0 mmol g⁻¹.



Figure 3.12: CO₂ uptake isotherms of PPI-derived carbon samples carbonised at 800 °C and various periods of time.

Sample	CO ₂ uptake (mmol g ⁻¹)					
	0.15 bar	1 bar	20 bar			
PPI-800-1	1.3	4.6	16			
PPI-800-2	1.2	4.2	15.7			
PPI-800-3	1.5	4.8	15.7			
PPI-800-4	1.3	4.6	15.3			

Table 3.8: CO₂ uptake of PPI-derived carbon samples carbonised at 800 °C and various periods of time.

In contrast, the set of PPI-700-Y samples (Figure 3.3 and Table 3.9) show similar CO₂ uptake capacities at 0.15 bar and 1 bar (1.5–1.7 mmol g⁻¹) and (4.7–5.2 mmol g⁻¹), respectively, but show a broader variation at 20 bar (12.9–15.7 mmol g⁻¹). The uptake of 1.7 mmol g⁻¹ at 0.15 bar and 5.2 mmol g⁻¹ at 1 bar are amongst the highest ever reported for porous carbon material.^{25,51,54,60–64} As previously mentioned, the PPI-700-Y samples have a narrow pore size and very high levels of microporosity; hence, the samples exhibit the best CO₂ uptake at 25 °C and low pressures (0.15 and 1 bar), while they show a modest CO₂ uptake than that of PPI-800-Y samples at 1 bar but have slightly lower uptake at 20 bar. This is in line with the fact that pore size plays a significant role in CO₂ absorption at low pressure, whereas the total surface area is more critical at higher pressure.

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Figure 3.13: CO₂ uptake isotherms of PPI-derived carbon samples carbonised at 700 °C and various periods of time.

Table 3.9: CO ₂ uptake of PPI-derived carbon samples carbonised at	700	°C
and various periods of time.		

Sample	CO ₂ uptake (mmol g ⁻¹)					
	0.15 bar	1 bar	20 bar			
PIP-700-1	1.7	4.8	12.9			
PIP-700-2	1.5	4.7	13.7			
PIP-700-3	1.7	5.1	14.5			
PIP-700-4	1.5	4.8	15.7			

3.5.2 Methane storage

The microporosity of porous materials with a high surface area along with low mesoporosity are critical requirements for methane storage efficiency at moderate to high pressure (35–100 bar).^{1,3,42,67–70} A high microporous volume is required to ensure strong adsorption of methane molecules, while some mesoporosity is necessary for effective sorption kinetics. Therefore, the mix porosity of current carbons is predicted to be an attractive candidate for attaining high methane storage at moderate pressures.^{1,3,35,67-70} Methane storage capacity of CKHP carbons was measured at 35 bar and 25 °C. Figure 3.14 shows the excess gravimetric isotherms for methane uptake of the CKHP carbons, and Table 3.10 lists the amount of excess methane adsorbed on a gravimetric basis (expressed as mmol g⁻¹ and g g⁻¹) and on a volumetric basis (expressed as cm³ (STP) cm⁻³) for all carbons at 25 °C and 35 bar. The gravimetric excess methane uptake is in the range of 3.1-7.9 mmol g⁻¹ (equivalent to $0.05-0.13 \text{ g g}^{-1}$). It is interesting to note that sample CKHP-800 (4.3 mmol g⁻¹) has a higher excess gravimetric methane uptake than the sample CKHP-900 (3.9 mmol g⁻¹) at 5 bar; however, the trend reverses with the latter storing 7.7 mmol g⁻¹ at 35 bar. This suggests that the pore size is more significant than the surface area in determining gravimetric CH₄ uptake at 5 bar. In addition, samples with a completely microporous structure (CKHP-600, CKHP-700) exhibit a reduction in the gravimetric excess methane uptake at 35 bar, consistent with their low surface area and pore volume. Nevertheless, the scenario entirely changes for materials having micropores and narrow mesopores. These materials with large surface area and pore volume have higher gravimetric uptake of 7.9 mmol g⁻¹ at 35 bar. The isotherms of excess CH₄ uptake show that the more highly microporous

samples approach saturation at 35 bar, while samples with larger micropores

are far from saturation and can store more methane at higher pressures.



Figure 3.14: Excess methane uptake at 25 °C and 35 bar of KHP-derived carbon samples (CKHP).

Sample	Excess uptake (35 bar)			Total uptake (35 bar)		
	mmol/g	g/g	cm ³ /cm ³	mmol/g g/g		cm³/cm
CKHP-600	3.1	0.05	80	3.4	0.05	88
CKHP-700	5.2	0.08	114	5.7	0.09	124
CKHP-800	7.2	0.12	118	8.3	0.13	135
CKHP-900	7.7	0.12	114	9.3	0.15	137
CKHP-1000	7.9	0.13	103	9.3	0.15	121

Table 3.10: CH₄ uptake of KHP-derived carbon samples (CKHP) at 25 °C and 35 bar.

Volumetric uptake is a critical measure of solids performance in methane storage, considering the adsorbent's packing density. According to the US Department of Energy (DOE), the methane storage target in porous materials has been set at a volumetric uptake capacity of 263 cm³ (STP) cm⁻³ at moderate pressure (35–100 bar) and room temperature (25 °C). In this work, although highly microporous samples show acceptable adsorption behaviour in gravimetric capacity and have a high packing density (Table 3.3), they exhibit a low volumetric capacity, indicating the importance of having a high gravimetric capacity, along with a large surface area for methane storage. In contrast, samples with a mix of microporosity/mesoporosity demonstrate a good methane uptake on a volume basis. Samples CKHP-800 and CKHP-900 achieve a volumetric uptake of 135 cm³ cm⁻³ and 137 cm³ cm⁻³, respectively, at 35 bar and 25 °C, which is higher than many MOFs.⁶⁴ It should be noted, at this point, that the volumetric uptakes for carbon materials were computed using the actual packing density, whereas the ideal crystallographic density was employed for MOFs. This means that the value is unrealistic as a single crystal of MOF fitting the tank is far from realistic; hence, overestimating the actual volumetric adsorption capacity of the MOFs.⁵ Carbon materials, unlike MOFs, can endure high pressures without loss or damage to the porosity and, thus, without a negative impact on adsorption performance. Consequently, carbon materials are highly appealing as a component for high-pressure storage tanks for both the automobile industry and long-distance transportation, on the condition that high-pressure compressors of around 10 MPa are compulsory to achieve the DOE goal.⁵ However, overall, the best uptake of 137 cm³ cm⁻³ at 35 bar for the present KHP-derived carbons is modest compared to the best carbons that can store up to 200 cm³ cm⁻³.^{41,42}

The modest surface area and pore volume of the KHP-derived carbons limits the gravimetric uptake with the consequence that the volumetric uptake is also low. This observation clarifies on the importance of surface area and pore volume in determining CH₄ uptake. Indeed, it was the motivation of this study that directed us to explore PPI-derived carbons, which as shown above achieve much higher porosity.

Given the importance of overall surface area and pore volume in determining the CH4 uptake, we only explored the performance of PPI-derived carbons that have high surface area, namely, PPI-800-2, PPI-900-2 and PPI-1000-2. Figure 3.15 shows the isotherms of excess methane adsorption for these PPI carbons, and Table 3.11 presents the excess methane adsorbed on a gravimetric and volumetric basis at 35 bar and 25 °C. The PPI carbons show a very high gravimetric methane uptake capacity in the range of 9–10.3 mmol g^{-1} (equivalent to 0.14–0.16 g g^{-1}), where sample having the high surface area and pore volume show better uptake. It is also obvious that the gravimetric methane capacity increases as the carbonisation temperature increases. Surprisingly, the excess methane uptake of 10.3 mmol g^{-1} (0.16 g q⁻¹) at 35 bar and 25 °C is among the best reported for porous materials.^{1,3,4,68,69-72} Total methane uptake ranges from 10.5–12.0 mmol g⁻¹ $(0.17-0.20 \text{ g g}^{-1})$. Accordingly, these samples have a remarkable uptake compared with the best benchmark materials reported to date. In addition, the excess methane adsorption isotherms show that saturation was not reached in the pressure range of 0-35 bar, indicating that the current PPI carbons, particularly the PPI-1000-2 sample, can potentially store more methane at higher pressures.

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Figure 3.15: Excess methane uptake at 25 °C and 35 bar of PPI-derived carbons.

Table 3.11: CH₄ uptake of PPI-derived carbons at 25 °C and 35 bar.

Sample	Excess uptake (35 bar)			Total uptake (35 bar)			Working capacity ^a		
	mm	iol/g_g/g	g cm ³ /cm ³	mmol,	/g g/g	cm ³ /cm ³	cm ³ /cm ³		
PPI-800-2	9	0.14	185	10.5	0.17	217	118		
PPI-900-2	9.1	0.15	178	11.2	0.18	218	125		
PPI-1000-2	10.3	0.16	191	12	0.20	227	138		

^{*a*} Working capacity is the difference in uptake between 35 bar and 5 bar.

As previously stated, the packing density of adsorbents is essential in determining the volumetric methane uptake. The self-activating nature of the present PPI carbons, and the fact that they are highly microporous means that

their packing density (Table 3.3) is high with the consequence that they maintain high performance with respect to volumetric uptake of CH₄ (Table 3.11). The excess and total volumetric uptake isotherms of PPI carbons are shown in Fig. 3.16. The samples appear to be not reaching saturation, which suggest that they can achieve more volumetric uptake at higher pressures (36-100 bar). The carbons have excess volumetric methane uptake of 185 to 191 cm³ cm⁻³ at 35 bar and 25 °C. These excess uptake values are better than the best porous carbons reported to date.^{2,5,69,73-75} More importantly, the carbons have total volumetric methane uptake of between 217 and 227 cm³ cm⁻³ at 35 bar and 25 °C. Up to now, activated carbons derived from date seeds (*Phoenix dactylifera*) that store up to 222 cm³ cm⁻³ are the best-performing porous carbons for volumetric methane storage at 25 °C and 35 bar.⁴² With a total storage capacity of up to 227 cm³ cm⁻³, the present PPI-derived carbons outperform all other porous carbons previously reported^{2,5,42,75} and are comparable to benchmark MOFs.^{2,5,74,75} Working capacity is a critical measure of a porous material's performance for methane storage, defined as the difference in the uptake between the adsorption and desorption pressures. A desorption pressure of 5.8 bar is recommended for methane storage, whereas an adsorption pressure of 35 bar has often been used. The present PPI-derived carbons show a high working capacity of 138 cm³ cm⁻³, which is comparable to the highest previously reported for any porous materials.^{41,42} The current carbons match the best MOFs concerning volumetric methane storage, but the carbons have the benefit of being more robust and much cheaper. The cost of an adsorbent is a crucial consideration, and the high price of MOFs is probable to impede their commercialisation.1,3,4,69



Figure 3.16: Excess and total volumetric methane uptake at 25 °C and 35 bar of PPI-derived carbons.

3.6 Conclusion

The synthesis of porous carbons with a convenient one-step method has been reported. Porous carbons were successfully prepared by heating carbon-rich metal salts, namely potassium hydrogen phthalate (KHP) and potassium phthalimide (PPI) at 600-1000 °C, followed by washing with water. All the samples presented a high carbon content. In contrast, the H, N and O content of the samples decreased with the increase in the carbonisation temperature. All the samples showed irregular, non-graphitic crystal structure expected for porous carbons. TGA analysis showed that the thermal stability of the samples corresponded to their amorphous structures. KHP-derived carbons (denoted as CKHP carbons) exhibited surface area and pore volume in the range of 488–1851 m² g⁻¹ and 0.20–1.03 cm³ g⁻¹, respectively. Even though

the simplicity of the synthesis method, the CKHP carbons are highly microporous, with a micropore surface area proportion is remarkably high at ca. 97%, and up to 94% of the pore volume arising from micropores. PPIderived carbons have high surface area and pore volume of up to 2889 m² g⁻ ¹ and 1.36 cm³ g⁻¹, respectively, for a sample carbonised at 900 °C for 2 h. The PPI-derived carbons have high levels of microporosity proportion regardless of the carbonisation temperature, and their porosity is dominated by micropores (5–15 Å), which is beneficial for CO_2 and CH_4 uptake. The PPIderived carbons captured up to 5.2 mmol g^{-1} of CO₂ at 1 bar and 25 °C, which is amongst the highest ever reported for any porous carbons. Under CO₂ postcombustion conditions (0.15 bar), the carbons stored 1.7 mmol q^{-1} of CO₂, which is also among the highest so far reported for porous carbons. Moreover, the PPI carbons also have attractive CO₂ uptake at moderate pressure (20 bar). The CO₂ uptake at 25 °C and low pressure was confirmed to be reliant on the pore size, while the total surface area is more essential at higher pressure, indicating that the carbons can be tailored for pre or postcombustion CO₂ uptake. The CKHP and PPI-derived carbons have high packing density, which aids their volumetric CO₂ or CH₄ uptake. The PPIderived carbons have volumetric CH₄ uptake of up to 227 cm³ (STP) cm⁻³ at 35 bar and 25 °C. Assuming that the deliverable methane amount is defined as the difference in the amount of methane adsorbed between 5 bar and 35 bar, PPI samples exhibited excellent deliverable methane capacity of 138 cm³ (STP) cm⁻³, comparable to the highest previously reported for MOF and porous carbon materials. According to the findings of this study, KHP and PPI are very competitive precursors for the simple synthesis of porous carbons

with an attractive and unrivalled mix of properties for CO_2 and CH_4 storage applications.

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Chapter 4: Polyethylene terephthalate (PET) waste as a promising source for carbons with superior performance for CO₂ and CH₄ storage

4.1 Abstract

The conversion of plastic waste into high value-added carbon has received widespread research attention because of the need for sustainable development and the ever-increasing outputs of plastic waste. This work used a single plastic waste component (polyethylene terephthalate, PET) as a source (starting material) for preparing activated carbon with outstanding CO₂ and CH₄ storage capabilities, following activation with varying KOH amounts at moderate temperature (600-800 °C). The elemental composition, thermal stability, morphology, textural properties, and gas storage capacity of the carbons were investigated. All PET-derived carbons, following simple hydrothermal carbonisation of PET, presented a very high carbon content and appeared to be suitable starting materials for activated carbon production. The resulting PET-derived activated carbons have a high surface area of up to 2828 m² g⁻¹ along with a pore volume of up to 1.47 cm³ g⁻¹. The carbon porosity can be tailored towards narrow and wide pore size distribution within the micropore to the small mesopore size range. The activated carbons were explored for CO_2 and CH_4 storage. CO_2 storage capacity of 4.3 mmol g⁻¹ at 1 bar and 25 °C was obtained, which is at a competitive level for porous carbons. Furthermore, enhanced CO₂ adsorption under typical flue gas conditions (i.e., 0.15 bar) is achieved with an adsorption capacity of 1.5 mmol g⁻¹, which is also among the highest so far observed for porous carbons.

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Samples with a high surface area showed better performance at 20 bar, indicating the CO₂ adsorption at 20 bar correlates with the total surface area. The capacity of methane storage at 25 °C and pressure up to 100 bar was explored. The carbons have high gravimetric methane uptake in the range of 11.1-13.4 mmol g^{-1} (0.18-0.21 g g^{-1}), depending on their surface area and pore volume. These methane uptake values are amongst the best reported for any porous material. The carbons were easily compacted to a high packing density of up to 1.13 g cm⁻³ with minor structural deterioration. Following compaction, the carbons achieve the best performance for volumetric CH₄ storage of up to 448 cm³ (STP) cm⁻³ at 100 bar, as well as an unrivalled working capacity of up to 273 cm³ (STP) cm⁻³, which is significantly higher than any currently available benchmark material. More significantly, these values substantially exceed the requirements set by the United States Department of Energy (US DOE). This work demonstrates for the first time that adequately designed porous carbons can attain methane storage above the US DOE targets without any of the drawbacks normally encountered with the use of MOFs.

4.2 Introduction

Due to the universal scale of environmental pollution from the accumulation of solid waste pollutants, attention has been drawn to the significance of reducing solid waste contamination. Consequently, intensive research has been conducted to address the serious concerns about its disposal.¹⁻¹² Plastic waste is one of the largest and most problematic solid waste sources.¹¹⁻¹⁴ Since the first industrial-scale manufacture of plastics in the 1940s, the rate of generation, consumption, and production of solid plastic waste has dramatically increased.⁵ According to reports, global plastic production augmented from 1.7 million tonnes in 1950 to 288 million tonnes in 2012, with 32.6 million tonnes of plastic waste being correspondingly produced in the United States.¹⁵ Plastic generation and pollution have, therefore, significantly increased over the past 50 years.¹² Sardon et al.⁹ expected that the plastic waste quantity would be greater than fish by 2050 due to the continued increase of plastic waste, rapid disposal and inadequate recycling mechanisms. This widely extensive use of plastic is attributable to its superior properties, including low cost, easy handling, design flexibility, high thermal stability, transparency, food inertness, negligible CO₂ permeability, malleability, and resistance to weak and strong mineral acids, oxidising agents and sunlight.¹⁰

Polyethylene terephthalate (PET), in particular, has been widely used in the manufacture of disposable soft drink bottles since the 1980s, and already over 320 000 tonnes of PET were used in various consumer goods applications in 1987.¹⁶ PET is the most important polyester resin presently generated because of its outstanding chemical and mechanical properties.¹⁷ This polymer is commercially derived from the reaction of terephthalic acid and

ethyleneglycol, and its properties are determined by its molecular structure, molecular weight, crystallinity and impurity content.¹⁷ The chemical structure of PET repetition unity is shown below in Fig. 4.1.



Figure 4.1: The chemical structure of polyethylene terephthalate (PET), used as a starting material.¹⁸

Recently, polyethylene terephthalate (PET) has become one of the more significant post-consumer plastic wastes.^{3,4,11,12,14,19} PET consumption has recorded the fastest growth rate in the global plastic market because of the continued expansion of the PET bottle market.¹³ Even though PET goods do not directly poison the environment, they have posed a problem of substantial concern because of the massive quantity of solid waste production.^{7,20} Thus, the use of PET products, as things currently stand, poses a significant ecologically unsustainable issue, as most plastics are non-biodegradable.^{2,21} PET is highly stable and resistant to hydrolytic degradation because of the aromatic ring in its chemical structure.²²

Landfill and incineration are the conventional PET waste disposal approaches, but they are far from being universally accepted due to land space limitations, waste of resources and environmental contamination.^{2,21,23} Therefore, the current situation needs simple, eco-friendly, and cost-effective methods of PET waste recycling to mitigate any further accumulation of plastic waste that would disrupt the ecosystem's balance due to its non-

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biodegradable nature.¹⁴ PET can be practically recycled using mechanical, thermal, and chemical recycling methods. The common recycling approaches for post-consumer PET waste are either mechanical or chemical.¹⁴ However, the low consistency of the recycled plastic mixture limits the mechanical recycling of plastic waste. Therefore, chemical recycling is a widely accepted recycling method for PET that adheres to 'sustainable development' principles.²⁴ Chemical recycling opens up new ways of generating high-valueadded carbon from PET waste for various commercial and industrial applications.²⁵

Activated carbons are extensively used as very effective adsorbents because of their large surface area, high storage capacity, low energy demand for regeneration, cost-effectiveness, and mature manufacturing.²⁶⁻³² Another advantage of activated carbons is their low potential environmental effect, as most industrial waste or biomass materials can be used as carbon sources for preparing activated carbons; this may enhance process sustainability.³³ Owing to the high carbon content in most plastics, special consideration has been given to the use of waste plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) to produce value-added porous carbons, providing an effective way of lowering solid polymer waste.¹¹ Several methods for producing activated carbons from plastic waste have been proposed and tested, including gasification/pyrolysis direct carbonisation supplemented with chemical or physical activation and hydrothermal carbonisation.^{6-8,15,33-36} Activated carbons obtained from industrial waste, particularly plastic waste, are regarded as promising gas sorbents, concurrently solving the serious

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environmental problems of greenhouse gas reduction and waste PET recycling.³

CO₂ accounts for more than 60% of total greenhouse gas emissions, and the current CO₂ levels contribute to anthropogenic climate changeand the global warming. More seriously, plastic bottles have contributed significantly to CO₂ emissions. According to a Pacific Institute report,³⁷ bottling water produced more than 2.5 million tonnes of CO₂ in 2006, with over 300 billion bottles sold and discarded. If urgent measures are not implemented, CO₂ emissions from plastic bottles are expected to double by 2030.¹² Thus, minimising CO₂ levels in the atmosphere is regarded as one of the most significant environmental and scientific challenges.^{33,38,39} Different proposed and complementary alternatives can be used to reduce CO₂ emissions, such as improvements in energy efficiency, replacing lower non-carbon fuels or CO₂ capture and storage (CCS), and developing renewable and clean energy sources.⁴⁰ Ideally, using renewable and cleaner fuels with lower or even zero carbon content is the best strategy for reducing CO_2 emissions. Natural gas, mainly composed of methane (CH₄), represents a cleaner and low-cost fuel due to the related environmental advantages (e.g., abundant reserves, lower greenhouse gas emissions and higher combustion efficiency).^{28,31,41-48} The main challenge that has prevented the widespread use of natural gas is its lower volumetric energy density under atmospheric conditions. The energy density can be improved by storing natural gas as compressed natural gas (CNG) or liquefied natural gas (LNG). However, both CNG and LNG are not applicable under ambient temperature and pressure, where the high cost of processes involved (cryogenics and compression) and the high safety risk complicate using these technologies. Adsorbed natural gas (ANG) is a promising technique that
involves the storage of fuels at low pressure and room temperature in an attempt to reduce the cost and offer improved ease of usage.^{45,49}

The US Department of Energy (DOE) has recently set a volumetric methane storage target of 350 cm³ (STP) cm⁻³ and gravimetric storage capacity of 0.5 g (CH₄) g^{-1} at room temperature and a pressure of 35 to 100 bar to enable widespread use of methane. It is noteworthy that the 350 cm³ (STP) cm⁻³ target was set at that level based on the crystallographic density of metalorganic framework (MOF) materials that are considered to be a leading class of methane storage materials. The reasoning behind this target is that MOFs have a crystallographic density that is at least 25% lower than their actual packing density. Therefore, this target (350 cm³ (STP) cm⁻³) allows for a 25% reduction in volumetric capacity (to ca. 263 cm³ (STP) cm⁻³) due to packing MOFs inside a storage tank. Accordingly, porous adsorbents must meet these storage targets to become practical for the ANG technology. To be attractive for methane storage, porous carbons should have a high surface area with appropriate porosity and a high packing density if they reach the methane storage capacity of current benchmark materials. Previous reports indicate that the chemical activation of PET can lead to significantly improved textural properties owing to the generation of micro/mesopores that are beneficial for gas storage.^{31,45,49,50} Moreover, PET plastic may be regarded as a novel carbon source as it is an abundant material with a high carbon content of over 60 wt%, which makes it suitable for porous carbon preparation.⁵¹ Other motivations for exploring PET plastic waste are (i) the growing demand for PET postconsumer reclamation to keep up with increasing consumption, and (ii) recent experimental studies that suggest that PET-derived activated carbons are ideal adsorbents with high cyclic stability, high CO₂/CH₄

adsorption capacity, good CO_2/N_2 selectivity and fast adsorption-desorption kinetics.^{3,4,12,51}

Consequently, this study investigates the production of activated carbons from PET waste for gas storage purposes. The key reason for using PET as a carbon precursor in this study is to explore inexpensive raw materials for the large-scale development of carbon-based structures, not only for waste processing but also for eliminating or alleviating critical environmental pollution. More importantly, porous carbons with a high surface area (2828 m² g⁻¹) and pore volume (1.47 cm³ g⁻¹) were produced and showed unprecedented methane adsorption capacity and working capacity of up to 448 and 273 cm³ (STP) cm⁻³, at 25 °C, respectively. These values significantly exceed the performance of all current benchmark materials and surpass the requirements set by the DOE, thus indicating that the generated carbons can be effectively used as an adsorbent for storing methane.

4.3 Expermental section

The PET waste used as a carbon matrix was obtained from post-consumer water bottles with the trademark (*Hamidiye*). PET bottles were first cleaned to be free of impurities and air-dried, then cut into small flakes with sizes less than 5 mm.

4.3.1 Material synthesis

Direct activation: the required KOH amount was thoroughly squashed, then distributed between PET flakes at a KOH/PET mass ratio of 2 or 4. The resulting mixture was placed in a ceramic boat and inserted inside a tubular furnace, and heated at a ramp rate of 3 °C min⁻¹ to temperatures ranging

from 600 to 800 °C under a flow of nitrogen. The furnace was held at the final temperature for 1 h, and then cooled to room temperature under nitrogen flow. The resultant activated carbon was stirred in 10% HCl at room temperature for 3 days. The final activated carbons were filtered, washed abundantly with deionised water until neutral pH, and dried in an oven at 100 °C. The resulting carbons were designated as PETxTD, where x is the KOH/PET ratio, T is the activation temperature, and D indicates direct activation.

Conventional activation via hydrothermal carbonisation (HTC): PET was first converted to hydrochar *via* HTC as follows: 4.6 g of PET was dispersed in 20 ml of deionised water and placed in a stainless-steel autoclave, which was then heated up to 250 °C, maintained at the target temperature for 2 h and cooled to room temperature. The resulting carbonaceous product, denoted as hydrochar, was filtered, washed abundantly with deionised water, and dried at 100 °C for 24 h. Then, the derived hydrochar was chemically activated as described above. The carbons were designated as PETx*T*HC, where x is the KOH/PET ratio, *T* is the activation temperature, and HC indicates activation of PET-derived hydrochar.

4.3.2 Material characterisation

CHN elemental analysis was performed on an Exeter Analytical CE-440 Elemental Analyser. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 analyser under flowing air conditions (100 mL/min). Powder XRD analysis was performed using a PANalytical X'Pert PRO diffractometer with a Cu-K α light source (40 kV, 40 mA) with a step size of

0.02° and 50 s time step. Nitrogen sorption analysis and textural properties of the carbons were determined at -196 °C using a Micromeritics 3FLEX sorptometer. Before analysis, the carbon samples were degassed under vacuum at 200 °C for 16 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on adsorption data in the partial pressure (*P*/*Po*) range of 0.02 – 0.22, and pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of (*P*/*Po* \approx 0.99). The micropore surface area and the micropore volume were obtained via *t*plot analysis. Non-local density functional theory (NL-DFT) was applied to nitrogen adsorption data to determine the pore size distribution. The morphology of the samples was examined by scanning electron microscopy (SEM) using an FEI Quanta200 microscope, operating at a 5 kV accelerating voltage.

4.3.3 Gas uptake measurements

 CO_2 uptake was investigated in the pressure range of 0–20 bar at room temperature using a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003). The carbons were outgassed under vacuum at a high temperature of up to 240 °C and a ramp rate of 5 °C/min for several hours before performing the CO_2 uptake measurements.

Methane uptake was determined using a Hiden Isochema XEMIS Analyser. Before the uptake measurements, the carbon samples were degassed at 240 °C under vacuum for several hours. Methane uptake isotherms were obtained at 25 °C over a methane pressure range of 0–100 bar.

4.4 Results and Discussion

4.4.1 The yield and elemental composition of PET carbons

The yield of activated carbons is crucial in evaluating new carbon sources.³¹ The activated carbon yield was monitored to assess if the activation method provided any benefits in terms of carbon balance. The experimental values of the yield and elemental composition of both sets of activated carbon samples are presented in Table 4.1. The activated carbons yield via direct activation was typically between 30-40%. By contrast, the carbon yield from PET to hydrochar derived from the conventional activation via HTC was ca. 73%. The yield of conventionally activated carbons with KOH ratios of 1:2 and 1:4 was between 34-62% and 37-42%, respectively. Thus, the yield of activated carbons is higher for the conventional route than the direct activation. In general, increasing the activating agent ratio (KOH) declines the overall yield of activated carbons for both methods. A similar trend was noticed in the yield of carbons activated at higher temperatures, where using higher activation temperatures reduces the yield of activated carbons. According to previous studies, the process yield suggests the activation degree of the carbon.⁵² Mendoza-Carrasco et al.⁵³ stated that the production yield for PET-derived activated carbon synthesised by physical activation is typically low, but a higher yield can be obtained by KOH chemical activation.

As presented in Table 4.1, the elemental carbon and hydrogen content of the PET waste was similar to that of PET bottles reported in previous studies.^{52–54} Moreover, the chemical formula of PET polymer $(C_{10}H_8O_4)_n$ is consistent with the elemental composition in Table 4.1.⁵² Before activation, the carbon content of the PET-derived hydrochar was determined and compared to that

of PET. As expected, the carbon content increased following hydrothermal carbonisation (HTC) from 62.1% for PET to 67.4% for the hydrochar. Higher activation temperatures generated greater carbon content for both the directly and conventionally activated samples. However, higher amounts of activating agent led to a decrease in the carbon content.⁴ In addition, activated samples present a decreased amount of H, owing to the removal of H-containing functionalities during the activation processes.⁵²

The chemical formula of PET polymer is $(C_{10}H_8O_4)_n$, and the C/H weight ratio of 15 is similar to the PET obtained value.⁵² An increase in the C/H ratio for activated carbons is likely due to the removal of H-containing functional groups as the amount of elemental C increases. In addition, An increase in the C/H ratio suggests a higher aromatic degree after activation. In both methods, samples with low KOH impregnation exhibit high aromaticity; however, the lowest aromaticity shown in the conventionally activated samples with the high ratio is likely due to severe activation conditions. The oxygen content of PET, on the other hand, decreases after hydrothermal carbonisation to hydrochar, and it reduces even more after chemical activation of the hydrochar, with the decrease being significant at higher activation temperatures. There is a noticeable increase in oxygen content as the KOH/precursor ratio rises from 2 to 4 for directly activated samples.^{4,51}

Sample	Yield [%]	C [%]	H [%]	N [%]	O [%]ª	C/H⁵	O/C ^c
PET	-	62.1	4.1	0.0	33.8	15.0	0.41
Hydrochar	73	67.4	3.9	0.0	28.7	1.44	0.32
PET2600D	40	66.2	0.1	1.2	32.5	61.25	0.37
PET2700D	37	70.4	0.1	1.1	28.4	55.17	0.30
PET2800D	35	74.6	0.1	1.0	24.3	62.17	0.24
PET4600D	39	60.7	0.1	0.2	39.0	50.58	0.48
PET4700D	35	68.4	0.1	0.6	30.9	57.00	0.34
PET4800D	30	70.3	0.1	0.2	29.4	58.58	0.31
PET2600HC	62	69.8	0.1	1.2	28.9	58.17	0.31
PET2700HC	53	73.3	0.1	0.8	25.8	61.08	0.26
PET2800HC	34	76.2	0.1	1.0	22. 7	63.50	0.22
PET4600HC	42	74.0	0.1	0.3	25.6	61.67	0.26
PET4700HC	39	77.1	0.2	0.1	22.6	32.13	0.22
PET4800HC	37	83.5	0.3	0.1	16.1	23.19	0.14

Table 4.1: The yield and elemental composition of directly andconventionally PET-derived activated carbons.

^acalculated by difference. ^{b,c} Atomic ratio

4.4.2 Thermal stability of PET carbons

TGA was conducted to evaluate the thermal stability of the carbons and confirm that the activated carbons were completely carbonaceous. The TGA curves of directly activated samples and analogous conventionally activated samples are shown in Fig. 4.2 and Fig. 4.3.

All the TGA curves indicate that the samples are stable up to 450 °C. A minor weight loss in the temperature range of 35–100 °C was observed due to the elimination of moisture content and volatiles. The majority of weight loss occurs between 550 and 650 °C, which corresponds to carbon burn off.⁵⁵ These temperatures are in the expected range for carbons, which are amorphous and non-graphitic.^{31,56} The rapid decrease in the weight (i.e. burn off) at \geq 500 °C indicates that the carbons are single-phase materials.⁵⁷ Moreover, the pyrolysis of PET-hydrochar (Fig. 4.3) exhibits an abrupt weight loss centred at 280 °C due to the single step degradation of aromatics of the PET polymer.⁵²

The TGA curves of the directly activated carbons show the residual mass of less than 2 wt%, indicating they are fully carbonaceous, with trace quantities of mineral matter. By contrast, the conventionally activated carbons show a range of residual masses. For example, sample PET2600HC shows a significant residual mass of ca. 15%, which may be attributed to inorganic residues resulting from the activating agent (KOH).^{57,58} However, the samples prepared at higher activation temperatures show a low residual mass of up to 8%, indicating the presence of low ash content. Since the polymer does not contain inorganic matter, the ash (oxides or inorganic impurities) in the PET is most likely the result of residues from the activation step.⁵² The amount of residual inorganic matter reduces at higher carbonisation temperatures, which may be attributed to the increasing decomposition of K₂CO₃ during carbonisation above 700 °C.^{26,30,59,60}



Figure 4.2: Thermal gravimetric analysis (TGA) curves of directly activated PET-derived carbons.



Figure 4.3: Thermal gravimetric analysis (TGA) curves of PET-hydrochar derived activated carbons.

According to the TGA curves, the conventionally activated carbons (i.e. via HTC) show higher thermal stability than analogous directly activated carbons,

suggesting high levels of graphitisation.^{26,30,59,60} Additionally, for both sets of samples, it seems that carbons activated at higher activation temperatures are more thermally stable, i.e. more resistant to combustion.^{26,29,60} Furthermore, samples activated at a KOH/precursor ratio of 4 have slightly higher thermal stability than equivalent (with respect to activation temperature) samples activated at a ratio of 2.

4.4.3 Structure ordering of PET carbons

X-ray diffraction (XRD) was performed to confirm the nature and purity of the carbons. The XRD patterns of directly and conventionally activated samples are shown in Fig. 4.4 and Fig. 4.5.

All the activated samples show broad and low-intensity peaks at $2\theta = 22^{\circ}$ and 44°, indicating that they are amorphous.^{26,29,56,59,60} The broad peaks at $2\theta = 22^{\circ}$ and 44° nominally correspond to the (002) interlayered spacing between adjacent graphite layers and (100) in-plane ordering of graphite, respectively.^{4,51,60,61} The intensity of the peaks corresponds to the average number of stacked graphene layers within a sample, and so does the regularity and graphitic of the sample; the very low intensity is consistent with the amorphous nature of the carbons. The XRD patterns of directly activated samples prepared at a KOH/PET ratio of 2 show some sharp peaks, even though the corresponding TGA curves (Fig. 4.2) indicate that they have very low amounts of impurities. The sharp peaks most likely arise from KCL residue from the washing process.²⁹ The XRD patterns show that the amount of KOH has no substantial effect on the nature of carbons. Furthermore, it appears that the activation temperature also has no significant effect on the

level of graphene stacking.³¹ The XRD patterns of all carbons, in general, are compatible with the amorphous nature of activated carbons.



Figure 4.4: Powder XRD patterns of directly activated PET-derived carbons.



Figure 4.5: Powder XRD patterns of PET-hydrochar derived activated carbons.

4.4.4 **Porosity and textural properties**

The nitrogen sorption isotherms and pore size distribution (PSD) curves of directly and conventionally activated samples are shown below in Fig. 4.6 and Fig. 4.7. The corresponding textural parameters are summarised in Table 4.2. As displayed in Fig. 4.6A, the nitrogen sorption isotherms of directly activated carbons at any given activation temperature (600, 700 and 800 °C) are predominantly type I, which is typical of microporous materials.^{26,29–32,60} The directly activated samples adsorbed a large amount of nitrogen at low relative pressure (P/Po < 0.05), which is further evidence of their microporosity. However, the isotherms of PET27D samples exhibit a type H4 hysteresis loop, suggesting the existence of larger pores.⁵² The PSD curves in Fig. 4.6B confirm that the samples are predominantly microporous, but with a wide relative pore size distribution that includes supermicropores (i.e., pore channels with a diameter of 7-20 Å). Similar trends are observed for directly activated PET47D samples (Fig 4.6A), which are mainly microporous but with a gentler adsorption knee consistent with the presence of a relatively broad distribution of micropore sizes that extends to supermicropores.

The isotherms of conventionally activated PET27HC samples (Fig 4.7A) are type I with considerable microporosity. It is interesting to note that although the quantity of adsorbed nitrogen increases for samples activated at higher temperatures, there is no change in isotherm shape; all the carbons display isotherms with a sharp adsorption knee, indicating the absence of pores of size larger than the micropore range (up to 20 Å).³¹ On the other hand, samples PET47HC (Fig. 4.7A) seem to adsorb extra nitrogen at relatively

higher pressures ($P/P_0 > 0.3$) compared to the analogous directly activated carbons.



Figure 4.6: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of directly activated PET-derived carbons.

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Figure 4.7: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of conventionally activated PET-derived carbons.

The change in the isotherm shape with a wider adsorption knee signifies that the pore size has changed to larger pores that extend into the small mesopore range.^{31,52,60} For example, the isotherms of samples activated at a higher

activation level (PET4700HC and PET4800HC) show a very wide adsorption knee with a linear increase at relative pressure up to a P/Po of 0.3, suggesting the presence of a significant proportion of small mesopores, which is confirmed by the PSD curves in Fig. 4.7B. The presence of larger pore sizes for sample PET4800HC is due to the gasification effects related to the decomposition of potassium salts at a higher level of activation.^{31,52,60}

Sample	surface area ^a	Pore Volume ^b	Pore size	
	m ² g ⁻¹	cm ³ g ⁻¹	Å	
PET2600D	590 (498)	0.61 (0.40)	5/8/11	
PET2700D	1028 (947)	0.64 (0.47)	5/6/8/11	
PET2800D	1331 (1148)	0.99 (0.62)	5/8/11	
PET4600D	1624 (1514)	0.80 (0.65)	5/8/10/11/20	
PET4700D	1617 (1516)	0.76 (0.63)	5/8/9/11/20	
PET4800D	1505 (1388)	0.75 (0.60)	5/8/9/11/20	
PET2600HC	819 (794)	0.35 (0.31)	5/8/13	
PET2700HC	1038 (985)	0.51 (0.38)	5/8/14	
PET2800HC	1482 (1359)	0.75 (0.54)	5/8/11/13/15	
PET4600HC	2154 (1758)	1.11 (0.78)	5/8/11/16/21/27	
PET4700HC	2650 (2129)	1.43 (0.96)	5/8/11/15/2/27	
PET4800HC	2828 (2352)	1.47 (1.07)	5/8/10/11/21/27	

 Table 4.2: Textural properties of directly and conventionally activated PETderived carbons.

The values in parenthesis refer to: ^a micropore surface area and ^b micropore volume.

The textural parameters of the directly and conventionally activated samples are summarised in Table 4.2. Generally, the surface area and pore volume increase for samples activated at higher temperature and amount of KOH. However, PETx*T*HC carbons generally have a higher surface area and a high

level of microporosity. The surface area of PET27D rises from 590 m² g⁻¹ for sample PET2600D to 1028 m² g⁻¹ for sample PET2700D and then increases further to 1331 m² g⁻¹ for PET4800D. A similar trend is observed for pore volume, which increases with activating temperature from 0.61 cm³ g⁻¹ to 0.99 cm³ g⁻¹. This trend is expected due to the higher activation levels at higher temperatures, wherein more developed porosity results in a larger surface area.⁶² The conventionally activated PET27HC samples show a high surface area of up to 1482 m² g⁻¹ but a lower pore volume ranging from 0.35 to 0.75 cm³ g⁻¹. Nevertheless, the pore size distribution of the PET27D and PET27HC sets of carbons is relatively similar.

The surface area and pore volume of directly activated PET4TD samples are in the range of 1505 to 1624 m² g⁻¹ and 0.75 to 0.80 cm³ g⁻, respectively. Sample PET4800D would be expected to exhibit a higher surface area than PET4700D due to being prepared at higher levels of activation. However, PET4800D has a lower surface area, which indicates that the 800 °C is beyond the optimum activation temperature for the relevant activation conditions. On the other hand, sample PET4800HC exhibits the highest surface area and pore volume of up to 2828 $m^2 q^{-1}$ and 1.47 cm³ q⁻¹, respectively. As expected, this increase in the surface area is due to the higher levels of activation arising from the greater extent of reactions between KOH and the carbon structure, releasing more gases and developing more pores.^{26,29,31,32,60,63} It is worth mentioning that the surface area of 2828 $m^2 g^{-1}$ is at the high end of all previously reported results for PET-derived activated carbons.^{3,4,6,21,35,51,53,64} In addition, activation at a high level of activation produces a significant proportion of larger pores in the small mesopore range than for PET27HC samples; this can be attributed to the higher amount of KOH, which increases

the K_2CO_3 generation, releasing more CO and CO_2 , which produces broader pores. It is noticeable that the porosity of directly activated samples at the most severe activation level is still predominantly in the micropore/supermicropore range, with no pores wider than 20 Å, as confirmed by the PSD curves (Fig.4.6B).

Moreover, the proportion of micropore surface area and pore volume for the directly activated samples ranges between 84 and 93%, and 63 and 83%. The conventionally activated samples have a proportion of micropore surface area and pore volume of up to 96% and 88%, respectively.

The pore size distribution (PSD) curves of directly and conventionally activated carbons are shown in Figs. 4.6B and 4.7B. As previously mentioned, samples prepared at a KOH/PET ratio of 2 are mainly microporous with directly activated samples possessing pores of size 5, 8 and 11 Å. In contrast, conventionally activated samples have slightly larger pores centred at 5, 8, 13 and 14 Å. Directly activated samples prepared at a KOH/PET ratio of 4 have pores mainly within the micropore range, while conventionally activated samples are microporous but with some mesopores in size range of 20 - 40 Å.

4.4.5 Morphologhy of PET carbons

The morphology of the activated carbons was monitored using SEM analysis. SEM images of the directly and conventionally activated carbons are shown in Fig. 4.8 and Fig. 4.9.

The morphology of the PET carbons is dominated by irregularly shaped particles with large conchoidal cavities and some sharp edges. This morphology is observed for all the activated carbons regardless of the precursor used, signifying that an extreme morphological transformation occurs through the activation process. The KOH activating agent reacts progressively on the carbon's surface before reaching the precursor carbon's interior.^{30,58,60,65,66} This suggests that the activated carbons do not retain the primary structure of the precursor. Moreover, the directly activated carbons exhibit much greater connectivity, creating the impression of larger monolith-like particles as opposed to the freestanding spherical particles for the conventionally activated carbons.⁶⁰

The amount of KOH used in the activation process appears to have an effect on morphology. Thus, carbons activated at a KOH/PET ratio of 2 show a higher degree of surface roughness, suggesting a microporous structure. Carbons activated at a KOH/PET ratio of 4 present smoother surfaces with larger particles. The activation temperature does not appear to have any substantial impact on the morphology.⁵⁸



Figure 4.8: SEM images of directly and conventionally activated PETderived carbons prepared at KOH/PET ratio of 2.



Figure 4.9: SEM images of directly and conventionally activated PETderived carbons prepared at KOH/PET ratio of 4.

4.5 Gas uptake measurements

4.5.1 Carbon dioxide uptake

The CO_2 uptake capacity of PET carbons was determined at pressure of up to 20 bar and room temperature (25 °C). The CO_2 uptake isotherms are shown in Fig. 4.10 and Fig. 4.11, and the uptake at various pressures (0.15, 1 and 20 bar) is presented in Table 4.3.

At 1 bar, carbons prepared at a KOH/PET ratio of 2 show CO₂ storage capacity ranging from 2.9 mmol q^{-1} to 4.3 mmol q^{-1} . The CO₂ uptake of 4.3 mmol q^{-1} is at the top end of what has been reported for all porous carbons.^{26,29-32,60} It is also higher than what has previously been reported for carbons derived from packaging waste materials,^{3,4,51,55,67} It is worth mentioning that while carbons synthesised at a KOH/PET ratio of 2 have narrower pores than those prepared at a ratio of 4 (Table 4.2), the former show considerably better CO_2 capture capacities at 1 bar. This clearly indicates that the CO₂ uptake at low pressure is significantly influenced by pore sizes. More specifically, samples that have narrow micropores store more CO₂ than those with supermicropores and mesopores. This is due to the narrow micropores having stronger adsorption potentials that enhance their fulling up with CO₂ molecules. These findings demonstrate that effective CO₂ sorbents need careful control of their porosity, which should ideally arise from micropores <10 Å.

Moreover, at typical flue gas conditions (CO₂ partial pressure of 0.15 bar), enhanced CO₂ adsorption (0.3 - 1.5 mmol g^{-1}) is achieved, emphasising the potential of these samples for post-combustion CO₂ captures. At such low

pressure, uptake of 1.5 mmol g^{-1} is amongst the best ever reported for porous carbons^{26,29–32,60} and corresponds well with the samples' microporosity.

However, the surface area is the dominating factor that determines uptake at 20 bar, and thus samples with a high surface area have better performance.

As shown in Figs. 4.10 and 4.11, the uptake of carbons prepared at a KOH/PET ratio of 2 seem to be approaching saturation at 20 bar, while the uptake isotherms for carbons activated at a ratio of 4 (Fig. 4.12) are far from saturation, indicating that higher capture capacities can be reached at high pressures.

Sample	CO ₂ uptake (mmol g ⁻¹)				
	0.15 bar	1 bar	20 bar		
PET2600D	1.2	3.1	5.2		
PET2700D	0.8	3.5	9		
PET2800D	1.5	4.3	10.2		
PET2600HC	1.2	4	8.8		
PET2700HC	1	2.9	6.3		
PET2800HC	1.1	4.3	11.8		
PET4600D	0.8	3.2	13.2		
PET4700D	0.8	3.4	12.6		
PET4800D	0.3	2.2	11.7		

Table 4.3: CO2 uptake of directly and conventionally activated PET-derivedcarbons.



Figure 4.10: CO₂ uptake isotherms at 25 °C bar of directly activated PETderived carbons prepared at KOH/PET ratio of 2.



Figure 4.11: CO₂ uptake isotherms at up to 20 bar of conventionally activated PET-derived carbons prepared at KOH/PET ratio of 2.



Figure 4.12: CO₂ uptake isotherms of directly activated PET-derived carbons prepared at KOH/PET ratio of 4.

4.5.2 Methane storage

High-pressure (up to 100 bar) adsorption was determined at room temperature (25 °C) to evaluate the methane storage potential of the PET-derived carbons. Considering that porous adsorbents targeted at achieving exceptional CH₄ storage should be predominantly microporous with high surface area, high microporous volume and some mesoporosity,^{28,31,41,42,45,46,48,49,68,69} the porosity data in Table 4.2 suggest that PET carbons could be ideal candidates for achieving high methane storage capacity at high pressures.

Figure 4.13 displays the total gravimetric adsorption/desorption isotherms for methane at 25 °C and up to 100 bar. Initially, the methane uptake increases

linearly with an increase in pressure, and all isotherms exhibit an absence of adsorption-desorption hysteresis, demonstrating that the physisorption process is entirely reversible.⁴⁴ The total gravimetric methane uptake isotherms show no saturation tendency even at 100 bar, indicating that the PET carbons can store a higher amount of methane at pressures above 100 bar. The PET carbons show very high gravimetric uptakes at 100 bar in line with the surface area trends, where the sample with the highest surface area presents the highest gravimetric CH₄ adsorption capacity.

Table 4.4 summarises the methane uptake at 25 °C and up to 100 bar on a gravimetric basis (mmol g⁻¹ and g g⁻¹) and volumetric basis (cm³ (STP) cm⁻ ³). All PET carbons show high gravimetric methane uptake at 100 bar, with excess in the range of 11.1 to 13.4 mmol g^{-1} (equivalent to 0.18 - 0.21 g g^{-1} ¹). The excess methane uptake at 100 bar has a clear relationship with surface area and pore volume. In this regard, the largest excess uptake (13.4 mmol g^{-1}) is for sample PET4800HC, which has the highest surface area (2828) $m^2 q^{-1}$) and pore volume (1.47 cm³ q⁻¹). Methane storage capacity of 13.4 mmol q^{-1} (0.21 $q q^{-1}$) at 100 bar and 25 °C is amongst the best previously reported values for any porous material.^{28,31,41,42,45,46,48,49,68,69} The total methane uptake varied between 16.4 and 20.4 mmol g^{-1} (0.26 - 0.33 g g^{-1}). In this sense, all samples show an uptake above 20.0 mmol q^{-1} (> 0.30 g q^{-1} ¹), which is very impressive and compares favourably with the best benchmark materials reported to date.^{28,31,41,42,45,46,48,49,68,69} The targeted porosity development in PET carbons enables achievement of very attractive gravimetric methane storage capacity at 25 °C and 100 bar.



Figure 4.13: Total gravimetric methane uptake at 25 °C of compacted PETderived activated carbons.

Table 4.4: Methane uptake at 25 °C and pressure of 100 bar for compacted
PET-derived activated carbons.

Sample	Excess uptake (100 bar)		Total uptake (100 bar)			Working capacity ^a	
	mmol/g	g/g	cm ³ /cm ³	mmol/g	g/g	cm ³ /cm ³	cm ³ /cm ³
CPET4600HC	11.1	0.18	281	16.4	0.26	415	257
CPET4700HC	12.73	0.20	288	19.5	0.31	441	273
CPET4800HC	13.39	0.21	294	20.4	0.33	448	273

^aWorking capacity is the difference in uptake between 65 bar and 5.8 bar

Regarding potential methane storage applications, the volumetric uptake is a better performance indicator than the gravimetric uptake. Apart from the gravimetric methane uptake, the packing density of an adsorbent is the other

key factor in determining the suitability of a porous material for a gas storage tank with a defined volume.⁵⁰ The packing density of the PET-derived carbons, given in Table 4.5, was obtained following compaction at 370 MPa of a known weight of carbon in a 1.3 cm diameter die for 5 minutes at ambient temperature. The PET carbons show a very high packing density between 0.98 and 1.13 g cm⁻³, depending on porosity.^{31,49,70} High packing density means that more adsorbent can be filled into the tank with minimal interparticle space, thus maximizing the tank volume.⁵⁰ Critically, the textural properties of the PET carbons are largely retained after compaction. As shown in Table 4.5, the surface area and pore volume are largely retained after compaction with the exception of sample CPET4700HC, whose pore volume slightly decreased. Furthermore, the pore size distribution does not alter after compaction except for a minor shift in pore size maxima to smaller mesopores. Given that the mechanical compression whilst improving packing density does not, however, alter the textural properties and gravimetric methane uptake, the expectation is that of significantly improved volumetric CH₄ uptake.

Sample	BET surface area ^a m ² g ⁻¹	Pore Volume ^b cm ³ g ⁻¹	Pore size Å	Packing density g cm ⁻³
CPET4600HC	2045 (1618)	1.11 (0.73)	5/8/11/15/21	1.13
CPET4700HC	2590 (2079)	1.38 (0.93)	5/8/10/11/15/21	1.01
CPET4800HC	2793 (2292)	1.47 (1.06)	5/8/10/11/15/21	0.98

Table 4.5: Textural properties and packing density of compacted PET-derived activated carbons.

The values in parenthesis refer to: ^a micropore surface area and ^b micropore volume

The key volumetric storage target in porous materials has been set by the US Department of Energy (DOE) at 350 cm³ (STP) cm⁻³ of volumetric storage capacity and 0.5 g (CH₄) g^{-1} of gravimetric storage capacity at ambient temperature (25 °C) and moderate pressure (35-100 bar). The total volumetric uptake of the PET carbons are shown in Fig. 4.14. Given the excess methane uptake and the packing density of the PET carbons, it is possible to estimate the volumetric storage capacity (cm³ (STP) cm⁻³). The volumetric storage capacity increases with increasing excess adsorption and material porosity. In general, the PET carbons appear to be much further away from saturation at 100 bar, indicating that much greater volumetric methane uptake can be achieved at pressures higher than 100 bar. All the tested PET carbons have exceptional volumetric methane storage with the uptake of up to 448 cm³ (STP) cm⁻³ at 25 °C and 100 bar. This volumetric uptake is far higher than that of any previously reported porous material.^{28,31,41,42,44-49,68,70-} ⁷⁹ To date, MOFs have been suggested as the most promising methane storage materials, and extensive research on their performance has been published.^{41,45,49,70,77,79} Despite their potential for high-pressure methane

storage, MOFs have low mechanical stability.⁵⁰ These MOF-related constraints have underscored the necessity to move towards efficiently packable materials. Carbon materials, unlike MOFs, have a higher mechanical strength, as demonstrated in this work, thereby avoiding any packing-related efficiency loss.⁵⁰ Consequently, PET carbons show exceptional and unrivalled total volumetric methane uptake capacities of between 415 and 448 cm³ (STP) cm⁻ ³ because of a combination of their porosity and particle morphology, which allow for effective particle packing. The PET carbons also exhibit a certain amount of mesopores, ensuring good adsorption/desorption kinetics.⁸⁰ Furthermore, the high packing density of the compacted PET carbons, along with their high gravimetric CH₄ uptake, results in unprecedented volumetric storage capacity. More significantly, the volumetric uptakes for the PET carbons are the highest ever reported. Finally, the PET carbons significantly exceed the requirements set by the DOE, meaning that they can be effectively used as an adsorbent for storing methane.^{28,31,41,42,44-49,68,70-79}

Working capacity is the main measure of porous material performance for methane storage. The US Department of Energy (DOE) recently set a target methane working capacity (the difference between adsorption and desorption from 65 to 5.8 bar at room temperature) of 315 cm³ cm⁻³ for ANG technology, at which point it will be competitive with the commercially available compressed natural gas vehicles.^{31,81} Table 4.4 presents the working capacity of PET carbons at pressures ranging from 65 bar to 5.8 bar. Despite enormous efforts to find porous materials with the desired performance, the current world record values are 214 cm³ cm⁻³ (for MOF-96)⁸¹, and is 208 cm³ cm⁻³

(for MOF-519)⁸². However, the present PET carbons have considerably higher methane working capacity that reaches 273 cm³ (STP) cm⁻³.



Figure 4.13: Total volumetric methane uptake at 25 °C of compacted PETderived activated carbons.

4.6 Conclusion

The ever-increasing production of plastic waste has wreaked terrible environmental problems and further exacerbated the energy crisis. Therefore, the development of simple, economically feasible and sustainable approaches to the long-term transformation of plastic waste into high valueadded products is important for competitiveness and motivating waste plastics utilisation progress. This work is within the context of reducing the environmental impact of the massive amounts of residues produced by PET consumption. Polyethylene terephthalate (PET) bottles were explored since

they are among the most common post-consumer plastic wastes. The PETderived carbons were successfully prepared via two activation methods; conventional activation via hydrothermal carbonisation (HTC) and direct activation. Both methods involved KOH-mediated activation under mild (KOH/PET = 2) or severe (KOH/PET = 4) conditions at 600-800 °C. All activated carbons presented a very high carbon content and appeared to be suitable starting materials for activated carbon production. A maximum surface area of 2828 m² g⁻¹ was achieved, along with a maximum pore volume of 1.47 cm³ g⁻¹. Carbons prepared at a KOH/PET ratio of 2 showed CO₂ storage capacity of up to 4.3 mmol g⁻¹ at 1 bar and room temperature (25 °C), which is at the top end of what has been observed for all porous carbons, and comparable to what was previously reported for carbons derived from packaging waste materials. Samples with a large surface area showed better CO_2 uptake performance at 20 bar, indicating the CO_2 uptake at 20 bar correlates with the total surface area. The PET-derived carbons have high excess gravimetric methane uptake in the range of 11.1 - 13.4 mmol g⁻¹ (0.18-0.21 g g⁻¹) at 100 bar and 25 °C. The carbons were easily compacted to a high packing density of up to 1.13 g cm⁻³ with no textural property penalties. The compaction to high packing density when combined with the high gravimetric uptake offer unprecedented volumetric methane storage capacities of up to 448 cm³ (STP) cm⁻³ at 100 bar, and an unrivalled working capacity of up to 273 cm³ (STP) cm⁻³. More significantly, these values are the highest observed to date for all benchmark materials and substantially exceed the requirements set by the DOE, demonstrating that PET carbons can be can be effectively used as adsorbents for methane storage. These findings

indicate that porous carbon materials, when suitably designed, can reach DOE gas storage targets.

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5.1 Abstract

This work shows how knowledge of any biomass and choice of carbonisation process can offer a generalised route to predictability in the preparation of activated biocarbons. We demonstrate that based on O/C ratio of carbonaceous matter, it is possible to predictably generate biocarbons with suitable porosity, surface area density, volumetric surface area and packing density targeted towards record levels of CO₂ and CH₄ storage capacity. Highly porous carbons with controlled levels of microporosity of up to 97% of the surface area and 92% of the pore volume are generated. The level of synthetic control is such that it enables, on the one hand, exceptional CO₂ storage at 25 °C and low pressure (1.5 and 5.4 mmol g⁻¹ at 0.15 and 1 bar, respectively) or moderate pressure (23.7 mmol g⁻¹ at 20 bar), indicating superior uptake under both post-combustion and pre-combustion CO₂ capture conditions. The carbons may also be directed towards storing record levels of methane; at 25 °C and 100 bar, volumetric methane uptake of between 309 and 334 cm³ STP cm⁻³ was obtained, which values are considerably higher than all current benchmark materials and, moreover, surpass the United States Department of Energy (US DOE) target of 263 cm³ (STP) cm⁻³. Crucially, the carbons also have very attractive working capacity (deliverable

methane for 100 – 5 bar) of 262 cm³ (STP) cm⁻³, 234 cm³ (STP) cm⁻³ (80 to 5 bar), and 210 cm³ (STP) cm⁻³ (65 to 5 bar).

5.2 Introduction

Growing concerns regarding climate change and related environmental issues have encouraged considerable efforts to control the emission of CO₂, a major greenhouse gas. To reduce the amount of emitted CO₂, there are considerable efforts aimed at carbon capture and storage (CCS) as an intermediate solution. However, the ever increasing global consumption of fossil fuels and rising concerns over the sustainability of oil reserves have stimulated research in alternative energy sources. In this regard, natural gas, with its better environmental sustainability properties compared to oil-based fuels, has been touted as a cleaner alternative energy source. However, methane's volumetric energy density at standard temperature and pressure conditions, being only 0.12% of that of gasoline has limited its practical applications.¹⁻⁶ Strategies for increasing the energy density of methane have included liquefaction or compression. However, both are generally viewed as not being viable under ambient temperature and pressure conditions; compressed natural gas needs high-pressure (typically 200-300 bar) conditions that require expensive holding vessels, while liquefied natural gas depends on costly cryogenic cooling techniques. Adsorbed natural gas is, on the other hand, regarded as a promising way forward as it presents advantages with respect to safety, high gravimetric and volumetric energy density and energy efficiency. In this context, it is necessary to find suitable adsorbent materials that are viable for storage of methane and other energy-related gases.¹⁻⁷

Porous carbons, amongst other materials, have been suggested as promising candidates for gas storage applications related to sustainable energy provision where they are explored in relation to other adsorbents, including zeolites and metal-organic frameworks (MOFs).^{1–6} Porous carbons, especially activated carbons, can have a competitive edge due to their large-scale availability, low cost, controllable porosity, high thermal and chemical stability, easy preparation, and variable packing density.^{7–10} Activated carbons, in particular, can be readily generated from an extensive range of carbon-containing materials.^{11–13} Considering the need for sustainability in large-scale gas storage applications of porous carbons, it is worthwhile to prepare them from renewable materials.¹⁴ To this end, biomass-derived porous carbonaceous materials have gained attention due to their ready availability, low cost, renewability, and simple preparation methods.^{14–19}

The amount of gas adsorbed and stored on a solid is influenced by the surface area and porosity of the absorbent.⁸ In this regard, exploring new trends in the synthesis of tailorable porous materials with large surface area and optimised porosity is one of the long-pursued objectives towards high-performance activated carbons for gas storage applications. The porosity of an activated carbon can be tailored by varying the carbonisation and/or activating processes.^{7,9,20} The carbonisation process can dramatically alter the characteristics of both the activatable carbonaceous matter and the final carbon products. Hydrothermal carbonisation (HTC) has long been established as a starting point in transforming biomass into carbon-rich carbonaceous matter that is suitable for activation. The HTC process has the attraction of being relatively simple, only requiring the heating of biomass in water at a typical temperature of 250 °C under autogenous pressure. HTC

provides superheated water conditions under which biomass is converted into so-called hydrochar that is amenable to activation.^{18,21,22} Air-carbonisation (AC), on the other hand, involves the transformation of biomass to carbonaceous matter at relatively low temperature of ca. 400 °C in the presence of air.^{7,18,23} Carbonised matter from either process can then be activated, which in this report is via a chemical activation step using potassium hydroxide (KOH) as an activating agent. KOH is a preferred activating agent and is widely used to produce carbons with a range of porosity characteristics that can be tailored for enhanced gas adsorption performance.^{10,11,18,24,25}

We have recently shown that the carbonisation phase can affect the elemental composition of biomass-derived carbonaceous matter.^{7,12,18,23,26} As a consequence, the atomic oxygen/carbon (O/C) ratio is heavily influenced by the nature of the biomass source and the carbonisation process.^{7,12,18,23,26} Furthermore, it has also recently been shown that the nature of a carbonaceous precursor has a significant impact on activation behaviour (i.e., susceptibility or resistance to activation) and, consequently, plays a key role in determining the nature of porosity (e.g., micropore/mesopore mix) in the resulting carbons.^{7,26} These recent advances are important because the ability to intentionally select or generate targeted biomass-derived carbonaceous precursors can provide activated carbons with predictable and tailored properties for specific applications.

More generally, extensive research findings have demonstrated that biomassderived activated carbons can show real-world application potential for gas storage.^{7,9,12,20,24,27} To this end, biomass-derived activated carbons have been explored for methane storage.^{7,28} A practical target for methane storage has

recently been set by the US Department of Energy (DOE) at 350 cm³ (STP) cm⁻³ of volumetric storage capacity and 0.5 g (CH₄) g⁻¹ of gravimetric storage capacity at room temperature and pressure of 35 to 100 bar. It is worth noting that the 350 cm³ (STP) cm⁻³ target was set at that level based on the crystallographic density of MOFs.^{3,4} MOFs have a crystallographic density at least 25% higher than their actual packing density. Hence, this target allows for a 25% reduction in volumetric capacity (to ca. 263 cm³ (STP) cm⁻³) due to the need to pack MOFs into a storage tank. It is important to note that, in the case of activated carbons, no reduction is anticipated as the volumetric uptake can be obtained using experimentally determined packing density. This means that the target for methane storage in carbons can be taken to be 263 cm³ (STP) cm⁻³. An adsorbent's density is key in determining volumetric storage capacity because the adsorbent must be confined in a specific volume (e.g. in a tank), and therefore the higher the adsorbent density, the higher the amount of material that can be restricted in a tank and thus the higher the storage capacity.^{3,4} To achieve a high packing density, an adsorbent's porosity should arise predominantly from micropores, which may be accompanied by the presence of some small mesopores.

This work demonstrates clear predictability in the synthesis of biomassderived activated carbons that are intentionally targeted to have properties suitable for CO₂ and CH₄ storage. Clove (*Syzygium aromaticum*) was selected as starting material because it has a relatively low elemental oxygen content. The carbonisation process (AC or HTC) was used along with variation in the activation temperature and the amount of activating agent, to control the textural properties of the resulting activated carbons. The motivation of the study is that cloves, based on their elemental composition and in particular

oxygen content and O/C atomic ratio, can be used to predictably generate activated carbons with the appropriate porosity and high packing density that are suited for achieving exceptional levels of CO₂ and CH₄ storage capacity. Although cloves have been used to demonstrate the predictability, the implications are more general and point to the use of either (i) biomass starting material with a low O/C ratio (such as cloves), which yield activateable carbonaceous matter with low O/C ratio or (ii) any biomass that can be transformed into activateable carbonaceous matter with low O/C ratio. In this regard, the cost of producing activated carbon in a predictable manner (from cloves or any other suitable biomass) should be no more expensive compared to that of already used biomass sources for any commercially available carbons.

5.3 Expermental section

5.3.1 Synthesis of biomass-derived activated carbons

Air carbonisation (AC): 2 g of cloves were placed in an alumina boat and heated in a horizontal tube furnace to 400 °C under a nitrogen atmosphere at a heating ramp rate of 10 °C min⁻¹. Once at 400 °C, the cloves were briefly (5–10 min.) exposed to a flow of air, after which the furnace was left to cool under a nitrogen flow. The resulting carbonaceous matter was designated as air carbonised clove, ACC.

Hydrothermal carbonisation (HTC): 4.6 g of cloves were dispersed in 20 ml of deionised water and placed in a stainless-steel autoclave, heated up to 250 °C, maintained at the target temperature for 2 h, and then cooled to

room temperature. The resulting solid product, denoted as hydrochar, was obtained via filtration, washed abundantly with deionised water, and dried at 100 °C for 24 h. The resulting hydrochar was designated as HCC – hydrochar from cloves.

Chemical activation: the required amount of KOH was thoroughly mixed with the carbon precursor (ACC or HCC) in an agate mortar at a KOH/carbon precursor ratio of 2 or 4. The resulting mixture was loaded onto an alumina boat, placed inside a tubular furnace, and heated at a ramp rate of 3 °C min⁻¹ to 600, 700 or 800 °C under a flow of nitrogen. The furnace was held at the final temperature for 1 h, and then allowed to cool under an atmosphere of nitrogen gas. The resulting activated carbons were washed with 20% HCl at room temperature and then filtered, following which they were washed severally with deionised water until neutral pH was achieved for the filtrate. The carbons were then dried in an oven at 100 °C.

The activated carbons was designated as ACCxT for air-carbonised carbonderived samples and HCCxT for hydrochar-derived samples, where x is the KOH/carbon precursor ratio, and T is the activation temperature.

5.3.2 Material characterisation

Elemental, CHN, analysis was performed on an Exeter Analytical CE-440 Elemental Analyser. A PANalytical X'Pert PRO diffractometer was used to perform powder XRD analysis using a Cu-Kα light source (40 kV, 40 mA) with a step size of 0.02° and 50 s time step. Nitrogen sorption analysis (at -196 °C) with a Micromeritics 3FLEX sorptometer was used for porosity assessment and determination of textural properties. Prior to analysis, the carbon

samples were degassed under vacuum at 200 °C for 16 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method applied to adsorption data in the relative pressure (P/P_o) range of 0.02 – 0.22, and pore volume was estimated from the total nitrogen uptake at close to saturation pressure ($P/P_o \approx 0.99$). The relative pressure range for the determination of surface area was monitored in all cases such that there was a positive y-axis intercept from multipoint BET fitting (i.e., C > 0) and also that $V_{ads}(1 - p/p_0)$ would rise with P/P_o.²⁹ The micropore surface area and micropore volume were determined via *t*-plot analysis. The pore size distribution (PSD) was determined using Non-local density functional theory (NL-DFT) applied to nitrogen adsorption data. The determination used SAIEUS software wherein the applied 2D-NLDFT heterogeneous surface kernel allowed adequate consideration of the chemical and energetic heterogeneity of the carbons. The fitting parameter, λ , within the SAIEUS software that controls the PSD's roughness was between 2.5 and 5.0.^{30,31} Scanning electron microscopy (SEM) images were recorded using an FEI Quanta200 microscope, operating at a 5 kV accelerating voltage.

5.3.3 Gas uptake measurements

 CO_2 uptake was determined in the pressure range of 0–20 bar at room temperature using a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003). The carbons were outgassed at 240 °C for several hours prior to performing the CO_2 uptake measurements.

Methane uptake was determined using a Hiden Isochema XEMIS Analyser. Before the uptake measurements, the carbon samples were degassed at 240

°C under a vacuum for several hours. Methane uptake isotherms were obtained at 25 °C over the pressure range of 0–100 bar.

5.4 Results and Discussion

5.4.1 Yield and elemental composition of activated carbons

The yields of air-carbonised clove (ACC), clove-derived hydrochar (HCC) and activated carbons are summarised in Table 1 and Table 2. The yield of activated carbons was monitored so as to enable a comparison between the air carbonisation route and the conventional HTC route. The yield of aircarbonised cloves (ACC) is similar to clove-derived hydrochar at 35%. However, the yield of ACC-derived activated carbons ranges from 25 to 50%, while that of HCC-derived samples was lower at between 11% and 40%. For any given activation conditions, the yield via AC is higher than for HTC, and in some cases is twice as high. It is clear that the air carbonisation route offers higher yields of activated carbons than the conventional HTC route, indicating that air carbonisation generates carbons that are relatively resistant to activation with KOH due to having a lower O/C ratio as confirmed in Table 1 and 2.^{7,18} Similar trends in yield between AC and HTC routes have previously been observed for activated carbons derived from other biomass sources such as date seed⁷ or sawdust.¹⁸ In general, the carbon yield decreases at greater levels of activation (i.e., higher amounts of KOH and/or activation temperature).

Sample	Yield [%]	C [%]	H [%]	N [%]	0 [%]]
Clove	-	49.7	5.9	0.9	43.5	0.66
ACC	35	66.1	4.3	1.9	27.7	0.31
ACC2600	50	76.5	1.1	0.6	21.8	0.21
ACC2700	47	84.3	0.5	0.3	14.9	0.13
ACC2800	44	87.3	0.2	0.3	12.2	0.11
ACC4600	42	78.4	0.6	0.3	20.7	0.20
ACC4700	37	89.3	0.2	0.3	10.2	0.09
ACC4800	25	90.9	0.2	0.2	8.7	0.07

Table 5.1: Carbonisation yield and elemental composition of raw clove, air-
carbonised clove (ACC) and ACC-derived activated carbons.

^aAtomic ratio

Table 5.2: Carbonisation yield and elemental composition of clove, clove
hydrochar (HCC) and HCC-derived activated carbons.

Sample	Yield [%]	C [%]	H [%]	N [%]	O [%]	O/C ^a
Clove	-	49.7	5.9	0.9	43.5	0.66
HCC	35	62.1	6.3	1.5	30.1	0.36
HCC2600	40	79.0	0.4	0.3	20.3	0.19
HCC2700	37	83.0	0.4	0.4	16.2	0.15
HCC2800	24	86.2	0.1	0.2	13.5	0.12
HCC4600	15	80.9	0.6	0.6	17.9	0.17
HCC4700	12	88.4	0.3	0.2	11.1	0.09
HCC4800	11	92.1	0.2	0.1	7.6	0.06

^aAtomic ratio

The primary aim of the carbonisation process is to enrich the carbon content of the resulting carbonaceous matter. The elemental composition of the raw clove, the carbonized matter (ACC and HCC), and activated carbons is given in Table 1 and Table 2. The elemental composition data is an average of at least three determinations. The elemental composition of raw cloves indicates an O/C atomic ratio of 0.66, which is relatively low compared to many other biomass sources for which the ratio is in the range of 0.75 to 1.0.^{7,18} The carbon content increases following the carbonisation step from 49.7 wt% for the raw clove to 66.3 wt% for ACC and 62.1 wt% for HCC, accompanied by a reduction in O content. Air carbonisation results in a reduction in O content from 43.5 wt% (raw clove) to 27.7 wt% for ACC, which is a lower O content compared to 30.1 wt% for HCC. It is noteworthy that the O/C ratio of ACC (0.31) is slightly lower than that of HCC (0.36), although, in general terms, both carbonaceous products have a relatively low ratio.^{7,18} The content of H, N and O, on the other hand, gradually reduces at higher levels of activation. Indeed, the O/C ratio for ACC and HCC are amongst the lowest observed for various biomass sources where the O/C ratio is typically in the range of 0.4 to 1.0.^{7,18} It is noteworthy that the elemental composition of ACC and HCC is comparable to that of carbonaceous matter that is known to exhibit resistance to KOH activation, including air-carbonised date seeds,⁷ lignin-derived hydrochar,⁷ air-carbonised sawdust¹⁸ and so-called CNL1 carbon.²³ In all cases, activation of both ACC and HCC increases the C content, with the rise being generally more significant at higher levels of activation. The low O/C ratio of the ACC and HCC offers an opportunity to predictably target the porosity and packing density of the resulting carbons as described in the

following sections. The expectation is that activated carbons derived from ACC and HCC, by virtue of the low O/C ratio, will be dominated by micropores and therefore exhibit both a high surface area density and enhanced packing density.

5.4.2 Structure and morphology of activated carbons

X-ray diffraction (XRD) was performed to ascertain the nature of the carbons and their purity with respect to the absence of any crystalline inorganic phases. This is important if any inferences are to be made on the link between O/C ratio of precursors with porosity (especially the surface area density) and packing density. Any inferences require that both the precursors (ACC and HCC) and activated carbons be fully carbonaceous with no inorganic matter. The XRD patterns of the raw clove, air-carbonised clove (ACC), clove-derived hydrochar (HCC) and activated carbons are shown in Figures 5.1, 5.2 and 5.3. The XRD pattern of the HCC and ACC show a broad peak at $2\theta = 22^{\circ}$, which may arise from minor graphitic/turbostratic carbon domains. The XRD patterns for all the carbons are featureless except for low intensity and broad peaks at $2\theta = 22^{\circ}$ and 44° , which are typically attributed, respectively, to the (002) and (100) diffractions related to graphitic/turbostratic carbon (Figure 5.1). The low intensity and broad nature of the peaks suggests the lack of planarity of graphitic domains.¹⁸ According to the XRD patterns of the activated carbons (Figure 5.2 and 5.3), the amount of KOH has no significant impact on the graphitic/turbostratic nature of the carbons. At any given activation temperature, the XRD patterns indicate a comparable level of graphitic ordering or graphene stacking.³² Crucially, all the XRD patterns show no sharp peaks, which confirms the absence of any inorganic matter.

Thus, according to the XRD patterns, ACC, HCC and the activated carbons are fully carbonaceous.



Figure 5.1: Powder XRD patterns of raw clove, air-carbonised clove (ACC) and clove hydrochar (HCC).



Figure 5.2: Powder XRD patterns of activated carbons derived from aircarbonised clove (ACC).



Figure 5.3: Powder XRD patterns of activated carbons derived from clove hydrochar (HCC).

Cloves have a bulky morphology with a compact surface lacking any conspicuous porous architecture (Figure 5.4). After air carbonisation, cavities or cracks appear on the external surface of the ACC sample (Figure 5.4). However, when clove is converted to hydrochar, some of the clove's original morphology appears to be preserved (Figure 5.4). Conversely, the morphology of activated carbons shows irregularly shaped particles with relatively smooth surfaces and randomly distributed craters and pores (Figure 5.5 and 5.6).¹⁴ Such cavities are consistent with generation of porosity via gasification processes.³³ It is interesting to note that this morphology is similar to that of most previously reported activated carbons. This is consistent with the fact that it is now well-recognised that activated carbons produced by KOH activation have similar morphology and that the type of precursor material used has little effect on particle shape.



Figure 5.4: SEM images of raw clove, air-carbonised clove (ACC) and clovederived hydrochar (HCC).



Figure 5.5: Representative SEM images of activated carbons derived from air-carbonised clove.



Figure 5.6: Representative SEM images of activated carbons derived from clove hydrochar.

5.4.3 Porosity and textural properties

The nitrogen sorption isotherms and the pore size distribution (PSD) curves of air-carbonised activated carbons (ACCxT) are displayed in Figure 5.7 and Figure 5.8. All the carbons exhibit type I isotherms, which indicates their microporous nature. Although the quantity of nitrogen adsorbed increases with the severity of activation (i.e. higher activation temperature), all ACC27 carbons (Figure 5.7A) show no variation in the shape of the isotherm. All ACC2*T* carbons have a type I isotherm with a sharp adsorption knee wherein virtually all nitrogen sorption occurs at very low relative pressure (P/Po < 0.01). A sharp knee indicates the presence of a significant proportion of microporosity and the absence of pores larger than the micropore range (up to 20 Å). As shown in Figure 5.7B, the porosity of the ACC2T carbons is dominated by 5–20 Å pore channels, with all pores being less than 20 Å in diameter. Despite the non-changing shape of the isotherms, the level of porosity, as measured by the amount of nitrogen adsorbed, increases modestly for samples generated at higher activation temperature. The isotherms of ACC4T carbons (Figure 5.8A) are consistent with a predominantly microporous nature but with a broader knee. Knee broadening, which is greater at higher activation temperature (i.e., more severe activation), indicates presence of larger pores. This is confirmed by the PSD curves in Figure 2B. Unlike ACC2*T* carbons (Figure 5.7B), the ACC4*T* set (Figure 5.8B) possess a greater proportion of wider micropores and some small mesopores.



Figure 5.7: (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of activated carbons derived from air-carbonised clove at KOH/ACC ratio of 2.



Figure 5.8: (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of carbons derived from air-carbonised clove (ACC) at KOH/ACC ratio of 4.

The nitrogen sorption isotherms and PSD curves of hydrochar-derived activated carbons (HCCxT) are shown in Figure 5.9 and Figure 5.10. The isotherms of HCC2T carbons (Figure 5.9A) are type I, with a pronounced sharp adsorption knee at low relative pressure, which is characteristic of essentially microporous materials. The sample activated at 800 °C (HCC2800) exhibits a gentle adsorption knee, implying the presence of supermicropores (pore channels with diameters ranging from 7–20 Å) in addition to micropores. This is confirmed by the PSD curves in Figure 5.9B; HCC2*T* carbons show few pores larger than 10 Å and no pores wider than 20 Å. Activation at a KOH/HCC ratio of 4 produces a higher proportion of larger pores than activation at a ratio of 2. For example, the isotherms of samples HCC4600 and HCC4700 show a broad adsorption knee, while the sample activated at 800 °C (HCC4800) exhibits a very wider adsorption knee with a linear increase in adsorption at relative pressure (P/Po) up to a of 0.4, indicating the presence of a significant proportion of small mesopores. The PSD curves (Figure 5.9B) confirm that HCC47 samples have relatively wide PSD but still mainly in the micropore/supermicropore to mesopore range, with pore channels of up to 34 Å.

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Figure 5.9: (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of activated carbons derived from clove hydrochar (HCC) at KOH/HCC ratio of 2.



Figure 5.10: (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of activated carbons derived from clove hydrochar (HCC) at KOH/HCC ratio of 4.

The textural properties of both sets of activated carbons are given in Table 5.3. In the context of all known activated carbons, the surface area and pore volume are moderate to high, depending on the severity of activation. The surface area of ACC2T carbons gradually increases from 1500 m² g⁻¹ for ACC2600 to 2150 m² g⁻¹ for ACC2800, and from 2229 m² g⁻¹ for ACC4600 to 3175 m² g⁻¹ for ACC4800. This modest increase in surface area for activation at higher temperature is consistent with the resistant to activation nature of ACC.⁷ A similar trend is observed for pore volume, which is in the range of 0.63 to 0.94 cm³ g⁻¹ for ACC2*T* carbons and up to 1.65 cm³ g⁻¹ for sample ACC4800. It is worth noting that the air-carbonised samples possess a very high proportion of surface area and pore volume arising from micropores, which for ACC2*T* samples is typically ca. 96% of the surface area and ca. 87% of pore volume, while for ACC4T samples it is 81 – 89% of surface area and 71–79% of pore volume. It is remarkable that the most severely activated sample (ACC4800), still has a proportion of microporosity at 81% (surface area) and 71% (pore volume). For samples prepared via hydrothermal carbonisation (HCCxT), the surface area of HCC2T carbons ranges from 1396 to 2414 m² g⁻¹, and the pore volume is in the range of 0.57–1.13 cm³ g⁻¹, with a very high proportion of micropore surface area of 97%, while micropore pore volume is between 80% and 92%. After the severest activation, sample HCC4800 has the highest surface area and pore volume of 3116 m² g⁻¹ and 1.75 cm³ g⁻¹, respectively, with relatively high microporosity; 70% of surface area and 56% of pore volume.

Sample	Surface area	Micropore surface area ^a	Pore volume	Micropore volume ^b	Surface area density ^c	Pore size ^d
	(m² g⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(m ² cm ⁻³)	(Å)
ACC2600	1500	1418 (95%)	0.63	0.55 (87%)	2381	5,8,13
ACC2700	1953	1866 (96%)	0.82	0.72 (88%)	2382	5,9,13
ACC2800	2150	2019 (94%)	0.94	0.81 (86%)	2287	6,9,14
ACC4600	2229	1983 (89%)	1.06	0.84 (79%)	2103	5,8,14,20
ACC4700	2773	2431 (88%)	1.42	1.01 (71%)	1953	5,8,14,21
ACC4800	3175	2568 (81%)	1.65	1.17 (71%)	1924	5,8,15,25
HCC2600	1396	1353 (97%)	0.57	0.52 (91%)	2449	5,8,13
HCC2700	1847	1784 (97%)	0.76	0.70 (92%)	2430	6,8,13
HCC2800	2414	2163 (90%)	1.13	0.89 (79%)	2136	6,9,14,19
HCC4600	1700	1499 (88%)	0.84	0.65 (77%)	2024	6,9,14,22
HCC4700	2743	2267 (83%)	1.35	1.05 (78%)	2032	6,9,15,24
HCC4800	3116	2190 (70%)	1.75	0.98 (56%)	1781	6,8,14,25

Table 5.3: Textural properties of activated carbons derived from air-
carbonised clove (ACC) and clove hydrochar (HCC).

^a Values in parenthesis are % of surface area from micropores. ^b Values in parenthesis are % of pore volume from micropores. ^c Surface area density is obtained as ratio of total surface area to total pore volume. ^d Pore size maxima from PSD curves.

The surface area and pore volume of air-carbonised ACC2*T* samples are comparable to those of analogous HCC2*T* carbons at any given activation level (i.e., similar temperature and KOH/carbon ratio). However, ACC2*T* have

higher levels of microporosity. This trend is also observed for carbons prepared at KOH/precursor ratio of 4, such that although the most severely activated carbons have a comparable total surface area, the air-carbonised sample ACC4800 has a lower pore volume and a significantly higher proportion of microporosity compared to sample HCC4800. This apparent resistance to the formation of larger pores suggests that ACC is relatively more resistant to activation in a manner similar to the recently reported air-carbonised ACSD and ACDS carbons.^{7,18} Nevertheless, HCCx*T* carbons also present high levels of microporosity when compared to most other activated carbons,^{7,18} which suggests a significant level of resistance to KOH activation consistent with the relatively low O/C ratio of HCC.

The surface area density (SAD) of the present carbons, which is the ratio of total surface area to total pore volume, is given in Table 5.3. The SAD of activated carbons is related to the susceptibility or resistance to activation of the carbonaceous precursor from which they are derived. Under any given activation conditions, a high SAD can be well matched with low O/C ratio for the precursor meaning resistance to activation and consequently a tendency to generate micropores rather than mesopores.⁷ The O/C ratio can, therefore, be used as a predictor for SAD (i.e., the balance of microporosity and mesoporosity). Moreover, both O/C and SAD may be used to predict the packing density of activated carbons.^{7,34,35} Given the low O/C ratio of both ACC and HCC, the expectation was that the resulting activated carbons would have high SAD, which is indeed confirmed in Table 5.3. The SAD is in the range of 2287 – 2382 m² cm⁻³ for ACC2*T* and 1924 – 2103 m² cm⁻³ for ACC4*T* samples. Given the similarity of the O/C ratio of ACC and HCC, relatively similar values are obtained for hydrochar-derived samples; 2136 – 2449

m² cm⁻³ for HCC2*T* and 1781 – 2032 m² cm⁻³ for HCC4*T* samples. These SAD values are, as predicted, on the higher end compared to that of many other biomass precursors⁷ including sawdust hydrochar,^{25,36} lignin hydrochar,³⁷ jujun grass hydrochar³⁸ and Camelia Japonica hydrochar.³⁸

The packing density of porous carbons plays a crucial role in determining the volumetric surface area and volumetric gas uptake, wherein the adsorbing material is filled into a tank with restricted space.³⁴ In such a scenario, increasing the packing density via compaction can improve the volumetric uptake of porous materials. However, such compression is only beneficial if it does not compromise the textural properties on which the gravimetric uptake depends.³⁴ To this end, and with a view of increasing packing density with respect to methane storage, a selection of high surface area HCC-derived carbons (HCC2800, HCC4700 and HCC4800) were compacted at ambient temperature in a 1.3 cm (diameter) die for 10 min at compaction pressure of 370 MPa. The compacted samples were designated as CHCC2800, CHCC4700 and CHCC4800. Only HCCxT carbons with the highest surface area (a criteria for good methane storage) were selected for compaction. Given the similarity in textural properties for the high surface area samples in both (HCCxT and ACCxT) series, the compaction was not duplicated for the latter series of carbons, as the expectation was that similar trends would be observed. As shown in Figure 5.11 and 5.12, the nitrogen sorption isotherms and PSD curves of the compacted samples are very similar to those of the noncompacted analogues. This indicates that the compaction does not cause any diminution of porosity or textural properties.³⁹ As shown in Table 5.4, in comparison to the data in Table 5.3 above, there are only minor changes in the textural properties of the carbons after compaction; both surface area

and pore volume are largely retained along with the proportion of microporosity, which is enhanced in some cases. As shown in Table 5.4, despite the retention of their textural properties, the compacted carbons show high packing density of 0.58 - 0.82 g cm⁻³.³⁵



Figure 5.11: (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves of compacted carbons derived from hydrochar (HCC).

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Figure 5.12: A comparison of representative hydrochar-derived carbons before and after compaction; (A) Nitrogen sorption isotherms and (B) pore size distribution (PSD) curves.

Table 5.4: Textural properties of compacted activated carbons derived from cloved from clo	ve
hydrochar.	

Sample	Surface area	Micropore surface area ^a	Pore volume	Micropore volume ^b	Surf. area density ^c	Packing density ^d	Vol. surface area ^e
	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(m ² cm ⁻³)	(g cm ⁻³)	(m ² cm ⁻³)
CHCC2800	2382	2170 (91%)	1.11	0.91 (82%)	2146	0.82	1953
CHCC4700	2643	2298 (87%)	1.31	1.02 (78%)	2018	0.75	1985
CHCC4800	3064	2162 (71%)	1.71	1.00 (59%)	1792	0.58	1777

^a Values in parenthesis are % of surface area from micropores. ^b Values in parenthesis are % of pore volume from micropores. ^c Surface area density is ratio of total surface area to total pore volume. ^d The packing density following compaction at 370 MPa. ^e Volumetric surface area determined as surface area x packing density.

The surface area density of the compacted samples is within the range of 1792 to 2146 m² cm⁻³ compared to 1781 to 2136 m² cm⁻³ for the noncompacted equivalents. Thus SAD does not change on compaction as the overall surface area and pore volume are retained. The volumetric surface area of the compacted carbons, which is defined as surface area x packing density, is also presented in Table 5.4. The volumetric surface area of porous materials has previously been used as a proxy for gas storage performance, especially for methane.^{1,7} The compacted carbons have a volumetric surface area of these carbons is amongst the highest reported for porous materials.⁷ Reports of MOFs with higher volumetric surface area exist (e.g., 2060 m² cm⁻³ for NU-1501-AI), but such values are likely to be overestimated as they are computed using crystallographic density rather than actual packing density.³⁹

5.5 Gas uptake measurements

5.5.1 CO₂ uptake

The CO₂ capture capacity was measured at 25 °C and a pressure range of 0 to 20 bar. The CO₂ uptake isotherms for ACCx*T* and HCCx*T* carbons are shown in Figure 5.13 and Figure 5.14, respectively, and Table 5.5 summarises the CO₂ uptake at various pressures (0.15 bar, 1 bar and 20 bar). Generally, the CO₂ uptake isotherms of the ACC2*T* and HCC2*T* carbons prepared at KOH/precursor ratio of 2 approach saturation at 20 bar, whereas those prepared at a ratio of 4 (ACC4*T* and HCC4*T*) are far from saturation, which indicates that they can reach greater storage capacity at higher pressures. As discussed above, the porosity of the ACC2*T* and HCC2*T* carbons is

dominated by micropores, while ACC4T and HCC4T samples have larger micropores and some small mesopores of size up to ca. 30 Å. Comparing the porosity data and CO₂ uptake reveals that the CO₂ uptake at low pressures of 0.15 bar and 1 bar is determined by the pore size rather than the total surface area, wherein carbons having narrow micropores show the higher uptake. Narrow micropores have been proven to be more effective at creating stronger interactions between CO_2 molecules and adsorbents than is possible for larger micropores and mesopores.²³ The CO₂ uptake of ACC2*T* samples at 1 bar ranges from 4.5 mmol g⁻¹ for ACC2600 to a high of 4.9 mmol g⁻¹ for ACC2700. The uptake of ACC2800 is the lowest at 4.2 mmol g⁻¹, which is consistent with the widening of the pore size for this sample (Figure 5.9B). The HCC2T set of samples show a similar trend; the CO₂ uptake at 1 bar being 4.3 mmol g^{-1} (HCC2600), 5.4 mmol g^{-1} (HCC2700) and 4.2 mmol g^{-1} for HCC2800. Overall, therefore, the ACC2T and HCC2T set of carbons show very high CO₂ uptake (4.2 – 5.4 mmol g^{-1}) at 1 bar and 25 °C. On the other hand, the uptake at 20 bar is dependent on surface area meaning that for the ACC2T and HCC2T set of carbons, it is samples ACC2800 and HCC2800 that have the highest storage capacity (Figure 5.13 and 5.14, and Table 5.5).

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Figure 5.13: CO₂ uptake isotherms at 25 °C of activated carbons derived from air-carbonised clove (ACC) prepared at KOH/ACC ratio of 2 (A and B) or 4 (C and D).

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Figure 5.14: CO₂ uptake isotherms at 25 °C of activated carbons derived from clove hydrochar (HCC) prepared at KOH/HCC ratio of 2 (A and B) or 4 (C and D).

Sample	CO ₂ uptake (mmol g ⁻¹)					
	0.15 bar	1 bar	20 bar			
ACC2600	1.1	4.5	13.3			
ACC2700	1.1	4.9	16.2			
ACC2800	0.9	4.2	18.0			
ACC4600	0.8	3.5	17.2			
ACC4700	0.7	3.6	21.1			
ACC4800	0.7	3.4	23.7			
HCC2600	1.3	4.3	10.7			
HCC2700	1.4	5.4	14.7			
HCC2800	0.9	4.2	19.0			
HCC4600	0.7	2.6	12.5			
HCC4700	0.7	3.3	20.3			
HCC4800	0.6	3.2	23.2			

Table 5.5: CO2 uptake of activated carbons derived from air-carbonisedclove (ACC) or clove hydrochar (HCC).

At lower pressure (0.15 bar), the CO₂ uptake of ACC2*T* carbons is in the narrow range of 0.9 and 1.1 mmol g^{-1} , with samples activated at 800 °C having the lowest storage capacity, again consistent with trends in pore size wherein widening of pores results in a reduction of uptake regardless of the variations in the overall surface area and pore volume. The HCC2*T* set of carbons shows a higher uptake of between 0.9 and 1.4 mmol g^{-1} . Generally, the trend matches that of uptake at 1 bar and is clearly related to the microporosity of the carbons.³² Thus, it is clear that for samples activated at
KOH/precursor ratio of 2, the ideal activation temperature for CO₂ uptake at such lower pressures is 700 °C. In particular, the CO₂ uptake for sample HCC2700, at 25 °C, of 1.4 and 5.4 mmol g⁻¹ at 0.15 and 1 bar, respectively, is at the very top end of what has been observed for all porous carbonaceous materials,^{9,12,18,27,32,35-38,40-42} hence, showing the potential of these carbons as post-combustion CO₂ storage materials. The uptake of HCC2700 is exceptional and one of the highest ever reported for carbons at ambient temperature and pressure, and is due to the sample having both the highest level of microporosity (97% of surface area and 92% of pore volume), and relatively high surface area for such a highly microporous material. Such a porosity combination, which is highly suited for low pressure CO₂ uptake, is unique to the extent that porous carbons rarely show uptake higher than ca. 4.8 mmol g^{-1} at 1 bar and 25 °C (Table 5.6).^{37,38,40-44} Uptake as high as 5.4 mmol g⁻¹ has seldom been observed (Table 5.6) and matches the record values reported to date, namely, 5.8 mmol g⁻¹ for compactivated carbons derived from sawdust,⁴⁵ 5.67 mmol g⁻¹ for fern-derived carbons,⁴⁶ and 5.5 mmol g⁻¹ for compactivated carbons derived from polypyrrole.⁴⁰

Sample	CO ₂ upt	ake (mmol g ⁻¹)	Reference
	1 bar	0.15 bar	
Hydrochar cloves HCC2700	5.4	1.4	This work
Sawdust-derived activated carbon	4.8	1.2	11
KOH-activated templated carbons	3.4	~1.0	42
Petroleum pitch-derived activated carbon	4.55	~1.0	47
Activated carbon spheres	4.55	~1.1	48
Phenolic resin activated carbon spheres	4.5	~1.2	49
Poly(benzoxazine-co-resol)-derived carbon	3.3	1.0	50
Fungi-derived activated carbon	3.5	~1.0	51
Chitosan-derived activated carbon	3.86	~1.1	52
Polypyrrole derived activated carbon	3.9	~1.0	41
Soya bean derived N-doped activated carbon	4.24	1.2	53
N-doped ZTCs	4.4	~1.0	54
Activated templated N-doped carbon	4.5	1.4	55
Polyaniline derived activated carbon	4.3	1.38	56
N-doped activated carbon monoliths	5.14	1.25	43
Activated N-doped carbon	3.2	1.5	57
Activated hierarchical N-doped carbon	4.8	1.4	58
Activated N-doped carbon from algae	4.5	~1.1	13
Compactivated carbons from sawdust	5.8	2.0	45
Fern-derived activated carbon	5.67	~1.7	46
Compactivated carbons from polypyrrole	5.5	2.1	40

Table 5.6: CO₂ uptake of of various porous carbons at 25 °C and 0.15 bar or 1 bar.

On the other hand, samples having the highest surface area do capture the largest amounts of CO_2 at 20 bar. Consequently, samples ACC4800 and HCC4800, with a surface area of 3175 and 3116 m² g⁻¹, respectively, show impressive CO_2 uptake of 23.7 and 23.2 mmol g⁻¹ at 20 bar. Rather unusually,

these high uptake at 20 bar is alongside attractive uptake at lower pressure of ca. 0.7 mmol q^{-1} (0.15 bar) and 3.4 mmol q^{-1} (1 bar). For many previous reports on CO₂ uptake in porous materials, a trend has emerged where materials with a large surface area have high uptake at a pressure of 20 bar or above, but have much lower uptake at a low pressure (≤ 1 bar). Furthermore, materials characterised by low to moderate surface area and having excellent low-pressure CO₂ uptake generally show low uptake at high pressure. This trend has been ascribed to the fact that the main determinant of CO₂ uptake at low pressure is pore size (and, consequently, the interaction between the gas molecules and pore walls), while the uptake capacity at high pressure is significantly dependent on surface area or space filling. Previous trends are, therefore, somewhat bucked for the present carbons that exhibit superior CO₂ uptake under conditions relevant to both pre-combustion and post-combustion CO_2 capture. Such unique CO_2 uptake is possible for the present carbons because they simultaneously achieve high surface area (and pore volume) and a high level of microporosity. The former ensures good CO₂ uptake at 20 bar while the latter is responsible for attractive low pressure (< 1 bar) uptake.

Although the present carbons show promise for both pre and post-combustion CO_2 uptake, their microporous nature, especially for ACC2*T* and HCC2*T* samples, is best suited for the latter (i.e., post-combustion CO_2 capture). We therefore further explored the low pressure CO_2 uptake of the ACC2*T* and HCC2*T* series of samples under conditions that mimic post-combustion CO_2 capture from flue gas streams. Table 5.5 shows the gravimetric uptake of the present carbons along with a comparison with benchmark carbons (Table 5.6). To better understand the performance of the present carbons we also

determined their volumetric CO₂ uptake. Volumetric uptake is important given that for application in CO₂ capture, the carbons would be packed into a column with limited space (i.e., volume) and therefore the amount of CO₂ stored as a function of the volume occupied by the adsorbing carbon should be optimised. The volumetric uptake takes into account the packing density of the carbons and their gravimetric uptake (Table 5.7). The low-pressure (up to 9 bar) volumetric CO₂ uptake of the ACC2*T* and HCC2*T* samples is impressive (Table 5.7), and is better than or matches that of benchmark carbons^{40,45,46,59} and MOFs.⁶⁰⁻⁶² In particular, the volumetric uptake of ACC2700 and HCC2700 is exceptional at pressures between 1 and 9 bar and reaches 197 g l⁻¹ (100 cm³ cm⁻³) at 1 bar, 409 g l⁻¹ (208 cm³ cm⁻³) at 5 bar, and 482 g l⁻¹ (245 cm³ cm⁻³) at 9 bar (Table 5.7).

Table 5.7: Packing (or tapping) density and low-pressure volumetric CO₂ uptake, expressed as g l⁻¹ (or cm³ (STP) cm⁻³), for clove-derived activated carbons compared to benchmark carbons and metal organic frameworks (MOFs). The values in parenthesis are volumetric uptake expressed as cm³ (STP) cm⁻³.

Sample	Density ^a	Volumetric	³ STP cm ⁻³)	Reference		
	(g cm ⁻³)	0.15 bar	1 bar	5 bar	9 bar	
ACC2600	0.92	45 (23)	182 (93)	390 (199)	463 (236)	This work
ACC2700	0.79	38 (19)	170 (87)	400 (204)	482 (245)	This work
ACC2800	0.72	29 (15)	133 (68)	349 (178)	450 (229)	This work
HCC2600	0.98	56 (29)	185 (94)	353 (180)	408 (208)	This work
HCC2700	0.83	51 (26)	197 (100)	409 (208)	476 (242)	This work
HCC2800	0.63	25 (13)	116 (59)	312 (159)	405 (206)	This work
SD2600	0.94	54 (27)	178 (91)	315 (160)	348 (177)	45
SD2600P	0.95	80 (41)	242 (123)	370 (188)	399 (203)	45
SD2650	0.89	47 (24)	161 (82)	294 (150)	338 (172)	45
SD2650P	0.81	54 (27)	189 (96)	371 (189)	427 (217)	45
Carbon A1	1.00	38 (19)	157 (80)	278 (142)	316 (161)	59
Carbon A3-3	0.87	27 (14)	128 (65)	302 (154)	378 (192)	59
MOF210	0.25 ^b	4 (2)	10 (5)	38 (19)	65 (33)	60
Mg-MOF-74	0.41 ^c	103 (52)	144 (73)			61,62

^a Packing density or tapping density. Packing density of ACC2*T* and HCC2*T* carbons may be determined from pellets compacted in a 1.3 cm die for ca. 5 min at 7 MPa. Similar values are obtained from the general equation; $d_{carbon} = (1/\rho_s + V_T)^{-1}$, where ρ_s is skeletal density and V_T is total pore volume from nitrogen sorption analysis. The skeletal density was determined from helium pycnometry from reference 25. ^b Crystal density of MOF210. ^c 'Tapping density' of Mg-MOF-74 from reference 62.

Similar to previous reports on biomass-derived carbons, the present clovederived carbons exhibit good regeneration and recyclability. Regarding recyclability, of particular interest is the amount of CO₂ that can be sequestered and delivered, i.e., the working capacity, over several cycles of use and reuse. The adsorption and regeneration cycles can be effected via pressure swing operations in the form of a pressure swing adsorption (PSA) process or vacuum swing adsorption (VSA) process.⁶³⁻⁶⁵ To work out the working capacity for the present carbons, we considered the following swing adsorption processes; PSA with adsorption at 6 bar and desorption at 1 bar, and VSA with adsorption at 1.5 bar and desorption at 0.05 bar.⁶⁵ Cognisant of the nature of flue gas streams from fossil fuel power stations, we determined the working capacity for two scenarios, namely, from a pure CO₂ stream, and from a flue gas stream in which CO₂ constitutes 20% of the gas flow so as to mimic real post-combustion flue gas stream conditions. The gravimetric working capacity is presented in Table 5.8 along with data for current benchmark activated carbons,⁴⁵ high performing MOFs (Mg-MOF-74 and HKUST-1),⁶⁶ and zeolite NaX.⁶⁷ For a pure CO₂ stream, the PSA working capacity of the present carbons is between 4.3 and 8.1 mmol g⁻¹, and thus is higher than that of Mg-MOF-74 (3.5 mmol g^{-1}), benchmark carbons (3.4 – 4.0 mmol q^{-1}) and zeolite NaX (1.6 mmol q^{-1}), and at the high end also surpasses that of HKUST-1 (7.8 mmol g^{-1}). For flue gas conditions, the PSA uptake of the present carbons is between 3.1 and 4.2 mmol q^{-1} , which matches the performance of HKUST-1 (4.5 mmol g⁻¹). The VSA uptake of the present carbons is also very attractive with sample HCC2700 reaching 6.1 mmol g^{-1} and 2.3 mmol g^{-1} , under pure CO₂ and 20% CO₂ conditions,

respectively, which when taken together compares favourably with all the

other benchmark materials (Table 5.8).

Table 5.8: Gravimetric working capacity for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) of CO₂ on clove-derived activated carbons compared to benchmark porous materials at ca. 25 °C for a pure CO₂ gas stream and a 20% partial CO₂ pressure flue gas stream.

Sample	Pure CO ₂ L	iptake ^a (mmo	ol g ⁻¹) Flue gas CO	2 uptake ^b	(mmol g ⁻¹) Reference
	PSA	VSA	PSA	VSA	
ACC2600	5.7	5.2	3.5	1.8	This work
ACC2700	7.4	5.8	4.0	1.9	This work
ACC2800	7.8	5.1	3.5	1.6	This work
HCC2600	4.3	4.6	3.1	2.0	This work
HCC2700	6.5	6.1	4.2	2.3	This work
HCC2800	8.1	5.2	3.6	1.7	This work
SD2600	3.7	4.6	3.0	2.1	45
SD2600P	3.4	6.0	4.1	2.9	45
SD2650	3.8	4.6	3.1	1.9	45
SD2650P	4.0	5.7	4.0	2.4	45
HKUST-1	7.8	6.4	4.5	1.6	66
Mg-MOF-74	3.5	3.9	2.1	4.1	66
NaX	1.6	2.8	1.8	2.5	67

^a1 bar to 6 bar for PSA; 0.05 bar to 1.5 bar for VSA. ^b0.2 bar to 1.2 bar for PSA; 0.01 bar to 0.3 bar for VSA.

Furthermore, the volumetric working capacity of the present carbons for both PSA and VSA processes is generally higher than that of the benchmark materials (Table 5.9). For pure CO₂, the PSA volumetric working capacity of the clove-derived carbons is exceptionally high ranging from 185 g l⁻¹ (94 cm³ cm⁻³) to a high of 257 g l⁻¹ (131 cm³ cm⁻³) compared to between 142 and 153 l g l⁻¹ (72 – 78 cm³ cm⁻³) for current benchmark carbons, and is much higher than for Mg-MOF-74 (63 g l⁻¹ or 32 cm³ cm⁻³) and HKUST-1 (147 g l⁻¹ or 75 cm³ cm⁻³). Sample HCC2700 has pure CO₂ VSA volumetric working capacity of 223 g l⁻¹ (114 cm³ cm⁻³) compared to 121 g l⁻¹ (62 cm³ cm⁻³), 70 g l⁻¹ (36 cm³ cm⁻³) and 78 g l⁻¹ (40 cm³ cm⁻³) for HKUST-1, Mg-MOF-74 and zeolite NaX, respectively. Sample HCC2700 also has PSA volumetric working capacity under flue gas conditions of 153 g l⁻¹ (78 cm³ cm⁻³), which is double that of HKUST-1 and much higher than for zeolite NaX and Mg-MOF-74.

Given that flue gas streams contain majority N_2 , it is important to understand the extent to which the present carbons are selective in adsorbing CO₂ over N_2 . We therefore determined the selectivity for a representative sample (HCC2700) by comparing the relative uptake at 25 °C and 1 bar of CO₂ and N_2 . The comparison (Figure 5.15) shows that at 1 bar the N_2 uptake is 0.25 mmol g⁻¹ compared to CO₂ uptake of 5.4 mmol g⁻¹. This gives an equilibrium CO₂/ N_2 adsorption ratio of 22, which is higher than typical ratios of 5 – 11 for carbon materials.^{11,34,42} The selectivity for CO₂ can also be estimated by considering a simulated post-combustion flue gas stream containing ca. 15% CO₂ with the remainder as N_2 by comparing the relative uptake of CO₂ at 0.15 bar and N_2 at 0.85 bar. This comparison can give a realistic estimation of selectivity for CO₂ from a scenario that closely mimics real application conditions. Determination of selectivity relies on the ideal adsorbed solution

theory (IAST), which is the established model for estimating the relative uptake (or selectivity) by an adsorbent for any two gases in a binary gas mixture.⁶⁸ The selectivity (S) for CO₂ can be derived using the IAST model according to the equation; $S = n(CO_2) p(N_2)/n(N_2) p(CO_2)$, where $n(CO_2)$ is CO₂ uptake at 0.15 bar, $n(N_2)$ is N₂ uptake at 0.85 bar, $p(N_2)$ is 0.85 and $p(CO_2)$ is 0.15. For sample HCC2700 (Figure 5.15), this determination yields a very high selectivity of 132. The selectivity may also be estimated from the ratio of the initial adsorption rates for CO₂ and N₂, which yields a selectivity factor of 38. The overall picture that emerges is that the clovederived carbons are highly selective for CO₂ adsorption under post-combustion capture conditions.

As previously postulated⁷ and confirmed here, the simultaneously attainment of high surface area and high microporosity, which is responsible for the exceptional CO₂ uptake, is possible due to the resistant to activation nature of the ACC and HCC precursors as indicated by their low O/C ratio. The implications of these findings are that the porosity of activated carbons can be predictably tailored by careful choice of the biomass precursor as guided by its elemental composition and in particular the O/C ratio. In essence, knowledge of the O/C ratio of a carbon precursor can embed predictability in the activation process thus making the synthesis of activated carbons more rational rather than being a random process that is based on trial and error or hit and miss.

Table 5.9: Volumetric working capacity, expressed as g l⁻¹ (or cm³ (STP) cm⁻³) for pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) of CO₂ on clove-derived activated carbons compared to benchmark porous materials at ca. 25 °C for a pure CO₂ gas stream and a 20% partial CO₂ pressure flue gas stream. The values in parentheses are the working capacity in cm³ (STP) cm⁻³.

Sample	Density	Pure CO ₂ ^a (g/l o	or cm ³ cm ⁻³)	Flue gas CO_2^{b} (g l ⁻¹ or cm ³ cm ⁻³) Refer		
	(g cm ⁻³)	PSA	VSA	PSA	VSA	
ACC2600	0.92	231 (118)	211 (108)	142 (72)	73 (37)	This work
ACC2700	0.79	257 (131)	202 (103)	139 (71)	66 (34)	This work
ACC2800	0.72	248 (126)	162 (82)	111 (57)	51 (26)	This work
HCC2600	0.98	185 (94)	198 (101)	134 (68)	86 (44)	This work
HCC2700	0.83	238 (121)	223 (114)	153 (78)	84 (43)	This work
HCC2800	0.63	225 (115)	144 (73)	100 (51)	47 (24)	This work
SD2600	0.94	153 (78)	190 (97)	124 (63)	87 (44)	45
SD2600P	0.95	142 (72)	251 (128)	171 (87)	121 (62)	45
SD2650	0.89	149 (76)	180 (92)	121 (62)	74 (38)	45
SD2650P	0.81	143 (73)	213 (108)	143 (73)	86 (44)	45
HKUST-1	0.43	147 (75)	121 (62)	85 (43)	30 (15)	66
Mg-MOF-74	0.41	63 (32)	70 (36)	38 (19)	74 (38)	66
NaX	0.63	44 (22)	78 (40)	50 (26)	69 (35)	67

^a1 bar to 6 bar for PSA; 0.05 bar to 1.5 bar for VSA. ^b0.2 bar to 1.2 bar for PSA; 0.01 bar to 0.3 bar for VSA.



Figure 5.15. Comparison of CO_2 and N_2 uptake at room temperature for sample HCC2700. The CO_2/N_2 adsorption ratio is 22 at 1 bar.

5.5.2 Methane storage

An efficient adsorbent for methane storage should have high surface area and pore volume arising from pore channels of size in the range of 8 to 15 Å, significant microporosity that is ideally above 85% of the total surface area and/or pore volume, with the rest being small mesopores.^{1–7} The present carbons should be ideal candidates to attain high methane storage capacity at moderate to high pressures, particularly given their combination of micro and mesoporosity (Table 5.4) and high surface area density and volumetric surface area. The methane uptake capacity of the carbons was determined at 25 °C and pressures of between 0 and 100 bar. The methane uptake measurements facilitated direct determination of the excess uptake. The total

methane storage capacity was then worked out from the excess data by taking into account the methane density at any given temperature and pressure, and the total pore volume of the activated carbon according to the following equation; $\theta_T = \theta_{Exc} + d_{CH4} \times V_T$, where θ_T is the total methane uptake, θ_{Exc} is the measured excess methane uptake, d_{CH4} is the methane gas density (g cm⁻³) at the prevailing conditions (temperature and pressure) as obtained from the National Institute of Standards and Technology website (http://www.nist.gov/), and V_T is the total pore volume (cm³ g⁻¹) of the activated carbon.

Figure 5.16 shows the excess and total methane uptake isotherms of the CHCCxT carbons, and Table 5.10 summarises the methane storage capacity at 35, 65 and 100 bar. At low pressure, the methane uptake increases sharply with pressure, while a gradual increase occurs in the medium-to-high pressure ranges, and the isotherms are fully reversible. The excess uptake isotherms indicate that the carbons approach saturation at ca. 60 bar. The excess uptake follows the trend in surface area, i.e., CHCC2800 < CHCC4700 < CHCC4800. At 35 bar, the excess uptake is in the range of 10.8 to 12.2 mmol g⁻¹, which increases to between 12.7 and 14.7 mmol g⁻¹ at 65 bar, and rises further to 13.1 – 15.5 mmol g⁻¹ at 100 bar. The excess methane uptake compares favourably with data from previous reports.^{1-7,39,62,69-75} The excess uptake is within a relatively narrow range, which is consistent with the spread of the porosity of the compacted carbons. The total uptake shows a wider range due to the impact of pore volume in its computation and is between 12.8 and 14.8 mmol g^{-1} at 35 bar, 16.0 and 19.8 mmol g^{-1} at 65 bar, and 18.5 to 23.8 mmol q^{-1} at 100 bar. This values translate to $q q^{-1}$ uptake, respectively at 35, 65 and 100 bar, of 0.21, 0.26 and 0.30 for CHCC2800,

0.21, 0.27 and 0.32 for CHCC4700, and 0.24, 0.32 and 0.38 for CHCC4800. It is noteworthy that, at 100 bar, the g g⁻¹ uptake is close to the US DOE target of 0.5 g g⁻¹ especially for sample CHCC4800. Such total gravimetric uptake is impressive and comparable to or surpasses that of the best benchmark materials reported to date.^{1-7,39,62,69-75}



Figure 5.16. Excess and total gravimetric methane uptake of compacted activated carbons at 25 °C.

	Gravimetric methane uptake (mmol g ⁻¹)								
Sample	Excess uptake Total uptake								
	35 bar	65 bar	100 bar	35 bar	65 bar	100 bar			
CHCC2800	11.1	12.7	13.1	12.8	16.0	18.5			
CHCC4700	10.8	12.8	13.5	12.8	16.8	20.0			
CHCC4800	12.2	14.7	15.5	14.8	19.8	23.8			

 Table 5.10: Excess and total gravimetric methane uptake for compacted activated carbons.

However, the amount of methane adsorbed per unit volume is the most important parameter in terms of the key considerations for methane gas storage applications. The packing density of the adsorbent, along with the gravimetric uptake, play a key role in determining the volumetric uptake. An adsorbent with a high packing density allows more of it to be packed into the restricted storage space (e.g. a tank), which effectively drives up the volumetric uptake. The volumetric methane uptake target, set by the US DOE, is 263 cm³ (STP) cm⁻³ at 25 °C and moderate pressure, i.e., 35–100 bar. Figure 5.17 shows the volumetric methane storage isotherms, and Table 5.11 summarises the uptake at various pressures. Interestingly, the volumetric uptake isotherms reveal no saturation at 100 bar, meaning that the present carbons may store greater amounts of methane at pressures higher than 100 bar. This contrasts with what has been observed for most benchmark MOFs, which saturate at ca. 80 bar.^{62,76} We attribute this observation to the contribution of the present carbon's mesoporosity to uptake high pressures, which also enables efficient at and adsorption/desorption kinetics.⁷⁷ All three compacted carbons exhibit

remarkably high volumetric storage capacity (cm³ (STP) cm⁻³) being, respectively, 235, 216 and 193 for CHCC2800, CHCC4700 and CHCC4800, at 35 bar. Such uptake at 35 bar is comparable or higher than has previously been reported for any porous carbon;^{7,78-87} the best uptake to date is 222 cm³ (STP) cm⁻³ for an activated carbon (ACDS4700) derived from aircarbonised date seed.⁷ More generally, the uptake is comparable to the best MOFs reported so far even though the latter's (MOF's) values, which are calculated using crystallographic density, are known be to overestimated.^{1,2,70–75,3–7,39,62,69} It is noteworthy that the uptake of CHCC2800 (235 cm³ (STP) cm⁻³) surpasses that of the best MOF value, i.e., 224 cm³ (STP) cm⁻³ for monoHKUST-1, where experimental packing density has been used. The monolithic monoHKUST-1 has a packing density of 1.06 g cm⁻³ and is claimed to be the current record holder with respect to volumetric methane storage in MOF materials.¹



Figure 5.17. Total volumetric methane uptake of compacted activated carbons at 25 °C.

Table 5.11: Total volumetric methane uptake and working capacity	for
compacted activated carbons.	

	Total v	olumetrio/	c uptake	Worki	Working capacity ^a			
Sample	(0	cm ³ (STP)	cm ⁻³)	(cm ³ (STP) cm ³)				
	35 bar	65 bar	100 bar	35 bar	65 bar	100 bar		
CHCC2800	235	293	339	142	200	246		
CHCC4700	216	282	334	144	210	262		
CHCC4800	193	258	309	132	197	248		

^a The volumetric working capacity is defined as the difference in uptake between the stated pressure (35, 65 or 100 bar) and 5 bar.

At 65 bar, the total methane uptake increases to 293 cm³ (STP) cm⁻³ for CHCC2800, 282 cm³ (STP) cm⁻³ for CHCC4700, and 258 cm³ (STP) cm⁻³ for CHCC4800. There are further increases with pressure such that at 100 bar,

the total methane uptake reaches exceptionally high values of 339 cm³ (STP) cm⁻³ for CHCC2800, 334 cm³ (STP) cm⁻³ for CHCC4700, and 309 cm³ (STP) cm⁻³ for CHCC4800. These volumetric uptake values, which are based on experimentally determined packing density, are by some margin the highest ever reported for any porous materials be they carbons or MOFs.^{1,2,70-75,3-} ^{7,39,62,69} For a clearer picture of the performance of the present carbons, Figure 5.18 shows how they compare with current benchmark MOFs, including HKUST-1, Ni-MOF-74 and PCN-14.^{2-4,88,89} The performance of the current carbons is also compared (Table 5.12) in terms uptake (total volumetric and gravimetric, as g g⁻¹) at 65, 80 and 100 bar to a suite of leading porous materials including Al-soc-MOF-1, MOF-210, NU-1500-Al, NU-1501-Fe and NU-1501-Al, amongst others.^{1,3,7,39,60,73,81,90-92} It is clear from Figure 5.18 that the uptake of the present carbons surpasses that of current benchmark carbons and MOFs. This is despite the use of crystallographic density rather than true packing density in calculating values for powder forms of MOFs. It is now accepted that application of crystallographic density overestimates volumetric uptake for MOFs and envisages an impractical scenario where MOFs are packed as single crystals into storage tanks. In practice the actual packing density of MOFs tends to be much lower than crystallographic density with the consequence that the volumetric uptake values for MOFs in Figure 5.18 (and Table 5.12) are overestimated by between 25 and 50%. Thus a more realistic comparison is presented is where reductions of 25% are applied to the values of powder MOFs (Figure 5.19). Comparison with recently reported monolithic forms of MOFs, namely monoHKUST-1 and monoUiO-66_D,^{1,91} removes the ambiguity arising from the use of crystallographic density. It is clear from Figure 5.18 and 5.19, and

Table 5.12 that the present carbons outperform the monolithic monoHKUST-1 and related monoUiO-66_D, both of which are claimed to be the current MOF record holders for methane storage at 25 °C and pressure of up to 100 bar.^{1,91} Furthermore, the present carbons also have much higher gravimetric uptake, which is almost twice as high compared to monoHKUST-1 and monoUiO-66_D as shown in Table 5.12. The exceptional performance of the present carbons, along with their attractive balance between gravimetric and volumetric uptake justifies the targeted synthesis wherein there is control of both the level of the micro/mesoporosity and the packing density via careful consideration of the O/C ratio of the biomass-derived precursor.





Table 5.8: Methane uptake for compacted activated carbons compared toselected benchmark MOFs and carbons reported in the literature.

Comula	Density	65	bar	80 bar		100 bar		Reference
Sample	(g cm ⁻³)	(g g ⁻¹) (cm ³ cm ⁻³)	(g g ⁻¹) ((g g ⁻¹) (cm ³ cm ⁻³)		(cm ³ cm ⁻³)	
CHCC2800	0.82	0.26	293	0.28	315	0.30	339	This work
CHCC4700	0.75	0.27	282	0.29	306	0.32	334	This work
CHCC4800	0.58	0.32	258	0.35	279	0.38	309	This work
CNL4800	0.67	0.26	241	0.29	269	0.31	291	60
PPYCNL124	0.52	0.30	217	0.33	238	0.36	260	60
PPYCNL214	0.36	0.36	183	0.41	204	0.46	229	60
ACDS4800	0.69	0.25	243	0.27	262	0.29	282	7,60
PPYSD114	0.47	0.32	211	0.35	231	0.39	254	60
AX-21 carbon	0.487	0.30	203	0.33	222	0.35	238	3
HKUST-1	0.881	0.21	263	0.22	272	0.23	281	3
Ni-MOF-74	1.195	0.15	259	0.16	267	0.17	277	3
Al-soc-MOF-1	0.34	0.41	197	0.47	222			70
MOF-210	0.25	0.41	143	0.48	168			71
NU-1500-Al	0.498	0.29	200	0.31	216	0.34	237	39
NU-1501-Fe	0.299	0.40	168	0.46	193	0.52	218	39
NU-1501-Al	0.283	0.41	163	0.48	190	0.54	214	39
monoHKUST-1	1.06	0.17	261	0.18	278	0.18	275	1
monoUiO-66_D	1.05	0.14	210	0.17	245	0.20	296	72

Volumetric uptake of powder MOFs is calculated based on crystallographic density.



Figure 5.19. Total volumetric methane uptake of compacted activated carbons at 25 °C compared to benchmark MOF materials. The uptake of powder MOFs was calculated using crystallographic density and a reduction of 25% was applied to simulate more realistic packing density.

To fully evaluate the performance of the carbons for methane storage applications, it is crucial to consider the amount (gravimetric and volumetric) of CH₄ that can be delivered, which is commonly referred to as the 'working capacity' or 'deliverable capacity'. In this study, the working capacity is taken as the difference between the adsorbing pressure (35 bar or above) and 5 bar as the desorbing pressure. The volumetric working capacity of the present carbons is given in Table 5.11, and Table 5.13 compares their performance to that of a suite of materials. Whilst the present carbons outperform the

current benchmark MOF and carbon materials (Table 5.13), the most relevant comparison is with monoHKUST-1, which is considered to be the current record holder for volumetric methane storage in porous materials and is claimed to be 50% better than any other MOF.¹ The highest deliverable CH₄ at 100 bar uptake pressure is 262 cm³ (STP) cm⁻³) is for sample CHCC4700 compared to 198 cm³ (STP) cm⁻³) and 253 cm³ (STP) cm⁻³) for monoHKUST-1 and monoUiO-66_D, respectively.

Table 5.9: Methane uptake working capacity for compacted activatedcarbons compared to selected benchmark MOFs and carbons reported in
the literature.

	6	5 bar	8	80 bar		0 bar	Reference
Sample	(g g ⁻¹) (cm ³ cm ⁻³)		(g g⁻¹)	(cm ³ cm ⁻³)	(g g ⁻¹)	(cm ³ cm ⁻³)	
CHCC2800	0.18	200	0.20	222	0.22	246	This work
CHCC4700	0.20	210	0.22	234	0.25	262	This work
CHCC4800	0.25	197	0.28	218	0.31	248	This work
CNL4800	0.19	182	0.22	202	0.24	224	60
PPYCNL124	0.23	167	0.26	188	0.29	209	60
PPYCNL214	0.29	146	0.34	167	0.39	192	60
ACDS4800	0.18	171	0.20	189	0.22	209	7,60
PPYSD114	0.25	162	0.28	182	0.32	205	60
AX-21 carbon	0.23	155	0.26	174	0.28	190	3
HKUST-1	0.15	179	0.16	198	0.17	207	3
Ni-MOF-74	0.08	148	0.09	152	0.10	162	3
Al-soc-MOF-1	0.36	176	0.42	201			70
MOF-210	0.38	134	0.45	157			71
NU-1500-Al	0.24	165	0.26	181	0.29	202	39
NU-1501-Fe	0.36	151	0.42	176	0.48	201	39
NU-1501-Al	0.37	147	0.44	174	0.50	198	39
monoHKUST-1	0.12	184	0.13	201	0.13	198	1
_{mono} UiO-66_D	0.11	167	0.14	202	0.17	253	72

5.6 Conclusions

Highly microporous activated carbons were generated from readily-available biomass precursors, cloves (Syzygium aromaticum) via either hydrothermal carbonisation or flash air-carbonisation followed by chemical activation with KOH. Both carbonisation routes yield carbonaceous matter with low O/C ratio and consequently on activation offer advantages with respect to carbon yield and suitable porosity for exceptional performance in CO_2 and CH_4 storage. The resulting activated carbons have high surface area of up to 3175 m² g⁻¹ and pore volume of up to $1.85 \text{ cm}^3 \text{ g}^{-1}$, and depending on activation conditions, present extremely high levels of microporosity of up to 97% of surface area and 92% of the pore volume. The activated carbons can simultaneously display high CO₂ uptake of 5.4 mmol g^{-1} at 1 bar, and 23.7 mmol g⁻¹ at 20 bar and room temperature, which are conditions that mimic post-combustion and pre-combustion CO₂ capture, respectively. Due to their suitably targeted mix of high surface area and pore volume, high packing density, and balance of microporosity-mesoporosity, the activated carbons are also suitable for the storage of methane. Record levels of volumetric methane storage capacity of up to 334 cm³ STP cm⁻³ were achieved at 100 bar and 25 °C, which is considerably higher than all the benchmark materials and surpass the volumetric CH₄ storage target set by the US DOE target (263 cm³ (STP) cm⁻³). Furthermore, they exhibit very high volumetric working capacity of up to 262 cm³ (STP) cm⁻³ for the pressure range of 100 bar (uptake pressure) to 5 bar (desorption pressure), and 25 °C. This work demonstrates that activated carbons can be predictably synthesised, based on the O/C ratio of biomass-derived activateable carbonaceous matter, in a

manner that deliberately targets porosity that is suitable for exceptional CO_2 and CH_4 storage.

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6.1 Abstract

A series of nitrogen-doped porous carbons were prepared from cloves (Syzygium aromaticum) and explored as adsorbents for CO₂ capture. The samples were synthesised using KOH or $K_2C_2O_4$ (PO) as activating agent. It was found that nitrogen doping promoted porosity development for both activating agents. Ultra-high surface area of up to 3430 m² g⁻¹ with a large pore volume of up to 2.37 cm³ g⁻¹ and bimodal porosity in the microppore and small mesopore range were obtained by KOH activation, while PO activation generated carbons with surface area and pore volume of up to 2641 $m^2 g^{-1}$ and 1.45 cm³ g⁻¹, respectively. The resulting N-doped carbons have attractive CO₂ capture performance of up to 1.5 mmol g⁻¹ and 4.7 mmol g⁻¹ at 25 °C and a pressure of 0.15 and 1 bar, respectively, which are pertinent to CO₂ capture from flue gas streams at ambient pressure or below. The high CO₂ capture capabilities at low pressures are among the highest reported for N-doped carbons, and can be ascribed to high levels of microporosity desite the overall high porosity. At 20 bar, samples with high surface area displayed the highest CO₂ uptake capacity of up to 24.9 mmol g^{-1} at 25 °C. Consequently, the porosity of the carbons may be directed towards either low pressure (post-combustion) or medium-to-high pressure (pre-combustion) CO₂ storage. Although N-doping may be beneficial for CO₂ uptake, the more critical factor is the porosity.

6.2 Introduction

Over recent decades, studies in sustainable energy have become a popular research field due to the worldwide energy deficit and growing awareness of the need for sustainable and environmentally friendly energy sources. Therefore, stabilising or reducing greenhouse gas levels in the atmosphere before permanent damage occurs to the climate system is critical. Considering the current energy situation, large-scale implementation of carbon capture and storage technologies is required to achieve the required reduction in greenhouse gas emissions, which are the primary contributor to climate change.¹⁻³ Among the developed technologies/processes for CO₂ capture and storage, physical adsorption of CO₂ utilising porous carbons as adsorbents is seen as a possible alternative technology to the traditional amine-based liquid phase absorption technique, since it requires less energy for adsorbent regeneration, is inexpensive and is more ecologically friendly.⁴⁻ ⁷ Porous carbon materials, as represented by activated carbons (ACs), are significantly showing a promising ability as catalyst carrier,^{8,9} energy production,^{10,11} and CO₂ capture or gas storage,^{5,12-14} besides environmental remediation^{15,16} because of their lower cost, readily available, good chemical, mechanical, and thermal stability, and their tuneable pore size and porosity.¹⁷⁻²³ One of the most appealing aspects of porous carbons is that their 'green' credentials can be improved if they are synthesised from sustainable resources. Given the wide range of porous carbon applications, using renewable materials to generate such materials would be even more beneficial in terms of economic, environmental, and societal concerns.^{20,24,25} As a renewable resource, biomass has been extensively employed to synthesise carbonaceous materials because of its abundance, cheap,

environmentally favourable and sustainable precursors, and they are used as gas adsorbents with high surface areas, complex pore structures and promising gas adsorption capacity.^{3,19,33,24,26-32}

Activated carbons can be generated by chemical or physical activation approaches. Chemical activation of carbon sources with KOH is gaining interest as a simple and effective choice for producing highly porous carbons with a high surface area (> 2000 $m^2 q^{-1}$), along with a relatively wellcontrolled PSD.^{4,21} The porosity, typically within the micro-supermicropore domain, can be controlled by varying the amount of KOH used and the activation temperature.^{4,21} It has also recently been demonstrated that by adding nitrogen sources such as melamine to the KOH and biomass mixture, the PSD can be extended into the mesopore region, resulting in hierarchical carbons that increase the possibility of using KOH-derived activated carbons in other applications such as high-pressure gas storage, adsorption of biomolecules, or ionic liquid-based supercapacitors where larger pores are required.^{24,34} Although KOH has favourable properties for the generation of advanced porous carbons, its large-scale industrial application as an activating agent is hindered by the fact that KOH-activation needs a relatively high temperature (> 600 °C) to function, which is not energy efficient.

Furthermore, KOH is corrosive, and its corrosiveness increases considerably with temperature.^{24,35-37}. In addition, most highly carbonaceous materials were prepared by using a KOH/carbon precursor ratio of nearly 4-6.^{35,38,39} Thus, the pursuit of more ecologically friendly methods to synthesise porous carbons by using less KOH amounts and less corrosive activating chemicals or procedures is a top priority in porous carbon preparation. Among the potential candidates, potassium oxalate (PO) is a good option as it is a less

corrosive and less toxic activating agent.^{4,27,40} Sevilla and Fuertes⁴¹ observed that using biomass products with potassium oxalate and melamine can be produced high surface area porous carbons (of up to 3000 m² g⁻¹) that match the electrochemical performance of KOH-ACs in conventional electrolytes and ionic liquids.⁴² Along the same lines, Schneidermann *et al.*⁴³ reported the synthesis of N-doped nanoporous carbons with a high surface area (ca. 3000 m² g⁻¹) by using lignin as a carbon precursor, K₂CO₃ as an activating agent and urea as a nitrogen source.

Based on this context, the heteroatom (S, N, O, P, etc.) doping can significantly increase the surface area and control the pore size distribution, enhancing gas storage capacity.^{44,45} Generally, nitrogen-doped carbons can be carried out using two strategies. One is the post-treatment of porous carbon with N-rich substances such as ammonia, amines or urea at high temperatures to introduce nitrogen functional groups on its surface, 1,25,46-48 while another is in situ (direct) doping using natural N-containing precursors, which can achieve homogeneous incorporation of nitrogen into the carbon material with controlled chemistry.^{1,25,46,49-51} The first strategy, on the other hand, tends to block pore structures and causes severe CO₂ uptake recession. It is also very tedious, expensive, and time-consuming.⁵² In contrast, Tan et al.⁵³ reported that in situ doping is more practicable and feasible since it's a simple synthesis that does not require multi-step treatment and high nitrogen content,¹ as well as it permits for a homogeneous distribution of nitrogen atoms and is more commercially viable, especially for future advancements in supercapacitor production.⁵⁴ Additionally, due to the nitrogen heteroatom derived from the precursors, the structure and functionalities of the synthesised materials will be more stable, resulting in excellent cycling

stability.⁵⁵ In-situ nitrogen doping can be applied in two different ways: (a) carbonisation of carbon precursors mixed with nitridation agents such as melamine or urea, and (b) utilisation of rich-nitrogen precursors including etc.⁴⁶ In melamine polyaniline, the context resin, of nitrogen functionalisation, urea has been expansively employed as a nitrogen source because of its high nitrogen content (> 46%), non-toxicity, low cost and environmentally inertness.^{46,56} The use of urea as a nitrogen source can improve the textural properties and assist in nitrogen doping by introducing a large amount of N groups into the porous carbon framework.^{2,45} As documented, urea decomposition upon thermal heating produces NH₃, biuret, cyanuric acid and various polymeric substances. The NH₃ generated during the urea decomposition acts as a key nitrogen donor.^{45,46,57–59} At high treatment temperatures, the nitrogen-containing radicals (such as NH and NH₂) formed by NH₃ could react with the carbon radicals and/or replace the oxygen-containing groups on the surface of carbons with nitrogen-containing groups. The resulting N-doped carbon has a significant amount of narrow micropores, which is attractive for gas capture. 45,46,57-59

Recently, much attention has been devoted to preparing N-doped carbons from biomass due to their sustainability, availability, and environmental friendliness. For instance, Tian *et al.*⁶⁰ synthesised N-doped porous carbons using enteromorpha prolifera as a precursor and demonstrated superior CO₂ adsorption performance. Rao *et al.*³ reported the one-step synthesis of nitrogen-doped porous carbon from water chestnut shell; carbons exhibit high CO₂ uptake of up to 4.5 mmol g⁻¹ at 25 °C and 1 bar. Wei *et al.*⁶¹ also synthesised N-doped carbons by KOH-activation of water chestnut shell as a carbon precursor and melamine as a nitrogen source. The obtained N-doped

carbons showed CO₂ adsorption capacities of up to 6.0 mmol g⁻¹ (at 0 °C and 1 bar) and 4.7 mmol g⁻¹ (at 25 °C and 1 bar). By carefully selecting the synthesis conditions, biomass-derived N-doped carbons can produce well-developed pore texture and N content, enhancing their positive impact on CO_2 capture.

This chapter reports the effective nitrogen doping strategy for preparing Ndoped carbons from biomass material as a carbon precursor and urea as a nitrogen source. As typical biomass, clove is widely available and is an encouraging precursor for preparing carbons with excellent physical proprieties, as reported in the previous chapter. This work also explores the effects of using a less corrosive and less toxic activating agent, i.e., potassium oxalate (PO), along with potassium hydroxide (KHP), on the porosity and the consequences for gas storage applications. The resulting N-doped carbons possess an ultra-high surface area of 3435 m² g⁻¹ and large pore volume of 2.37 cm³ g⁻¹, along with superior gas uptake performance in both low pressure (post-combustion) and medium-to-high pressure (pre-combustion) conditions demonstrating that both porosity properties and nitrogen doping influence CO₂ uptake, with the former being the decisive factor.
6.3 Expermental section

6.3.1 Synthesis of nitrogen-doped carbons

Air carbonisation: 2 g of the cloves (*Syzygium aromaticum*) were placed in an alumina boat and heated in a horizontal tube furnace to 400 °C under a nitrogen atmosphere at a heating ramp rate of 10 °C min⁻¹. Once at 400 °C, the cloves were briefly (5-10 min) exposed to a flow of air, after which the furnace was left to cool under a nitrogen flow. Then, the carbon product that is donated as (ACC) was doped with urea, as described below.

Urea treatment: the carbon product (ACC) was physically mixed with urea at a urea/carbon weight ratio of 1. The resulting mixture was crushed into a homogeneous powder in an agate mortar, then thermally treated under air flow (ca. 40 - 70 cm³ min⁻¹) at 350 °C, and a heating ramp rate of 10 °C min⁻¹ for 3 h. The furnace was then allowed to cool under a flow of air. The resulting product was washed thoroughly with hot deionised water to neutralise the pH and dried at 100 °C for 24 h. Then, the N-doped carbon that is named as (NAC-350) was chemically activated as described below.

Chemical activation: a potassium-based activating agent was added to the resulting N-doped carbon (NAC-350) and thoroughly mixed at a KOH/carbon ratio of 2. The resulting mixture was placed in a ceramic boat and inserted inside a tubular furnace and heated at a ramp rate of 3 °C min⁻¹ to 600–900 °C under nitrogen flow. The furnace was held at the final temperature for 1 h, and then the sample was left to cool under an atmosphere of nitrogen. The resultant activated carbons were stirred in 20% aqueous HCl at room temperature, and then washed with distilled water to neutral pH, and dried in an oven at 100 °C.

The N-doped carbons activated with KOH were labelled as NACPH-X, while the carbons activated with PO were labelled as NACPO-X, where X is the activation temperature.

6.3.2 Material charachterisation

Elemental, CHN, analysis was performed on an Exeter Analytical CE-440 Elemental Analyser. A PANalytical X'Pert PRO diffractometer was used to perform powder XRD analysis using Cu-K α light source (40 kV, 40 mA) with step size of 0.02° and 50 s time step. Nitrogen sorption isotherms and textural properties of the carbons were determined at -196 °C using a Micromeritics 3FLEX sorptometer. Before analysis, the samples were evacuated for 16 h at 200 °C under vacuum. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method applied to adsorption data in the relative pressure (P/P_o) range of 0.02 – 0.22, and pore volume was estimated from the total nitrogen uptake at close to saturation pressure ($P/P_o \approx 0.99$). Micropore surface area and micropore volume were obtained via t-plot analysis. The pore size distribution (PSD) was determined using a Non-local density functional theory (NL-DFT) model using nitrogen adsorption data. Xray photoelectron spectroscopy (XPS) was carried out using on a Specs spectrometer, using Mg K α (1253.6 eV) radiation from a double anode at 50 W. Binding energies for the high-resolution spectra were calibrated by setting C 1s to 284.6 eV. Data analysis was carried out using CASAXPS software with Kratos sensitivity factors to determine atomic % values from the peak areas. Scanning electron microscopy (SEM) images were recorded using an FEI Quanta200 microscope, operating at a 5 kV accelerating voltage.

6.3.3 CO₂ uptake measurements

 CO_2 uptake was investigated in the pressure range 0–20 bar at room temperature using a Hiden Isochema Intelligent Gravimetric Analyser (IGA-003). Prior to CO_2 uptake determination, the carbons were outgassed at a high temperature of up to 240 °C and at a ramp rate of 5 °C/min for several hours.

6.4 Results and discussion

6.4.1 The yield and elemental composition of N-doped carbons

The yields of urea, raw clove and N-doped carbons are summarised in Table 6.1. Product yield is an important factor to consider from an industrial standpoint.⁴¹ This is particularly the case when harmful and corrosive substances such as KOH are used. As shown in the table, there is a significant enhancement in the yield for the samples obtained via PO activation compared to those activated with KOH. The yields of N-doped carbons activated with KOH vary from 10 to 30 wt%, depending on the activation conditions. However, the yields obtained via PO activation are between 21 and 58 wt%, which is higher than what has been obtained by KOH activation. In this respect, using PO as the activating agent instead of KOH nearly doubles the yield (Table 6.1), which indicates a crucial economic feature in using a less corrosive and toxic activating agent to produce the same or more amount of product obtained by KOH.⁴¹ In addition, lower activation temperatures lead to higher carbon yield, such that samples prepared at 600 °C have twice the yield of samples activated at 900 °C. Increasing the

activation temperatures generally decreases the overall yield of activated carbons.

Sample	Yield [%]	C [%]	H [%]	N [%]	0 [%]	(0/C)*
Urea	_	20.0	6.7	46.2	27.1	1.01
Clove	-	49.7	5.9	0.9	43.5	0.66
ACC	-	66.1	4.3	1.9	27.8	0.31
NAC-350	-	65.9	2.2	11.7	20.2	0.23
NACPH-600	30	66.8	2.2	2.4	28.7	0.32
NACPH-700	21	82.5	1.1	2.3	14.1	0.13
NACPH-800	15	86.9	0.6	1.1	11.4	0.10
NACPH-900	10	90.7	0.0	0.4	8.9	0.07
NACPO-600) 58	71.4	2.3	3.2	23.1	0.24
NACPO-700	40	85.6	0.3	1.7	12.4	0.11
NACPO-800	32	92.4	0.1	0.6	6.9	0.06
NACPO-900	21	88.6	0.1	0.2	11.1	0.09

Table 6.1: Yield and elemental composition of urea, raw clove, aircarbonised clove (ACC), N-doped carbon at 350 °C and representatives Ndoped carbons.

*Atomic ratio

The chemical composition of the carbons was determined by elemental analysis, and the results are presented in Table 6.1, suggesting the successful incorporation of the heteroatoms. As shown, the carbon content increases following the air carbonisation process, from 49.7% for the clove to 66.3% for the air carbonised clove. Activation of both sets of samples increases the C content, with the increase being generally more significant at higher

temperatures (900 °C). On the other hand, H content reduces as the activation temperature increases, while O content decreases significantly from 43.5% (raw clove) to 6.9% for N-doped activated carbons. Cloves have a relatively low nitrogen content of 0.86%. After urea doping, nitrogen content increases to 11.74% for NAC-350. Upon further chemical activation, the amount of nitrogen in N-doped activated samples evidently changes with rising activation temperatures, in which some thermally unstable nitrogen species are decomposed/consumed during the chemical activation process.^{37,62,63} It is worth mentioning that the decomposition/incorporation of nitrogen species results in the generation of additional pores over the carbon surface, further enhancing porosity. Moreover, the samples have a maximum nitrogen content of \sim 3% at a lower activation temperature of 600 °C. However, an increase in the activation temperature causes a drop in nitrogen content, indicating that the N-groups are unstable at high temperatures.³⁶

The elemental composition of raw clove shows a low O/C atomic ratio of 0.66 with respect to many other biomass sources, for which the ratio is in the range of 0.75 to 1.0.^{19,64-67} The changes in the elemental composition reduced the atomic O/C ratio from 0.66 for the raw clove to 0.06 for N-doped activated carbons. This reduction is expected because the O/C ratio of the row clove is already low. The O/C ratio of 0.06 for the N-doped carbons is the lowest reported for porous carbon materials derived from biomass and other sources,^{19,64-67} which justifies the appropriate process parameters and conditions. It is noteworthy that the elemental composition of these carbons is comparable to that of air carbonised date seeds and sawdust.^{64,65} In general, the elemental composition of N-doped carbons indicates that air

carbonisation of biomass produces rich-carbon porous materials but with relatively low O and N amounts.

6.4.2 Structural ordering of N-doped carbons

The structure of the N-doped carbons was investigated using XRD analysis. The XRD patterns of of the raw clove, N-doped carbon (NAC-350) and both sets of N-doped activated carbons presented in Fig. 6.1, which show no traces of inorganic compounds, proving that they are entirely eliminated by acid washing. The XRD patterns of all the N-doped carbons exhibit two broad and low-intensity peaks at $2\theta = 22^{\circ}$ and 44° , typically attributed, respectively, to the (002)and (100)peaks of diffractions from graphitic domains.^{4,27,35,51,64,66,67} As observed, there is a shift in the prominent peak towards a lower angle and a decrease in the intensity of the peak after chemical activation, suggesting an increase in the d spacing. An increment in the *d*-spacing implies the addition of nitrogen and oxygen.⁶⁸ The general flattening and broadening of the $2\theta = 22^{\circ}$ peak from 600 °C to 900 °C support the proposed amorphous structure of the porous carbons that become more irregular and less graphitic as activation temperature increases.^{19,66} However, at higher temperatures, the intensity of the (100) diffraction peak slightly increases, indicating that increased temperature creates several graphitic layers.⁶¹ Generally, samples obtained by KOH activation show much broader and weaker diffraction peaks than those activated with PO, which demonstrates that KOH activation causes much more turbulent carbon structural.52



Figure 6.1: XRD patterns of (A) raw clove and N-doped carbon (NAC-350) (B) N-doped carbons prepared by KOH activation and (C) carbons obtained by PO activation.

6.4.3 **Porosity and textural properties**

The nitrogen sorption isotherms and the corresponding pore size distribution (PSD) curves of both sets of N-doped carbons are shown in Fig. 6.2 and Fig. 6.3.

The N-doped carbons activated with KOH (Fig. 6.2) show type I isotherms, indicating expected adsorption behaviour of the а microporous structure,^{19,24,27,69} except for samples activated at 900 °C. High adsorption was observed at low relative pressure ($P/P_{o} < 0.01$), which suggests the existence of plenty of micropores, and no substantial adsorption takes place at P/P_o greater than 0.1, except for samples activated at 900 °C. At an activation temperature of 800 °C, a slight widening of the adsorption knee in the isotherms has been observed, which denotes limited broadening in the pore size distribution.²⁷ However, there is an evident widening in the knee for samples prepared at 900 °C, showing a nearly linear increase in adsorption up to a P/P_{\circ} of 0.4, suggesting the presence of larger micropores and a significant proportion of mesopores.²⁷ In addition, samples activated at a very high temperature (900 °C) exhibit a type IV isotherm with a slight hysteresis loop at a medium P/P_o range, demonstrating capillary condensation phenomena, which is known to take place in mesoporous materials.^{11,70}



Figure 6.2: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of N-doped carbons prepared by KOH activation.

Sample	surface area ^a	Pore Volume ^b	Pore size
	m² g ⁻¹	cm ³ g ⁻¹	Å
NACPH-600	2753 (2167)	1.28 (0.84)	5/8/10/12/14/18
NACPH-700	3118 (2043)	1.46 (0.79)	5/8/10/11/15/20
NACPH-800	3363 (963)	1.69 (0.34)	5/8/11/15/21
NACPH-900	3435 (817)	2.37 (0.36)	5/7/11/15/27/34
NACPO-600	1072 (949)	0.45 (0.37)	5/7/8/11
NACPO-700	1842 (1307)	0.86 (0.52)	5/7/11/14/20
NACPO-800	2641 (1518)	1.26 (0.61)	5/7/9/11/14/21/27
NACPO-900	2547 (703)	1.45 (0.28)	5/7/11/14/21/27/34

Table 6.2: Textural properties of N-doped carbons prepared by KOH and POactivation.

The values in parenthesis refer to: ^a micropore surface area and ^b micropore volume.

As shown in Table 6.2, increasing activation temperatures increases the surface area and pore volume of carbons activated with KOH. This series of N-doped carbons show a surface area ranging from 2753 to 3435 m² g⁻¹, and a pore volume in the range of 1.28–2.37 cm³ g⁻¹, with the micropore volume representing 66% of the total pore volume. Generally, the high surface area and pore volume of N-doped carbons support the previous findings that the introduction of the N groups via urea treatment followed by KOH activation results in a significant pore structure development through reaction with N groups and the promotion of KOH penetration into the deeper layers of the sample structure.^{62,68,71} Sample NACPH-900 was expected to show a lower surface area than NACPH-800, due to the collapse of the structure. However, the former offers a higher than expected surface area, indicating that the thermal decomposition of intermolecular forces has no affected the overall surface area of sample NACPH-900.

In contrast, the micropore surface area and pore volume decrease as the activation temperature rise. Correspondingly, the pore size distribution (PSD) curves in Fig. 6.2B show that the micropores dominate the samples prepared by KOH activation at 600 °C and 700 °C with a wider pore size centred at ca. 20 Å (Table 6.2), while sample prepared at 800 °C is still dominated by micropores but with a small proportion of mesopores centred at 21 Å. With a further rise in the activation temperature, the sample displays a broadening pore size distribution with a significant proportion of 34 Å pores. The larger pores present in the samples activated at higher temperatures can be ascribed to a higher level of activation caused by greater gasification.^{4,19,27}

For samples activated with PO, the nitrogen sorption isotherms and the corresponding pore size distribution (PSD) curves are shown in Fig. 6.3, and

the textural properties are summarised in Table 6.2. The isotherms of all the N-doped carbons are type I, reflecting the presence of microporous solids.^{19,24,27,69} The isotherms of samples activated at 600 and 700 °C exhibit a sharp adsorption knee at relatively low pressure $P/P_0 = 0.1$, suggesting the presence of abundant micropores.¹ The isotherm of a sample activated at 800 °C displays a gentle adsorption knee, whereas the isotherm of a sample activated at 900 °C exhibits a wide adsorption knee with a nearly linear increase in adsorption up to a P/P_0 of 0.4, indicating the presence of significant mesoporosity.²⁷



Figure 6.3: Nitrogen sorption isotherms (A) and corresponding pore size distribution curves (B) of N-doped carbons prepared by PO activation.

In terms of textural properties (Table 6.2), samples activated at temperatures between 600 and 800 °C show surface areas in the 1072-2641 m² g⁻¹ range and pore volumes of 0.45-1.26 cm³ g⁻¹. A further increase in the activation

temperature slightly decreases the surface area by up to 2547 m² g⁻¹, which is ascribed to the strengthening of the activation process at a very high temperature (900 °C); the sample pore structure is destroyed and PSD becomes wide, resulting in a reduction in surface area.⁶¹ However, increasing the activation temperature to 900 °C, considerably enhances the pore volume by up to 1.45 cm³ g⁻¹ and causes a pore size enlargement due to the progressive gasification of carbon by the CO₂ evolved from K₂CO₃ decomposition, as the following reactions:^{4,27}

 Decomposition of potassium oxalate at temperatures ranging from 500-600 °C:

$$K_2C_2O_4 \rightarrow K_2CO_3 + CO$$

2) The redox reaction between the C and the generated potassium carbonate occurs at a temperature of up to 700 °C, resulting in C atoms etching (i.e., pore formation) according to the following reaction:

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

3) At a temperature above 800 °C, slow partial decomposition of potassium carbonate takes place according to the following reaction:

$$K_2CO_3 \rightarrow K_2O \,+\, CO_2$$

The gases produced by carbonate decomposition cause the pore formation via partial carbon gasification at a temperature above 800°C, along with the following reaction:

$$C + CO_2 \rightarrow 2CO$$

Moreover, a decrease in the proportion of micropore surface area and pore volume has been noticed with increasing activation temperatures. Fig. 6.3B

presents the pore size distributions (PSDs) of carbons prepared by PO activation, and Table 6.2 summarises the pore size maxima values. The samples activated at 600 and 700 C show pore sizes in the range of 5-20 Å, whereas the pore size system for sample NACPO-800 is slightly larger and centred at 20 Å and above. At the highest activation temperature of 900 °C, the PSD of sample NACPO-900 displays a significant proportion of mesopores of size 34 Å, corresponding with the expected effects of activation temperature.

The effect of the urea treatment or nitrogen content on the pore structure formation is inferred by PSDs. In case the nitrogen content is decreased, the PSDs exhibit a broader pore size distribution, the proportion of large micropores is increased and small mesopores are newly generated. For example, samples having high nitrogen content are mainly micropores and the pore diameter is concentrated at 20 Å. However, samples with very low nitrogen content show wide PSDs larger than 20 Å (Table 6.2). This could be because the carbon reacts with urea decomposition products at high temperatures, etching carbon fragments and forming large pores. Considering the low activation temperatures, however, nitrogen species might create steric hindrances and partially block the small pores. Therefore, the nitrogen content has a significant and far-reaching impact on the PSDs of the resulting samples.^{18,72-74}

Overall, the surface area of the N-doped carbons obtained by KOH activation is higher than that of PO activation, indicating the KOH treatment's role in enhancing the surface area. The surface area and the pore volume of the samples remarkably increased at high activation temperature (800 °C),

regardless of the activating agent used. This improvement in textural properties is due to the decrease in N, H, and O content (Table 6.1), which creates porous carbon samples with a large surface area and high porosity.²⁰ Moreover, potassium oxalate, a less corrosive and less toxic activating agent, can offer porosity control by simply adjusting the activation temperature. The ability to tailor the pore size of porous carbons is one of the challenges to the widespread use of carbons in energy-related applications.²⁷ Interestingly, the activation temperature is an essential factor in determining the textural properties of the activated carbons.^{22,27}

6.4.4 Nature of nitrogen in N-doped carbons

X-ray photoelectron spectroscopy (XPS) was used to characterise the chemical nitrogen state in the N-doped carbons. Figure 6.4 shows the XPS spectra of the N 1s of the selected carbon samples.

Combined with the data in Table 6.1, the clove has a low nitrogen content (0.86%). Upon urea treatment, the amount of nitrogen in sample NAC-350 increased to 11.74%. N-doping has accomplished during the urea treatment through chemical reactions of the urea with surface functional groups and subsequent heat conversions, resulting in N integration into the graphite lattice.⁶² These N atoms are probably presented on the edges as shown in Fig. 6.4; the N 1s XPS spectra of the samples depict three individual peaks with the binding energies centred at 398.7, 400.1 and 401.5 eV (1 eV = 1.602×10^{-19} J), consistent with pyridinic (N-6), pyrrolic/pyridine (N-5) and quaternary nitrogen species (N-Q), respectively. The forms of amine, N-5 and N-6 are usually presented at the initial stage of pyrolysis and then transformed to N-Q at higher temperatures. After KOH activation, the

nitrogen content reduces to 0.35% with increasing activation temperature because most nitrogen functionality is destroyed at high temperatures.^{62,75,76} Indeed, the doped nitrogen from urea is reported primarily as N-5 and N-6 species, with the proportion of N-5 becoming more significant at temperatures above 400 °C. This is because N-6 is more stable than N-5, and N-5 can be converted into N-6 and N-Q at high temperatures.^{77,78} Accordingly, the dominant nitrogen form at high temperatures is N-Q since it has the best stability⁷⁹, and the heat treatment favours the graphitisation process and the formation of N-Q species in the interior of the graphene layers.^{72,80}

Noticeably, the N-5 content is higher than that of N-6 in all carbon samples, consistent with previous reports stating that N-5 is the dominant N-containing species after KOH activation.^{52,81,82} It should be noted that the high percentage of N-5 form in the samples would be favourable for capturing CO_2 since N-5 significantly contributes to CO_2 capture more than other nitrogen species forms.^{1,37,45}



Figure 6.4: XPS spectra of the N-doped carbons obtained by KOH activation.

6.4.5 Morphology of N-doped carbons

Scanning electron microscopy (SEM) was employed to monitor the changes in the morphology of the raw cloves following air carbonisation, urea treatment and chemical activation. The SEM images of the clove, air carbonised clove and representative N-doped carbons are shown in Fig. 6.5, Fig. 6.6 and Fig. 6.7. As shown in Fig. 6.5, cloves have a bulky morphology with a tight surface without obvious porous structures. After air carbonisation, cavities or cracks can be found on the external surface of the ACC sample. Further urea treatment, a similar morphology as that of ACC appears to be retained, with a smooth surface and small particle sizes. After KOH activation, the morphology of N-doped carbons (Fig. 6.6) essentially consists of particles with relatively smooth surfaces, distinguished by the presence of randomly distributed craters and pores, which may have resulted from potassium leaching during the activation process.²⁰ This morphology is similar to that of carbons previously reported.^{65,67} Conversely, after PO activation (Fig. 6.7), the morphology of the original particles is transformed; the surface becomes rough, and the particle size turns into larger and looser ones. The ability to retain the original morphology after activation represents a potential advantage for KOH.⁴² Regardless of the activating agent used, broadening of the pore distribution has been observed as increasing the activation temperatures, which can be ascribed to the precursor gasification by CO_2 evolved during the decomposition of K₂CO₃.²⁰



Figure 6.5: The morphology of raw clove, air-carbonised clove (ACC) and N-doped carbon at 350 °C (NAC-350).



Figure 6.6: The morphology of N-doped carbons prepared by KOH activation.



Figure 6.7: The morphology of N-doped carbons prepared by PO activation.

6.4.6 CO₂ uptake of N-doped carbons

The CO₂ uptake capacity was measured at a pressure range of 0–20 bar and ambient temperature (25 °C). The CO₂ uptake isotherms of N-doped carbons prepared by KOH activation are presented in Figure 6.8, and the corresponding uptake at various pressures (0.15, 1 and 20 bar) is given in Table 6.3.

At 1 bar, the conditions relevant to post-combustion CO₂ capture,²⁷ samples with a PSD mostly centred below 20 Å have large CO_2 uptakes in the range of 3.7–4.0 mmol g⁻¹, where sample NACPH-700 shows the highest capacity. The CO₂ uptake slightly increases from 3.7 mmol q^{-1} for the sample prepared at 600 °C to 4.0 mmol g⁻¹ for the sample prepared at 700 °C, and then decreases to 2.4 mmol g⁻¹ for the sample NACPH-900. According to the uptake data, the total surface area does not determine the CO₂ uptake capacity at low pressure and 25 °C; however, the pore diameter is a key determinant.⁷¹ This trend agrees with previous reports that the CO₂ uptake at low pressure is determined by the preponderance of micropores.^{27,81} In addition, the N-doped carbons (NACPH-600 and NACPH-700) that store high CO₂ at low pressure, have N content of up to 2.36%, and their pyrrolic N content is higher than those of the other samples. This suggests that the amount of N may also affect the CO₂ uptake at low pressure because N doping can significantly improve the surface polarity of the carbons,⁸³ and pyrrolic N typically has much greater contribution to CO₂ capture.⁸² The CO₂ uptake capacity of 4.0 mmol g⁻¹ at 25 °C and 1 bar is competitive compared to many biomass-derived carbon materials, MOFs and ZIFs. For example, Wang et al.⁸⁴ reported that corncob-derived activated carbons adsorbed 3.56 mmol g⁻¹ of CO₂ at 28 °C and 1 bar. Sevilla and colleagues reported biomass-derived

porous carbons with CO₂ uptake capacity of 3.50 mmol g⁻¹ at 25 °C and 1 bar.²⁸ Under the same condition, Xia *et al*.⁸⁵ synthesised zeolite-template nitrogen-doped carbons with a CO₂ adsorption capacity of 3.86 mmol g⁻¹. Some COFs and MOFs have CO₂ uptake of less than 3.0 mmol g⁻¹ at 25 °C and 1 bar.^{86,87}



Figure 6.8: CO₂ uptake isotherms at 25 °C of N-doped carbons prepared by KOH activation.

Sample	CO ₂ up	CO ₂ uptake (mmol g ⁻¹)			
	0.15 bar	1 bar	20 bar		
NACPH-600	0.9	3.7	15.5		
NACPH-700	0.8	4.0	22.8		
NACPH-800	0.6	3.3	24.9		
NACPH-900	0.4	2.4	21.0		

Table 6.3: CO2 uptake at 25 °C of N-doped carbons prepared by KOHactivation.

A similar trend can be observed at lower pressure of 0.15 bar, where the sample with the largest surface area gives the lowest CO₂ uptake capacity, demonstrating the critical importance of pore size. Nevertheless, the trend is reversed at a pressure of 20 bar, which are conditions relevant to precombustion CO₂ capture, where the highest uptake of 24.9 mmol g⁻¹ is for the sample having the highest surface area. This is in line with the fact that the CO₂ uptake at high pressure is determined by the total surface area rather than the pore size.²⁷ The uptake of 24.9 mmol g⁻¹ at 20 bar is at the high end of what has previously been reported for carbon materials.^{78,88-92} As shown in Fig. 6.8, the isotherms of the samples exhibit fine reversibility with no hysteresis, and no saturation in the pressure range of 0-20 bar, except for sample NACPH-600, indicating that a greater amount of CO₂ can potentially store at very high pressure.

The CO₂ uptake of PO activated samples (Figure 6.9 and Table 7.4) show excellent CO₂ capture capacities ranging from 3.1 to 4.7 mmol g^{-1} at 25 °C and 1 bar. The CO₂ uptake of these samples is higher than most known N-

doped porous carbons. For instance, Ma *et al.*¹ synthesised nitrogen-doped porous carbons with HNO₃ and achieved a CO₂ adsorption capacity of up to 4.3 mmol g⁻¹ at 25 °C and 1 bar. Sevilla *et al.*⁹³ reported a CO₂ uptake of 4.4 mmol g⁻¹ for biomass-derived N-doped carbons. Xing et al.⁹⁴ prepared Ndoped carbons that adsorbed 4.24 mmol g⁻¹ at 25 °C and 1 bar. The CO₂ uptake of the PO activated carbons, at 0.15 bar, is between 0.7 and 1.5 mmol q^{-1} , with the highest CO₂ uptake being for sample NACPO-600, whereas sample NACPO-900 shows the lowest uptake despite having a large surface area. The uptake of 1.5 mmol g⁻¹ at 0.15 bar is competitive compared to the highest reported uptakes to date^{19,22,27,28,81,83,85,91,93} and correlates well with the high microporosity of the present samples. However, the carbons with a high surface area display the highest CO₂ uptake of 19.5 mmol g⁻¹ at 20 bar, indicating the CO_2 uptake correlates with the total surface area at high pressure. Importantly, all the samples, except NACPO-600, are far from saturation at 20 bar, indicating much more uptake can be adsorbed at higher pressures.



Figure 6.9: CO₂ uptake isotherms at 25 °C of N-doped carbons prepared by PO activation.

Sample	CO ₂ u	CO ₂ uptake (mmol g ⁻¹)	
	0.15 bar	1 bar	20 bar
NACPO-600	1.5	4	8.5
NACPO-700	1.4	4.7	15
NACPO-800	0.8	3.8	18.8
NACPO-900	0.7	3.1	19.5

Table 6.4: CO ₂ uptake at 25 °C of N-doped carbons prepared by PO
activation.

Upon comparison of potassium-based activating agents, KOH and PO, it can be seen that the N-doped carbons prepared by PO activation show better CO₂ uptake at low pressure (0.15 and 1 bar), which highlights the advantage of using a less corrosive and toxic activating agent in generating high surface areas and optimising their PSDs. In general, activation temperature has a pronounced influence on CO₂ adsorption at high pressure, suggesting that activation temperature can be used to tailor or optimise the textural properties of porous carbons for energy-related applications.⁷⁶ Furthermore, samples with higher N content show better CO₂ uptake at low pressure. Overall, the uptake capacity of N-doped carbons prepared by either KOH or PO activation is impressive because the samples perform well at low pressure (post-combustion) and medium-to-high pressure (pre-combustion) conditions.

6.5 Conclusion

A series of N-doped porous carbons were synthesised via air carbonisation of cloves, followed by urea treatment and then activation using either KOH or PO. The samples obtained by KOH activation showed textural characteristics with highly developed micro-mesopores and an ultra-large surface area of up to 3435 m² g⁻¹ with a large pore volume of up to 2.37 cm³ g⁻¹. In contrast, PO activation micro-mesoporous carbons with a surface area of up to 2641 m² g⁻¹ and a pore volume of up to 1.45 cm³ g⁻¹. Notably, a relatively low PO/carbon ratio of 2, along with temperature variations, can be used to produce a series of carbons with varying porosities. The optimal pore structure and presence of N contribute to enhanced CO₂ uptake capacity at low pressure conditions

that mimic post-combustion CO_2 capture, reaching up to 1.5 mmol g⁻¹ and 4.7 mmol g⁻¹ at 0.15 bar and 1 bar, respectively. This is ascribed to a combination of large surface area, appropriate porosity and the existence of nitrogen surface functionalities. Samples with a high surface area are attractive for moderate to high pressure CO_2 capture conditions that mimic pre-combustion capture, and have storage capacity of up to 24.9 mmol g⁻¹ at 25 °C and 20 bar. Notably, at 20 bar, the samples are far from saturation, indicating much more uptake can be adsorbed at higher pressures. It can be concluded that the synthetic parameters such as urea treatment, low activating agent ratio and activation temperatures were beneficial to improving CO_2 uptake, but the appropriate porous properties were the most significant factors.

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Chapter 7: Conclusions and future research directions

The syntheses, characterisations, and applications of micro/mesoporous carbonaceous materials prepared using various carbon precursors have been systematically studied. Novel porous materials have been developed, and different synthesis approaches have been investigated, i.e., one-step carbonisation, direct chemical activation, air carbonisation, hydrothermal carbonisation and direct N-doping of porous materials to improve the textural properties for gas storage applications. Furthermore, the effects of various process parameters on the activation stage, as well as the impact of activating conditions on activated carbon properties, are studied.

Chapter 3 reports the synthesis of porous carbons via an appropriate novel one-step strategy. Porous carbons were successfully prepared from the direct carbonisation of potassium hydrogen phthalate (KHP) and potassium phthalimide (PPI), which only required heat treatment of the high carbon-containing metal salts under a nitrogen atmosphere at 600–1000 °C, followed by washing with water. All samples have high thermal stability, which corresponds to their amorphous structures. The PPI-derived carbons exhibited high surface area (2889 m² g⁻¹) and pore volume (1.36 cm³ g⁻¹) after carbonisation at 900 °C, while those obtained using KHP as a carbon precursor have a surface area and pore volume in the range of 488–1851 m² g⁻¹ and 0.20–1.03 cm³ g⁻¹, respectively. The carbons showed an ideal porosity for CO₂ uptake to the extent that the PPI-derived carbons showed a CO₂ capture capacity of up to 5.2 mmol g⁻¹ at 1 bar and 25 °C, and stored 1.7

mmol g⁻¹ of CO₂ at CO₂ post-combustion conditions (0.15 bar), which are among the highest so far reported for porous carbons. In addition, CH₄ storage at 25 °C and 35 bar was also investigated. Both sets of carbons, form KHP and PPI, have high gravimetric CH₄ uptake. An important finding is that the carbons may be readily compacted to a high packing density of up to 1.15 g cm⁻³ with retention of their textural properties. The consequence of the compaction is that the high packing density of the PPI carbons, coupled with their high gravimetric CH₄ uptake, gives high volumetric uptake of up to 227 cm³ (STP) cm⁻³, at 25 °C and 35 bar, which is significantly higher than any previously reported carbon, and comparable to the best metal-organic frameworks (MOFs).

Considering the results of porous carbons derived from the direct carbonisation of potassium salts, the behaviour of other metal salts such as sodium, calcium, and zinc can be explored as possible precursors. The simplicity of the synthesis route, the scope to vary the preparation conditions and textural properties, the readily achieved optimal pore size, and the excellent gas sorption properties mean that the metal salt-derived carbons can offer an attractive and unrivalled mix of characteristics for CO₂ and CH₄ storage applications. The simple method and a combination with heteroatoms and metal salts offer a prospect for obtaining highly porous carbons materials with exciting properties that might enhance their overall performance and open numerous application possibilities and business opportunities. Moreover, future research should be directed towards CH₄ storage at high pressure to know how far these materials are from applicability in ANG and other real-world industrial applications.
Chapter 4 presents the preparation of cost-effective porous carbons from polyethylene terephthalate (PET) using conventional hydrothermal carbonisation (HTC) and direct KOH activation, under mild or severe activation conditions at 600-800 °C. The properties of PET-derived carbons and their gas storage capacity were investigated. All the samples presented a very high carbon content and appeared to be suitable starting materials for activated carbon production. A maximum surface area of 2828 m² g⁻¹ was achieved, along with a maximum pore volume of 1.47 cm³ g⁻¹, associated with narrow and wide pore size distributions. The activated carbons were explored for CO₂ and CH₄ storage. CO₂ storage capacity of up to 4.3 mmol g⁻ ¹ at 1 bar and room temperature (25 °C) was obtained, which is at a competitive level for porous carbons, and comparable to what was previously reported for packaging waste materials. Furthermore, enhanced CO₂ adsorption under typical flue gas conditions (i.e., 0.15 bar) is achieved with an adsorption capacity of 1.5 mmol g⁻¹, which is also among the highest so far observed for porous carbons. Samples with a high surface area showed better performance at 20 bar, indicating the CO₂ uptake at 20 bar correlates with the total surface area. The methane storage capacity of the PET-derived carbons was also evaluated. A suitable adsorbent for CH₄ storage needs to combine high surface area and pore volume, high material (packing) density, and suitable micro/mesopore size distribution. The PET carbons showed high gravimetric methane uptakes of 11.1-13.4 mmol g^{-1} (0.18-0.21 g g^{-1}), following the surface area and pore volume trends. The carbons were easily compacted to a high packing density of up to 1.13 g cm⁻³ with minor penalties on textural properties. Following compaction, the carbons achieve the best performance for volumetric CH₄ storage of up to 448 cm³ (STP) cm⁻³ at 100

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bar, as well as an unrivalled working capacity of up to 273 cm³ (STP) cm⁻³, which is significantly higher than any currently available benchmark material. More significantly, these values substantially exceed the requirements set by the United States Department of Energy (US DOE). This work demonstrates for the first time that adequately designed porous carbons can attain methane storage above the US DOE targets without any drawbacks usually encountered with the use of MOFs.

For future work, PET carbons were prepared using well-established synthesis procedures, but with a twist wherein a limited amount of inorganic matter is judiciously retained. More emphasis should be given to investigating the impact of the presence of inorganics on enhancing their packing density, with the consequence that they have extraordinary levels of volumetric uptake. Furthermore, this study is limited to a single component plastic, which is polyethylene terephthalate (PET). However, due to the requirement of sustainable development and the ever-increasing generation of waste plastics, more attention should be paid to converting mixed plastics consisting of polypropylene, polyethylene, polystyrene, and others into valuable porous carbon materials, which could be an effective and promising approach. It is believed that the further work is expected to not only open up a novel way to recycle waste plastics and pave the way for large-scale use of mixed plastic waste, but also advance the sustainable production of valuable porous carbons for a variety of applications such as energy storage, environmental remediation, catalysis, etc.

Chapter 5 reports the production of biomass-derived activated carbons with high porosity development and specific properties suitable for carbon dioxide

capture and methane storage. Highly microporous activated carbons have been successfully generated via two carbonisation methods from an environment-friendly and abundantly available biomass precursor, cloves (*Syzygium aromaticum*), followed by KOH chemical activation. Both carbonisation routes yield carbonaceous matter with a low O/C ratio and, consequently, on activation offer advantages with respect to carbon yield and suitable porosity for exceptional performance in CO₂ and CH₄ storage. Remarkably, the activation of cloves generated carbons with a high surface area and a large pore volume of 3175 m² g⁻¹ and 1.85 cm³ g⁻¹, respectively. The activated carbons, depending on the activation conditions, presented high levels of microporosity, with up to 97% of the surface area and 92% of the pore volume arising from micropores. Such a unique combination of porosity implies that the produced carbons simultaneously show an interesting CO₂ uptake at both low pressure (1.4 and 5.4 mmol g^{-1} at 0.15 and 1 bar, respectively) and high pressure (23.7 mmol g^{-1} at 20 bar), indicating superior uptake under both pre-combustion and post-combustion CO_2 capture conditions. Under ambient conditions, uptake of 5.4 mmol g⁻¹ is comparable and better than that of current benchmark porous materials, including carbons, zeolites or metal-organic frameworks. Significant gravimetric and volumetric methane uptake at high pressure have also been gained, confirming a highly competitive uptake and delivery efficiency. At 100 bar, volumetric methane uptake values of up to 334 cm³ STP cm⁻³, which is considerably higher than all the benchmark materials and surpass the volumetric CH₄ storage DOE target (263 cm³ (STP) cm⁻³) at room temperature and 100 bar. Furthermore, they exhibit a very high volumetric working capacity of up to 262 cm³ (STP) cm⁻³ for the pressure range of 100 bar

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(uptake pressure) to 5 bar (desorption pressure) and 25 °C. This work demonstrates that activated carbons can be predictably synthesised, based on the O/C ratio of biomass-derived activatable carbonaceous matter, in a manner that deliberately targets porosity that is suitable for exceptional CO_2 and CH_4 storage.

In term of sustainability, the use of cloves as a waste to produce carbons seems to be very promising, which can resolve issues like low synthesis cost of activated carbons containing high surface area, pore density and attractive performance as sustainable energy materials. Another future research direction would involve the use of the direct activation process of biomass that negates the need for HTC or pyrolysis or use a potassium oxalate (PO) as activating agent which can offers a direct and mild non-hydroxide activation process that is simpler, cheaper, and more sustainable. In addition, a variety of biomass precursors with low O/C atomic ratio can be used for the preparation of versatile biomass derived carbons thus increasing their scope of application in various fields including energy storage and environment.

Chapter 6 details the synthesis and characterisations of N-doped porous carbons by direct urea doping and chemical activation using either KOH or PO. KOH activation generated samples with highly developed micromesopores and an ultra-large surface area of up to 3435 m² g⁻¹ with a large pore volume of up to 2.37 cm³ g⁻¹. In contrast, PO activation produced micromesoporous materials with a surface area of 2641 m² g⁻¹ and a pore volume of 1.45 cm³ g⁻¹. The optimal pore structure and nitrogen content (up to 3.24 wt%), in addition to pore size distribution, contribute to enhanced CO₂ adsorption capacity at low pressure conditions that mimic post-combustion

 CO_2 capture, reaching up to 1.7 mmol g⁻¹ and 4.7 mmol g⁻¹ at 0.15 bar and 1 bar, respectively. Samples with a high surface area are attractive for moderate to high pressure conditions that mimic pre-combustion capture, showing a high CO_2 adsorption capacity of 24.9 mmol g⁻¹ at 25 °C and 20 bar. Notably, at 20 bar, the samples are far from saturation, indicating much more uptake can be adsorbed at higher pressures. It can be concluded that the synthetic parameters were beneficial for improving CO_2 uptake, but the appropriate porous properties were the most significant factors.

In future work, the textural parameters of the resulting activated carbons could be more controlled by varying the amount of activators or urea ratio. With a high specific surface area and a mix of micro and moderate mesoporosity, the prepared porous carbon may enhance methane adsorption capacity and working capacity since the abundant mesoporosity ensures higher capture at high uptake pressure. Another interesting aspect that requires further research is the synthesis of multi-heteroatom doped porous carbons, where the high amount of heteroatom doping may result in adsorbents with high porosity and excellent structural stability that are tailored to the targeted application, i.e., low or high pressure gas adsorption. In addition, one step of N-doping and activation of biomass carbon can provide an effective approach to new high-efficiency adsorbents through the use of NaNH2 instead of KOH as a chemical activator, which can not only avoid the corrosion of the reactor to a large extent, but also using NaNH2 as both an activator and a nitrogen source can effectively reduce the preparation cost and complexity of the adsorbent in the activation process. This can provide a promising heteroatom-doped activated carbon for both energy and gas storage.