

Adsorption properties of South African bituminous coals relevant to carbon dioxide storage

GN Okolo
22006303

Thesis submitted in fulfillment of the requirements for the degree *Philosophiae Doctor* in *Chemical Engineering* at the Potchefstroom Campus of the North-West University

Supervisor: Prof. RC Everson

Co-supervisor: Prof. HWJP Neomagus

Prof. R Sakurovs (CSIRO Energy, NSW, Australia)

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“Winning means you're willing to go longer, work harder, and
give more than anyone else”

- Vince Lombardi-

Dedication

This dissertation is gratefully dedicated to the loving memory of my late sister,

Miss Juliana Okolo, who passed on to glory on the 13th of April, 2008.

May her gentle soul rest in perfect peace!

Eternal rest grant unto her Oh Lord..., And let perpetual light shine upon her..., May she rest
in peace.... Amen

Declaration

I, **Gregory Nworah Okolo**, hereby declare that this thesis title: “Adsorption properties of South African bituminous coals relevant to carbon dioxide storage”, submitted in fulfilment of the requirements for the degree *Philosophiae Doctor* (PhD) in *Chemical Engineering* is my work and has not previously been submitted to any other institution in whole or in part. Written consent from authors had been obtained for publications where co-authors have been involved.

Signed at Potchefstroom on the 22nd of January, 2017



.....
Gregory Nworah Okolo

Preface

Format of thesis

The format of this thesis is in accordance with the academic rules of the North-West University (approved on November 22nd, 2013), where rule **A.5.4.2.7** states: “Where a candidate is permitted to submit a thesis in the form of a published research article or articles, or as an unpublished manuscript or manuscripts in article format and more than one such article or manuscript is used, the thesis must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.”

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Format of numbering and referencing

It should be noted that the formatting, referencing style, numbering of tables and figures, and general outline of the manuscripts were adapted to ensure uniformity throughout the thesis. The format of manuscripts which have been submitted and/or published adhere to the author guidelines as stipulated by the editor of each journal, and may appear in a different format to what is presented in this thesis. The headings and original technical content of the manuscripts were not modified from the submitted and/or published versions, and only minor spelling and typographical errors were corrected. The bibliography (reference list) was included at the end of each chapter, and the Appendices.

Supplementary data

Relevant supplementary data, where necessary, were included in the Appendices.

Nomenclature

The description of the nomenclature (notations/symbols, Greek symbols, and relevant abbreviations) were included at the end of each chapter, unless stated otherwise. It should be noted that notations/symbols and Greek symbols may vary between chapters, following the format of the published papers.

Statement from co-authors

To whom it may concern,

The listed co-authors hereby give their consent that **Gregory Nworah Okolo** may submit the following manuscripts as part of his thesis entitled: **Adsorption properties of South African bituminous coals relevant to carbon dioxide storage**, for the degree *Philosophiae Doctor in Chemical Engineering*, at the North-West University:

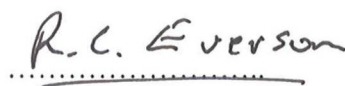
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Okolo GN, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. 2015. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel*, **141**:293-304.

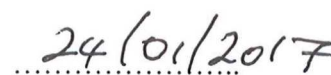
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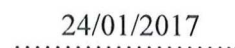
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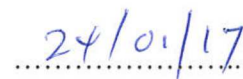
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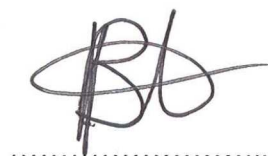
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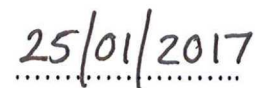
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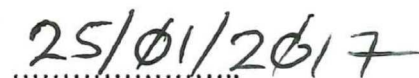
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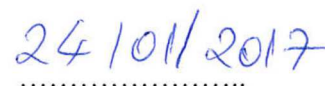
Mokone J. Roberts



Date



Mihaela Grigore



Date

List of publications

Journal articles

1. **Okolo GN**, Everson RC, Neomagus HWJP, Bunt JR, Sakurovs R, Mihaela G. 2015. Correlation of coal properties with the carbon dioxide, methane and nitrogen high-pressure sorption capacity of South African bituminous coals. 2017. **Submitted to Fuel (Submission No.: JFUE-D-17-00148)**.
2. Uwaoma RC, Strydom CA, Bunt JR, **Okolo GN**, Matjie R. 2017. The catalytic effect of Benfield waste salt on CO₂ gasification of a typical South African Highveld coal. **(Submitted to Waste Management)**.
3. **Okolo GN**, Neomagus HWJP, Everson RC, Roberts MJ, Bunt JR, Sakurovs R., Mathews JP. 2015. Chemical-structural properties of South African bituminous coals: Insights from wide angle XRD-carbon fraction analysis, ATR-FTIR, solid state ¹³C NMR, and HRTEM techniques. *Fuel*, **158**:779-792.
4. **Okolo GN**, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. 2015. Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques. *Fuel*, **141**:293-304.
5. Roberts MJ, Everson RC, Domazetis G, Neomagus HWJP, Jones JM, Van Sittert CGCE, **Okolo GN**, Van Niekerk D, Mathews JP. 2015. The DFT molecular modelling and particle kinetics studies of the mechanism for CO₂-char gasification. *Carbon*, **93**:295-314.
6. Roberts MJ, Everson RC, Neomagus HWJP, **Okolo GN**, Van Niekerk D, Mathews JP. 2015. The characterisation of slow-heated inertinite- and vitrinite-rich coals from the South African coalfields. *Fuel*, **158**:591-601.

Conference proceedings

1. **Okolo GN**, Neomagus HWJP, Everson RC (presenter), Roberts MJ. Advanced characterisation of South African coal deposits for determination of CO₂ captive and reactive properties. **Oral presentation** at the IEA 6th International Conference on Clean Coal Technology (CCT 2013). Thessaloniki, Greece. 12-16th May, 2013.
2. **Okolo GN (presenter)**, Neomagus HWJP, Everson RC, Roberts MJ. 2013. Characterising the porosity and surface areas of coal by gas adsorption, MIP and SAXS techniques. **Poster presentation** at the IEAGHG International Interdisciplinary CCS Summer School; University of Nottingham. Nottingham, UK. 21 -26th July 2013.

3. **Okolo GN (presenter)**, Neomagus HWJP, Everson RC, Roberts MJ. 2013. Advanced characterisation of selected South African coals for CO₂ capture. **Poster presentation** at the IEAGHG International Interdisciplinary CCS Summer School; University of Nottingham. Nottingham, UK. 21 -26th July 2013.
4. **Okolo GN (presenter)**, Rambuda M, Roberts MJ, Chiyanzu I. 2013. Natural resources of South Africa: Minerals & Mining. **Invited oral presentation** at the South African Association of Science and Technology Educators (SAASTE) Conference. Wolmaransstad, South Africa, 19th October, 2013.
5. **Rambuda M (presenter)**, Neomagus HWJP, Everson RC, Bunt JR, **Okolo GN**. 2013. Gasification and combustion kinetics of typical South African coal chars. **Oral presentation** at the Fossil Fuel Foundation of Africa 18th Southern African Coal Science & Technology Indaba: Latest Research & Developments in Universities and Industries. Parys, South Africa, 13-14th November, 2013.
6. **Okolo GN (presenter)**, Neomagus HWJP, Everson RC, Roberts MJ. 2013. Structural characterisation of typical South African coals. **Oral presentation** at the Fossil Fuel Foundation of Africa 18th Southern African Coal Science & Technology Indaba: Latest Research & Developments in Universities and Industries. Parys, South Africa, 13-14th November, 2013.
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8. **Okolo GN (presenter)**, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. 2014. Characterising the porosity and surface areas of coal by gas adsorption, mercury intrusion and SAXS techniques. **Oral presentation** at the Particle Technology Workshop. University of Cape Town, Cape Town, South Africa, 4th November, 2014.
9. **Okolo GN (presenter)**, Everson RC, Neomagus HWJP, Roberts MJ, Sakurovs R. 2014. Carbon dioxide, methane and nitrogen high pressure sorption capacities of bituminous South African coals. 2014. **Oral presentation** at the FFF Coal, Energy and Sustainability Conference, Cape Town, South Africa, 27-28 November, 2014.

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Abstract

An investigation was undertaken to determine the sorption properties of South African bituminous coals relevant to carbon dioxide storage in unmineable coal seams. Four bituminous coal samples from underground coal seams of Witbank, Highveld, and Tshipise-Pafuri coalfields were selected for this study. Detailed sample characterisation was conducted on the coal samples using both standard and advanced techniques. The coal samples were further subjected to high pressure CO₂, CH₄, and N₂ sorption experiments at 55 °C and up to 16 MPa pressure to simulate in-situ coal seam conditions, using a high pressure gravimetric sorption system.

Petrographic data of the samples revealed that three of the samples (coals FOZ, DEN, and OGS) are iso-rank (bituminous medium rank C) coals (0.63 – 0.68 Rr.%), while coal TKD is classified as bituminous medium rank B (1.20 Rr.%). All three samples were found to be relatively high in ash yields (16.8 – 25.9 wt.%, adb). Using different techniques, it was found that the surface areas and porosity properties of the samples obtained from SAXS analysis were comparatively greater than similar data acquired from the more widely used techniques (CO₂- and N₂- LPGA, and MIP), and these results were observed to be significantly rank dependent.

Characterisation results from solid state ¹³C NMR, WAXRD-CFA, and ATR-FTIR show that the lower iso-rank coal samples contained more aliphatic moieties; while the higher rank sample (coal TKD) contained higher fractions of polyaromatic moieties and saturated long chain hydrocarbons, hence, higher aromaticity. Furthermore, HRTEM data revealed that the lower iso-rank coals exhibited higher frequency of lower molecular weight fringes; while the higher rank coal TKD possessed more of the higher molecular weight fringes, and tend to be more preferentially aligned with more ordered carbon crystallites.

Results from the high pressure sorption experiments show that the coal samples can store up to 4.1 – 8.7% of CO₂, 1.0 – 1.8% of CH₄, and 1.0 – 2.2 % of N₂ relative to its weight at the experimental conditions. A new model, based on a hybrid DR and Henry law approach (DR-HH), provided better fits to the experimental isotherm data than the previously used modified DR (M-DR) model. Physisorption was found to be the dominating sorption mechanism, with neat heat of sorption generally ≤ 12.8 kJ/mol. The sorption capacities of the samples were found to be rank dependent, while the micropore properties of the samples significantly impacted the sorption properties of the samples, more than both the mesopore and macropore properties. The sorption capacities of the samples were also found to be relatively influenced by the intermediate maceral abundance, suggesting that lithotype bandings enhances either the fluid transport processes or the micropore properties of the coal matrix.

Extended abstract

Carbon capture and sequestration or storage (CCS) in geological locations has been demonstrated as a viable and strategic option for global climate change mitigation, and continued utilisation of the relatively cheap and more evenly distributed fossil fuels, especially coal. CO₂ sequestration in deep unmineable coal seams has been identified as one of the geological storage options for captured CO₂ and has been found to be an attractive CO₂ storage sink as the CO₂ can be stored as super-critical fluid, which is expected to be stable for a geologically significant period. This may also enable the synergy of enhanced coal bed methane (ECBM) production that will add to the energy resource and generate income to offset some of the capital expenditure of the sequestration infrastructure. It has been reported that up to 1.30 Gton of CO₂ can be stored in identified unmineable coal seams of South Africa, with an estimated gas content of about 0.14 - 0.28 trillion m³. Moreover, a good source-sink match exists between the emission point sources and the unmineable coal seams of South Africa.

The understanding of the physical, chemical and structural properties of coal seams is necessary in identifying the chemical and physical interactions between the coal and the sequestered gases during its utilisation as a geological storage site. For CO₂ storage in coal seams, this is necessary to determine the suitability of the coal seams and the stability of the adsorbed CO₂ in the geological disposal site. Furthermore, a fundamental knowledge of the sorption properties of the coal seam to various adsorptive gases, especially CO₂ and CH₄ is necessary in determining the storage capacity of the unmineable coal seams and the displacement and or desorption of in-seam gas-in-place. Although enormous amount of sorption data abound for northern hemispheres' coals, information on South African coals at supercritical conditions is still limited. The current investigation examines the CO₂, CH₄, and N₂ high pressure sorption properties of four selected bituminous coals from underground coal seams of South Africa. The characteristic properties of the samples were studied using proximate, ultimate, total sulphur, and petrographic analyses. The micro-, meso-, and macro-pore properties and other physical-structural properties of coal samples were investigated using helium pycnometry, CO₂ and N₂ low pressure gas adsorption (LPGA), mercury intrusion porosimetry (MIP), and small angle x-ray scattering (SAXS) analytical techniques. The chemical-structural properties of four coals were probed using wide angle X-ray diffraction-carbon fraction analysis (WAXRD-CFA), attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR), solid state ¹³C nuclear magnetic resonance spectroscopy (ss ¹³C

NMR), and high resolution transmission electron microscopy (HRTEM). Mineralogy of the samples was studied using LTA-XRD analysis. The coal samples were further subjected to CO₂, CH₄, and N₂ high pressure (up to 16 MPa) sorption experiments at 55 °C to determine the sorption properties and sorption capacities of the coals.

Results from both CO₂ LPGA and SAXS techniques gave good insights into the micropore properties of the coals samples and the results were found to be significantly rank dependent. Consistent with previous findings, N₂ LPGA method underestimated the surface area and porosity of the samples compared to results obtained using the other techniques, but it provided a good insight on the mesopore properties of the samples. The surface areas and porosities of the samples determined from SAXS were found to be larger than any of the values from the other techniques. This is attributed to SAXS probing a wider range of pores, including pores that are closed to, or restricted in access by gas adsorption or mercury intrusion and also capturing the properties of pores in the range: $5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$; not readily measured by any of the other three techniques used in this investigation. However, since each technique responds to the pores in coals differently, a combination of SAXS with other techniques provides a richer picture of the nature of the porosity in coals.

The aromaticity of the samples determined by solid state ¹³C NMR ranged from 0.74 to 0.87 and compared well with the WAXRD-CFA results (0.73-0.86). WAXRD-CFA, ATR-FTIR and ¹³C NMR data showed that the lower iso-rank coal samples contained more aliphatic moieties; while the higher rank sample contained higher fractions of polyaromatic moieties and saturated long chain hydrocarbons. The lattice parameters determined from WAXRD-CFA show that the lower rank coals investigated are structurally less well-ordered than the higher rank coal. Also, the HRTEM aromatic fringe image analysis shows that the aromatic fringes of the higher rank coal were quantified as having the greatest preferential alignment than the fringes of the other three lower iso-rank coals examined. Furthermore, HRTEM data revealed that the carbon lattice of the samples consist of aromatic fringes of varying lengths, L ($3 \text{ \AA} \leq L \leq 95 \text{ \AA}$), which corresponded to a molecular weight distribution ranging from 75 to 1925 amu, assuming circular catenation. The coal with the highest volatile matter yield was found to exhibit a higher frequency of lower molecular weight fringes; while the higher rank coal possessed the most higher molecular weight fringes. It was demonstrated that, for the characterisation methods used in this study; that coal maturity impacts the chemical-structural properties of these coals more than maceral composition and abundance does.

LTA-XRD data reveals that kaolinite and quartz were the most abundant mineral phases in all four coal which corroborates the findings from the petrographic analysis. Smaller amounts of dolomite, calcite, pyrite, and illite were identified in the samples.

The sorption capacities (by weight) of the samples with respect to the gases decreased in the order: $\text{CO}_2 > \text{CH}_4 \approx \text{N}_2$. A new model, based on a hybrid Dubinin-Radushkevich and Henry law approach (DR-HH), provided better fits to the experimental sorption isotherm data than the previously used modified DR (M-DR) model. Obtained uncertainty metrics show that the DR-HH model generally returned lower error sum of squares (ESS) and root mean square (RMS) residuals, and higher quality of fit (QOF) compared to the M-DR model. The net heat of sorption, βE_s , of the samples for the three adsorptive gases were generally low (8.5 - 12.8 kJ/mol), indicating that physisorption was the dominating sorption mechanism. The sorption capacities of the samples were found to be rank dependent as they decreased with increasing vitrinite reflectance and elemental carbon. The micropore properties of the samples as measured by both CO_2 low pressure gas adsorption (LPGA) and small angle X-ray scattering (SAXS), significantly impacted the sorption properties of the sample more than both the mesopore and macropore properties determined from N_2 LPGA, SAXS, and mercury intrusion porosimetry. The sorption capacities of the samples were found to relatively increase with increasing intermediate maceral abundance, suggesting that lithotype bandings enhances either the fluid transport processes or the micropore properties of the coal matrix. Mineralogical analysis of the samples showed that, of the minerals present, only pyrite and calcite showed a trend with sorption capacity.

Keywords: *Anthropogenic GHG emissions; carbon capture and sequestration; coal properties; physical structural properties; micro-, meso-, and macro-pore properties; chemical-structural properties; sorption capacity, Dubinin-Radushkevich-Henry law hybrid.*

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Chapter 1

1.0 General introduction

1.1 Introduction

This brief introductory chapter is sub-divided into four sections: background information and motivation, problem statement, objective of the research, and scope of the research work (thesis).

1.2 Background information and motivation

Increasing anthropogenic greenhouse gas (GHG) emissions emanating from the utilisation of fossil fuels for energy production (power and liquid fuels) and other industrial processes (cement production, metallurgical uses, etc.), has largely contributed to global climate change [1-7]. The major GHGs are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), halocarbons (HCs), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and Sulphur hexafluoride (SF₆) [1, 6,

8]. The absolute and relative contributions of these GHGs to climate change can be defined and quantified using emission metrics such as radiative forcing (RF), global warming potential (GWP) and global temperature change potential (GTP). Although unit CO₂ concentration has been found to possess lower GWP with respect to the unit concentrations of the other GHGs, its higher abundance and ubiquity in emitted anthropogenic GHGs means that it exhibits higher effective RF, GWP and GTP, compared to the total effects of the other GHGs [6, 8].

Data from the Earth System Research Laboratory (ESRL) at Mauna Loa, Hawaii (last updated on the 11th of January, 2017) show that the mean global CO₂ concentration in the atmosphere has increased from 278 parts per million (ppm) during the pre-industrial era to 404.48 ppm as at December, 2016 [9]. This represents a 0.65% (2.63 ppm/yr) increase above the December, 2015 value (401.85 ppm) [9], with an annual growth rate well above the 1.63 ppm/yr average accumulation rate over the last 45 years (1970 – 2014) [9].

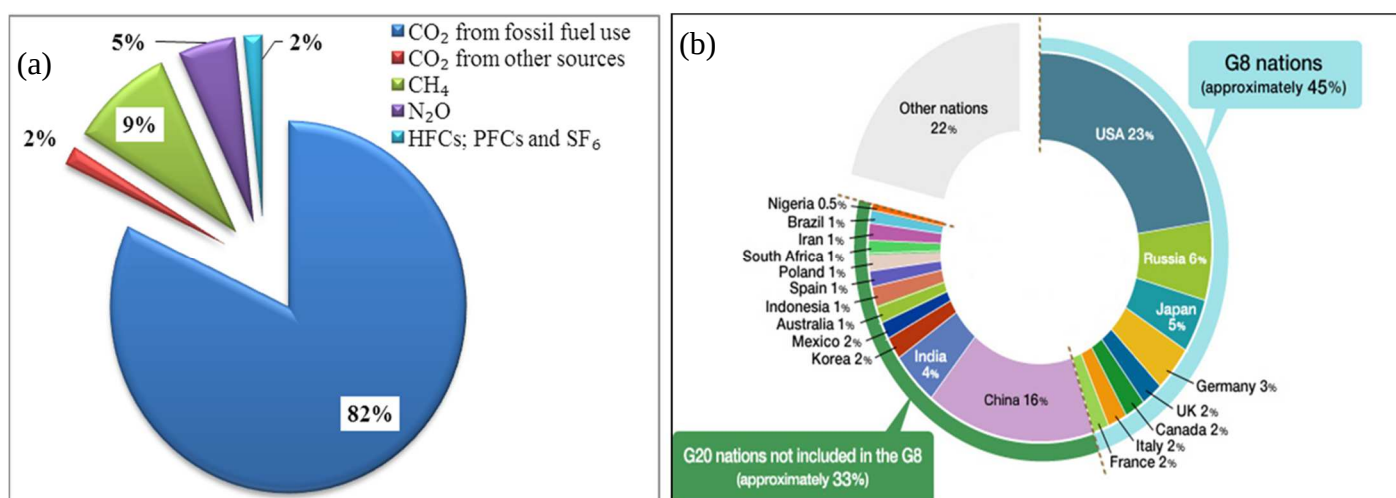


Figure 1.1: Global accounting for anthropogenic greenhouse gas (GHG) emissions (Adapted from [3]).

Figure 1.1 (a) shows the global accounting of anthropogenic greenhouse gas emissions adapted from IPCC [3]. It can be observed from Figure 1.1 that CO₂ emission accounts for a significant proportion of total emitted GHGs (84%) on the global scale, with a massive 82% of the total GHGs emanating for fossil fuel use alone, and only 2% resulting from other industrial sources

and agriculture. Other GHGs excluding CH₄, only accounted for just 6% of the total emitted GHGs on the global scale [3].

This increase in emissions has effectively resulted in a range of climate change effects including: melting glaciers, sea ice and snow cover; increasing ocean heat content, sea surface temperature and temperature over ocean and land; increasing air temperature in the troposphere; increasing humidity; and increasing uncertainties in medium to long term climate systems and predictions [1, 3, 4, 6, 10-16]. The inter-play of these effects over time has led to global warming with a predicted increase of 1.8 - 3.9 °C by 2100 [5, 6]. Model predictions from various investigators has shown that CO₂ emissions will continue to increase over the coming decades as fossil fuels continue to be a significant contributor of the global energy mix [3, 5, 6, 17, 18].

South Africa operates a highly energy-intensive economy, with considerable dependency on fossil fuels to meet its energy needs. This, together with its relatively small population, means that South Africa is a significant contributor with respect to per capita emissions of CO₂ on the global scale [18, 19]. Considering electricity production alone, 92% of electricity produced in South Africa is from coal combustion, complemented by nuclear energy [17, 18, 20]. South Africa emits about 440 Million tonnes (Mton) of CO₂ per annum [16, 18], and is responsible for over 40% of CO₂ emitted in the African continent. Thus, South Africa accounts for about 1% of global emission and is ranked 11th CO₂ emitter in the world [16-19, 21]. Figure 1.2 shows the distribution of large-scale industrial CO₂ emissions in South Africa. It is apparent from Figure 1.2 that emissions resulting from use of coal for electricity generation primarily by Eskom accounts for over 50% of South Africa's total CO₂ emission, followed by Sasol (15.9%). Rogue emissions from moving sources: transportation, agriculture, waste sector, etc. that cannot easily be captured account for about 21% (92 Mton) of the total CO₂ emissions.

Of the 440 Million tonnes of CO₂ emitted per annum in South Africa, About 320 Mton of emitted CO₂ (72.7%) is sequestrable, while about 32 Mton CO₂ (7.2%) resulting from Sasol coal-to-liquid (CTL) operation is capture-ready with about 95-98% CO₂ [17, 18]. Emissions from moving sources: transportation, agriculture, waste sector, etc. account for about 92 Mton (21%) of the total CO₂ emissions.

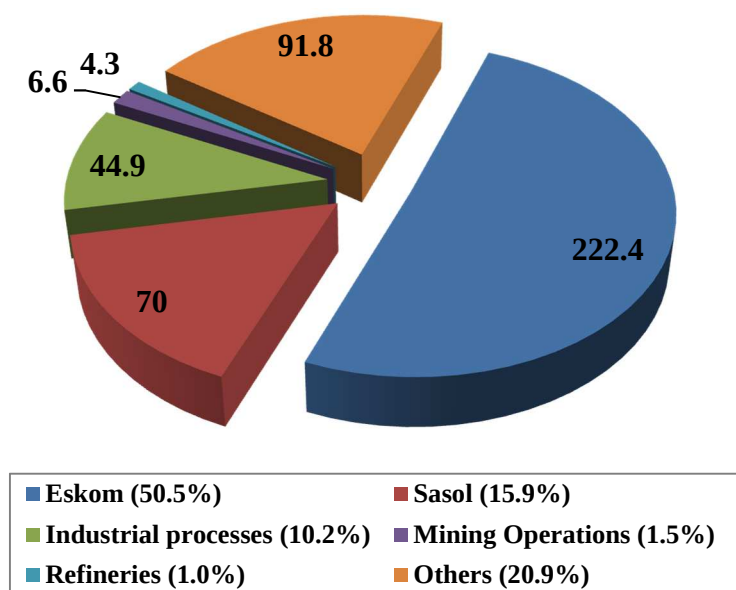


Figure 1.2: Distribution of large-scale industrial CO₂ emissions in South Africa (Adapted from [17])

South Africa has ratified the United Nations Framework Convention on Climate Change (UNFCCC) and its Kyoto Protocol, and plays a very active role in the climate negotiations on the global scale [16, 18]. The main objective of the UNFCCC and the Kyoto protocol is “to achieve the stabilization of greenhouse gas (GHG) concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Such a level should be achieved within a time-frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development to proceed in a sustainable manner” [22]. Under the Kyoto Protocol, carbon constraints were placed on industrialised countries [23]. In the first commitment period (2008 to 2012), South Africa, along with other larger developing countries such as Brazil, China and India, may continue to grow without any cap on emissions. However, once the developed nations take the lead with more ambitious emissions reductions, they will expect at least some developing countries to take a fair share of our common, albeit still differentiated responsibility [16, 18, 24]. Pressing for total exemption from any mitigation effort was not an option for South Africa [16]. To this end, the South African government and the Department of Energy, launched the South African Centre for Carbon Capture & Storage (SACCCS) to further the technical understanding of CCS potential in South Africa. Furthermore, CCS is part of the Long Term Mitigation Scenarios (LTMS) developed by the then Department of Environmental Affairs and Tourism, and one of South Africa’s eight Near-term Priority Flagship Programmes

of the National Climate Change Response White Paper, which addresses both greenhouse gas (GHG) mitigation and climate change adaptation [25]. The South African government endorsed the South African CCS Road Map in May, 2013; and included CCS in the National Development Plan 2030. In 2011, South African government in collaboration with UNFCCC hosted COP17 - the annual UN-led international climate change talks and negotiations that seek to shape the future architecture of the global climate change regime. At COP 17, South Africa committed to reduce carbon emissions by 34% by 2020 and by 42% by 2025 [24].

This increasing anthropogenic CO₂ emitted into the atmosphere can be controlled by implementing different decarbonisation options identified globally [3]. These include: reducing CO₂ production and release into the atmosphere by improved energy efficiency, implementing cleaner coal utilisation technologies, rapid deployment of renewable and nuclear energy systems, and capturing and sequestering the produced CO₂ in a safe geological locations [1, 3, 7, 26-29]. Various CO₂ sequestration options have been proposed including: storage in the deep oceans [7, 26, 28, 30], placement in geological formations (deep saline aquifers, depleted oil or gas reservoirs, and unmineable coal seams) and consumption via advanced chemical and biological processes [3, 7, 27-29, 31-34]. Storage of CO₂ in depleted oil and gas well seem to be the most lucrative option given the vast data available on these geological locations from previous years of oil and gas exploration activity. This option has since been commercialised with the added advantage of enhanced oil and gas recovery [3, 7, 35]. CO₂ storage in deep saline aquifers has also reached a commercial stage with the North Sea project in Norway as a good example [35].

Geological storage of CO₂ in deep “unmineable” coal seams is one of the geological storage options, and has been identified to be attractive as the CO₂ can be stored in the adsorbed supercritical fluid phase that is expected to be stable for geologically significant period [3, 7, 20, 31, 36-39]. This may also enable the synergy of enhance coalbed methane (ECBM) production which will add to recoverable energy resource and generate income to offset some of the capital expenditure (CAPEX) of the sequestration facility [7]. Unmineable or unprofitable coal seams are those coal seams considered too deep or too thin in thickness to be mined economically [3, 17, 20, 40]. It is worthy of note that this definition of “unmineable” may likely change with technological development, technological advancement, or economic conditions [3, 35]. Hence, long-term sequestration of CO₂ in coal seams might be more cost-effective than the other options. CO₂ storage in coal seam with ECBM had reached advanced stage of pilot testing and execution in USA, Canada, Japan, Mexico and Poland [31, 41]. A

schematic representation of CO₂ sequestration in coal seam is shown in Figure 1.3. CCS is comprised of three main value-chain processes: capture and compression of CO₂ from flue gases, transport of the CO₂ to storage sites, and permanent storage of the CO₂ in deep geological formations.

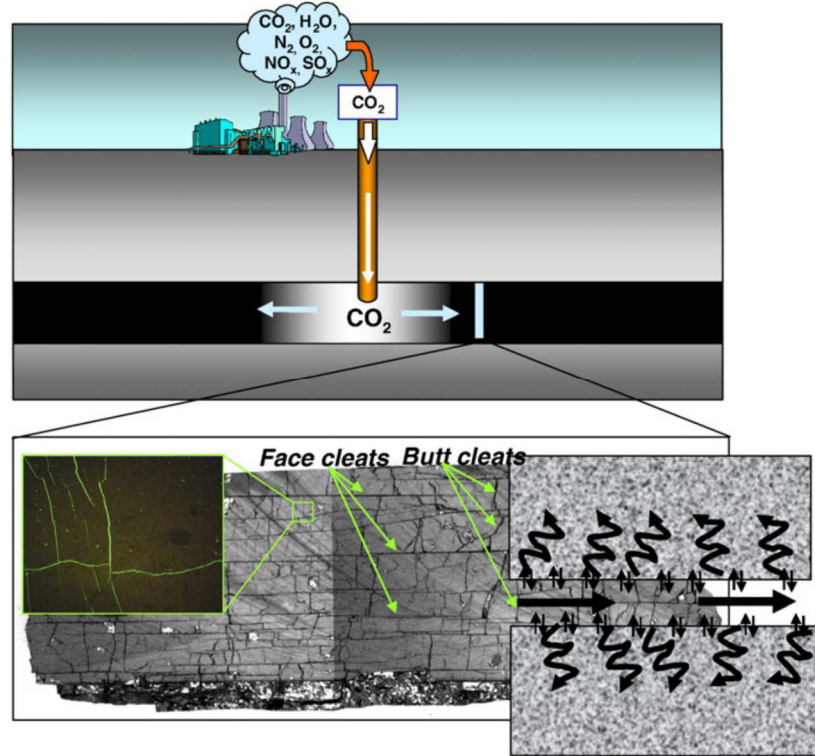


Figure 1.3: A schematic representation of CO₂ sequestration in coal seam [42].

The unmineable coal seams in South Africa can be used for carbon sequestration, with the synergy of coalbed methane production. Using the volumetric equations (Equations 1.1 and 1.2) proposed by DOE [43] for the calculation of CO₂ storage capacity in coal seams and limited data earlier published by Saghafi et al. [44, 45] and Billenkamp [46], Viljoen and co-workers [17] estimated that about 1.30 Gton of CO₂ can be stored in identified unmineable coal seams of South Africa, with an estimated gas content of about 0.14 - 0.28 trillion m³ (4.9 - 9.9 Tft³).

$$M_{CO_2} = Ah_g C\rho_{CO_2} E_{coal} \quad (1.1)$$

$$E_{coal} = \left(\frac{A_n}{A_t} \right) \left(\frac{h_n}{h_g} \right) E_A E_I E_g E_d \quad (1.2)$$

M_{CO_2} , is the CO₂ storage capacity of one or more coal seam(s) (kg); A , is the geographical area that defines the basin or region being assessed for CO₂ storage calculation (m²); h_g is the gross thickness of coal seams for which CO₂ storage is assessed within the basin or region defined by A (m); C , is the concentration of CO₂ in standard volume per unit volume of coal ($m^3_{CO_2}/m^3_{coal}$) (adsorption capacity at a given pressure or depth as determined by Langmuir volume or alternative method); assuming 100% CO₂-saturated coal conditions. If presented on dry-ash-free (daf) basis, then A and h must be corrected for daf; ρ , is the standard density of CO₂ (kg/m³); E_{coal} , is the CO₂ storage efficiency factor, determined from Equation 1.2; A_n/A_t , is the net to total area; h_n/h_t , is the net to gross thickness; E_A , is the areal displacement efficiency; E_I , is the vertical displacement efficiency; E_g , is the fraction of efficiency due to gravity (density difference between CO₂ and in situ water); E_d , is the microscopic displacement efficiency.

The spatial location and distribution of potential South African coal fields suitable for CO₂ storage and their capacities is given in Figure 1.4, while a summary of estimated CO₂ storage capacity of South Africa's "unmineable" coal fields is presented in Table 1.1 [17].

Besides, a good source-sink match exists between some of the large industrial emission point sources (especially power stations and Sasol's CTL facilities) and the unmineable coal seams [17], which may further lower captured CO₂ transport costs and contingencies. However, a fundamental knowledge of the sorption properties of these coals to various adsorbate gases, especially CO₂ and CH₄ is necessary in determining the storage capacity of unmineable coal seams. Although, enormous sorption data abound for northern hemispheres' coals, information on South African coals at and above supercritical conditions is still limited.

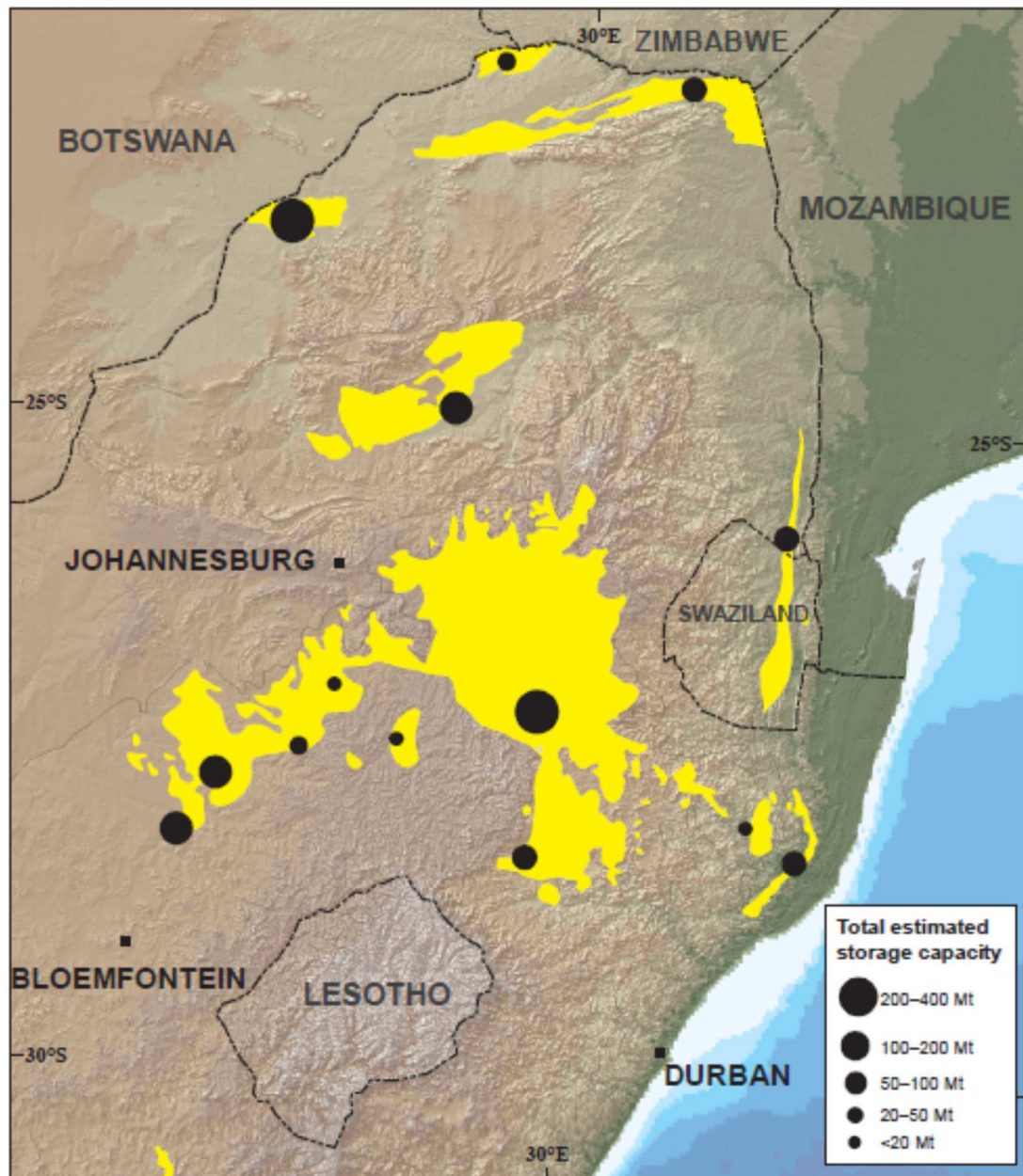


Figure 1.4: Spatial distribution of potential South African coal fields for CO₂ storage and their CO₂ storage capacity ranges [17].

Table 1.1: Estimated CO₂ storage capacity of South Africa's unmineable^a coal fields [17]

Coal basins / Coalfields	Coal seam area (km ²)	Coal seam thickness (m)	Coal seam depth range (m)	CO ₂ adsorption Capacity/tonne of coal seam (m ³)	CO ₂ storage Capacity of coal seam (MtCO ₂)	Coal seam gas content (wt %, adb)
Nongoma	75	1.5	300 - 550	22 - 27	5.2	7 - 24
Frankfort	216	1	300 - 550	22 - 27	10	NA
Heilbron	288	1	300 - 550	17 - 21	10.3	NA
Tuli	150	3	300 - 550	22 - 27	20.7	32 - 36
Edenville	360	2	300 - 550	17 - 21	25.7	NA
Newcastle/Ladysmith	936	1	300 - 550	22 - 27	43.1	NA
Kangwane	195	6	300 - 800	22 - 26	52.8	7 - 24
Pafuri	420	3	300 - 800	22 - 26	56.9	22 - 27
Somkele	360	5	300 - 800	22 - 27	82.9	6 - 8
Springbok Flats	2300	1	300 - 550	17 - 22	84.4	28 - 35
Kroonstad	936	3	300 - 550	17 - 21	100.3	NA
Welkom/Hennenman	1440	3	300 - 550	17 - 21	154.4	NA
Ellisras	800	10	300 - 800	17 - 22	293.4	23 - 26
Amersfoort/Utrecht	3600	2	300 - 550	22 - 27	331.8	NA
Total Estimated CO₂ Storage capacity of “unmineable” coal seams					1271.9	

^a - Unmineable or unprofitable coal seams are those coal seams considered too deep or too thin in thickness to be mined economically. It is worthy of note that this definition of unmineable may change with technological development or economic conditions.

1.3 Problem statement

One of the most important tools for the characterisation of solid adsorbent materials is the adsorbent's adsorption isotherm. The surface area, adsorption capacity, heat of adsorption, average pore size, and the volumetric changes (swelling or shrinkage), can be evaluated from well resolved adsorption isotherms [47]. The adsorption isotherms of coals are affected by both coal properties (rank, moisture content, swelling properties, etc.) and environmental factors (temperature of geological media, hydraulic pressure gradient, pH, etc.) [7, 42]. In order to develop an efficient approach for coal seam sequestration, variables that affect the coal-CO₂ interactions need to be investigated. Coal is an extremely complex material in terms of its pore structure and surface area. Coal has been described as a 'highly porous, glassy solid rock' below its glass transition temperature of ≈ 600 K [48]. However, the glassy macromolecular network is transformed into a rubbery material at temperatures above its glass transition temperature. Similar observation has been made when coal is brought into contact with adsorptive gases and vapours [49, 50].

The adsorption of CO₂ on coals is one of the techniques used to determine the micropore surface areas and micropore- structures and properties of coals [32, 51-55]. However, these measurements are usually conducted at pressures far below atmospheric pressure and at low temperatures (0 °C for CO₂, and -78 °C for N₂ adsorption) [47, 55]. Despite the fact that data from these measurements give significant insights into the storage capabilities of coal seams and are important to current sequestration efforts, low-pressure, low temperature adsorption isotherm data do not represent the geological, in-seam conditions [7, 41, 42].

Furthermore, low temperature, low pressure gas adsorption isotherm data does not consider volumetric changes (swelling or shrinkage) due to coal swelling [56], although this may not be significant at these conditions [47]. However, at high pressure, volumetric changes due to swelling may range from 0.36% to 5.14% of coal volume [56-60]. Results obtained by fitting the high pressure isotherm data of coals to empirical isotherm model equations may be deceptive due to the fact that these models are mainly based on a rigid adsorbent structure [59] with regular pore surface [47]. Thus, it is essential to develop a more rigorous mathematical

model based on an analysis of the physical phenomena that occur during adsorptive gas-coal interaction at high pressure and conditions similar to coal seam conditions.

Adsorption capacities of coals and mass transport of gases through the coal matrix are influenced by coal seam properties including: temperature, pressure, coal petrography and rank, moisture content, mineral matter content and composition [57, 61-66]. Yet, the influence of microlithotype composition and abundance have not received much attention. It is well known that coal microlithotype which is a reflection of the variety of combination(s) of maceral groups is not evenly distributed in coal; but tend to occur in band or layers, which gives coal its layered luster. Banding develops or rather becomes more apparent with the increased compaction during rank advance from lignite to bituminous coal. Thus, microlithotypes are characteristic of bituminous coals, and decrease significantly as the rank approaches anthracite [67, 68]. Cleats in coal matrices and fractures often occur along these bands; and are the conduits and principal pathways for the mass transfer and migration of fluids in coal seams [67, 69-71], which may aid in the accessibility of remote pores [47, 71], and enhance the pore volume of the geological storage media [71]. The impact of the macro-, meso-, and micro-pore structures and properties of coals and their influence on the sorption properties of coals also needs to be evaluated.

Due to the fact that CH_4 is the dominant gas in coal seams, the coalbed methane reservoir capacity and the factors that influence the adsorption capacity of CH_4 at high-pressures have been investigated in order to determine the gas-in-place and to enhance the safety of coal mining [29, 72, 73]. The adsorption of other gases, such as N_2 , C_2H_6 , H_2 , and their mixtures on coals have also been investigated at elevated temperatures and pressures [74-77]. The strategic injection of CO_2 into coal seams as a viable option to mitigate the increasing global CO_2 emissions has inspired interest in developing a better understanding of coal- CO_2 interactions at high pressures [62, 63, 73, 74, 78-82]. However, the adsorption isotherms of CO_2 on coals at high pressures (at or over the critical point) have been reported to display unusual behaviour that many investigators are yet to adequately understand [56, 57, 82-86].

1.4 Aim and objectives of the study

The aim of the study is to investigate the CO₂ sorption properties of four South African bituminous coals selected from underground coal seams relevant to CO₂ sequestration in coal seams; and correlate the sorption properties of these coals to the coal properties.

To achieve this, the following specific objectives were attained:

- Determine the physical-structural properties of the coals using both conventional and advanced analytical techniques.
- Perform an extensive study of the chemical-structural properties of the coal samples using various characterisation methods.
- Measure the CO₂, CH₄, and N₂ adsorption isotherms of the coals under conditions similar to in-seam conditions at pressures up to 16 MPa and at isothermal temperature of 55 °C, and develop a fitting isotherm model to adequately describe the adsorption isotherms of these adsorptive gases at high pressure.
- Determine the CO₂, CH₄, and N₂ maximum sorption capacities of the coal samples using the fitting isotherm model.
- Evaluate and distinguish between the CO₂, CH₄, and N₂ sorption properties of the samples at the experimental conditions to establish the sorption mechanism(s) and the adsorptive gas-coal interaction(s), and validate the sorption mechanism.
- Correlate the obtained sorption data with the determined coal properties to determine the influence of coal properties on the maximum sorption capacities and sorption properties of the samples.

1.5 Structure of thesis

This thesis is structured into 6 chapters.

Chapter 1 is concerned with the introduction, motivation, and the aims and objective of this research work.

In Chapter 2, a review of published works relevant to the aims and objective of this thesis is presented.

In chapter 3, the analytical techniques and results obtained from the physical-structural characterisation of the coal samples is given. This chapter has been published in the journal, *Fuel* (Volume 141, Pages 293 – 304: 2015).

Chapter 4 presents the analytical techniques, procedures and data resulting from the chemical-structural analysis of the 4 samples used in this work. This chapter has been published in the journal, *Fuel* (Volume 158, Pages 779 – 792: 2015).

The experimental methods, data analysis and results from the CO₂, CH₄, and N₂ high pressure sorption experiments on the four coal samples conducted on a high pressure gravimetric sorption system (HPGSS) are presented in Chapter 5. The obtained sorption properties of the coals were also correlated with the coal properties and the critical properties of the gases. This chapter has been submitted to the journal, *Fuel*.

In Chapter 6, the main conclusions drawn from the sample characterisation, and HPGSS experiments are presented and further research directions not covered within the scope of this thesis are highlighted.

Nomenclature

<u>Symbol</u>	<u>Definition</u>
A	Geographical area of basin (m^2)
A_n/A_t	Net to total area
C	Concentration of CO ₂ in standard volume per unit volume of coal ($m_{CO_2}^3/m_{coal}^3$)
E_A	Areal displacement efficiency (-)
E_{coal}	CO ₂ storage efficiency factor (-)
E_d	Microscopic displacement efficiency (-)
E_g	Gravitational displacement efficiency (-)
E_t	Vertical displacement efficiency (-)
h_g	Gross thickness of coal seams (m)
h_n/h_t	Net to gross thickness (m)
M_{CO_2}	CO ₂ storage capacity of one or more coal seam(s) (kg/ton)

Greek symbols

<u>Symbol</u>	<u>Definition</u>
ρ_{CO_2}	Standard density of CO ₂ (kg/m ³)

Abbreviations

<u>Acronym</u>	<u>Definition</u>
Adb	Air dry basis
CAPEX	Capital expenditure
CBM	Coalbed methane
CCS	Carbon capture & storage (or sequestration)
CFCs	Chlorofluorocarbons

CH ₄	Methane
CO ₂	Carbon dioxide
CTL	Coal to liquid
Db	Dry basis
DEA	South African department of environmental affairs
DEAT	South African department of environmental affairs & tourism
DOE	US Department of energy
ECBM	Enhance coalbed methane
ESRL	Earth system research laboratory, at Mauna Loa, Hawaii
GHG	Greenhouse gas
GTP	Global temperature change potential
GWP	Global warming potential
HCFCs	Hydrochlorofluorocarbons
HCS	Halocarbons
HFCs	Hydrofluorocarbons
IPCC	Intergovernmental Panel on Climate Change
LTMS	Long Term Mitigation Scenarios
Mton	Million tonnes
N ₂ O	Nitrous oxide
PFCs	Perfluorocarbons
ppm	Parts per million
RF	Radiative forcing
SACCCS	South African Centre for Carbon Capture & Storage
SF ₆	Sulfur hexafluoride
UNFCC	United Nations Framework Convention on Climate Change

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Chapter 2

2.0 Literature review

2.1 Introduction

In this chapter, a literature review of research conducted in the area of coal properties and sorption properties of coals relevant for CO₂ sequestration in coal seams was carried out. The physical- and chemical-structural properties of coals impacting their sorption properties were discussed. Isotherm models used to describe and determine the sorption properties of coals were highlighted. The survey presented in this chapter was considered to provide the necessary background for the execution of this research work.

2.2 Coal Structure

2.2.1 Origin and formation of coal

The origin, formation, and structure of coal have been extensively studied [1-9]. Coal is an extremely heterogeneous, non-uniform, complex material consisting of organic matter, mineral

matter, moisture, and a complex and complicated pore network [3, 6-8, 10, 11]. It is generally accepted that the organic portion of coal was formed from concentrated deposits of swampy organic matter originally derived from terrestrial plants [2, 3, 5, 6]. Plant debris including plants' leaves and stems were transformed into coal through complex biological, chemical, and geochemical processes driven initially by selective microbial action and later by the temperature and pressure gradient generated by overlaying sediments over geological time (several hundred millions of years) [5, 6]. This organic sedimentary rock is composed of these fossilised plant remains called macerals and mineral inclusions. The macerals are the morphologically distinct features of coal, usually distinguished by their physical form and reflectivity under the optical microscope [1]. Macerals are classified into three main maceral groups: liptinite (exinite), vitrinite, and inertinite [4, 6-8, 10]. Vitrinite is typically derived from the metamorphosis of woody plant tissue and material and is the most prevalent maceral in bituminous coals. Liptinite is formed from resinous lipids and waxy plant materials and other hydrogen-rich substances. Inertinite is considered to probably originate from partially oxidised or combusted carbons and are distinguished by their greater reflectivity and retention of plant structures. [1, 12]. The process of conversion of the plant matter into peat, lignite, bituminous coal, and anthracite is called "coalification". During the coalification process, large volumes of volatiles, mainly CH_4 , CO_2 , and water are released [8, 13]. Although CO_2 is more strongly adsorbed to the coal matrix than the other volatiles, it is more easily dissipated due to its solubility in the moisture or water present throughout the coalification process. Hence, CH_4 is the most prevalent gas in coal beds accounting for about 95% of coal bed gas [3, 8, 13]. However, CH_4 is less strongly adsorbed to the coal matrix, a property exploited by CO_2 -enhanced coal bed methane production process.

Coals are classified by their rank, which is a measure of the extent of the heat and pressure, the coal was subjected to during its formation. Vitrinite reflectance ($\text{Rr.}\%$), fixed carbon and volatile matter contents are used to distinguish higher-rank coals, while calorific value and moisture content may be used to differentiate lower-rank coals [4-7]. As coal progresses through the coalification or maturation process, its physical and chemical properties change. As coal rank increases, from lignite to anthracite, carbon content increases, oxygen and hydrogen contents decrease, slowly at first, then rapidly during the later stages of coalification. The volatile matter content of coal decreases, while the calorific or heating value tends to increase with increasing rank [1, 3, 10, 11]. Furthermore, as coal rank increases, the aromaticity

and molecular cluster size increases; vitrinite reflectance increases; moisture content decreases, rapidly in the early stages, but slowly in the later stages of coal maturation [1, 3, 10, 11].

2.2.2 Molecular organic structure of coal macerals

Coal has a highly complex chemical structure, consisting of macerals and minerals that reflect the depositional environment and the nature of the organic precursors [11, 14]. There have been substantial efforts aimed at elucidating the molecular organic structure of coal. This task is made difficult due to the large variety of coals, the heterogeneity of a single coal and the complexity of individual constituents [10, 11]. Instead, many ‘average molecular structures’ have been constructed based on the elemental analysis and chemical functionality determined by various analytical methods. These methods include: proximate and ultimate analysis, wide angle X-ray diffraction, spectroscopy (^{13}C NMR, HRTEM, IR, and FTIR), solvent swelling and extraction, and adsorption methods [11, 15-22].

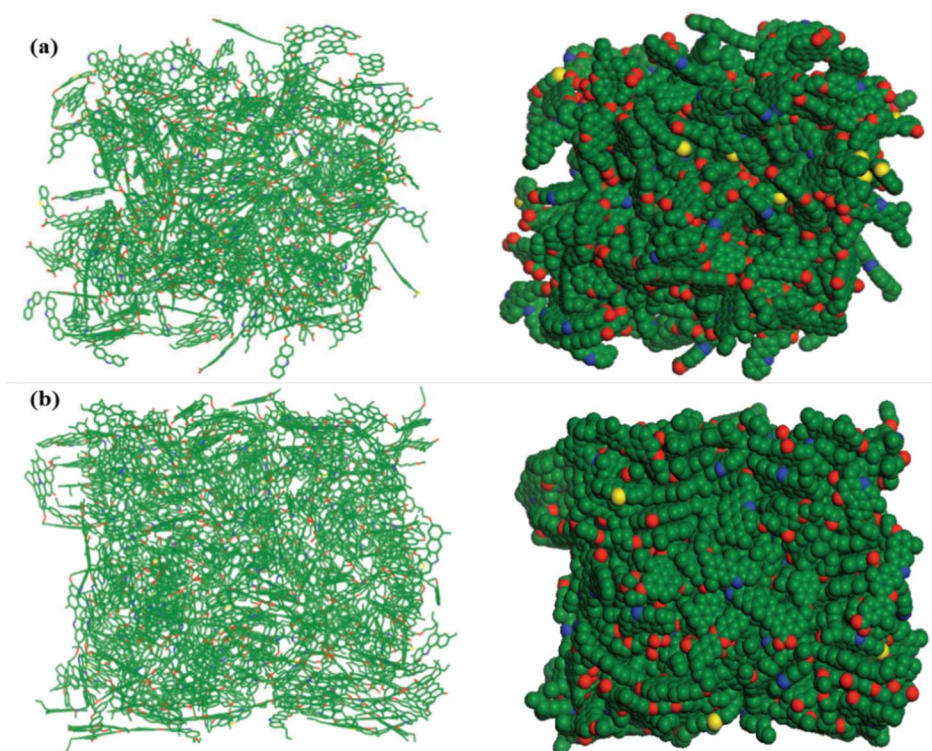


Figure 2.1: Molecular model for (a) inertinite-rich Highveld coal and (b) vitrinite-rich Waterberg coal [20]. Colour code: carbon- green, oxygen- red, nitrogen- blue, and sulphur- yellow. Hydrogen is not shown.

Early modelling efforts concentrated on developing an ‘average’ structure but nevertheless proved useful in explaining elements of coal properties [23-25]. Given [23] proposed a hypothetical structure for a bituminous coal vitrinite with 82% carbon content as one possible arrangement of the atoms present in coal molecule in line with the data available at that time. Given’s model illustrated the importance of functionality and the three dimensional structure of coal. The structure was based to a large extent on an array of connected polycyclic aromatic systems. Advances in the area of molecular modelling as applied to coal structure have evolved over the years. These advances have helped in the investigations and development of coal molecular models [17-20] that can be used to study different utilisation processes in coal including adsorption of CO₂ in coal [19, 21, 26-35]. The molecular representations of two South African, Permian-age vitrinite-rich Waterberg and inertinite-rich Highveld coals were elucidated by Van Niekerk & Mathews [20]. They reported an elemental composition of $C_{1000}H_{846}O_{69}N_{16}S_2$ and $C_{1000}H_{673}O_{78}N_{20}S_4$ for the vitrinite-rich Waterberg and inertinite-rich Highveld coal respectively. The molecular models of these coals are shown in Figures 2.1 in line and van der Waals radii rendering [20].

2.2.3 Physical structural properties of the coal

Coal as mined is anisotropically strained and ‘glassy’ [1, 36] and is compressed perpendicular to its bedding plane due to overburden pressure and expanded in the bedding plane as a result of tectonic movements [1, 37-40]. Coal as a ‘porous rock’ is thus, in a ‘glassy’ or pseudo-polymer state [41]. Many coal properties are similar to those of glassy polymers [42, 43]. The mobility of the macromolecular chains is highly constrained. The structure is very dense and there is very little void space in the structure. Therefore, diffusion in the glassy state is low. However, upon exposure to a swelling solvent, coal behaves as a ‘pseudo-polymer’ and its structure has been described as rubbery by Peppas [40]. In this state, the macromolecular chains are highly flexible. Large segments of the macromolecular network become mobile and occupy a larger portion of the free volume due to chain rotation, translation, and vibration [1]. These constraints and the complex physical structure of coal influences its physical-structural properties as density, surface area, porosity, and swelling properties of coals.

2.2.3.1 *Surface area and porosity properties of coal*

Coal is composed of highly cross-linked and entangled networks of macromolecular chains whose poor alignment in three dimensions produces various pore sizes and networks, resulting in usually low porosity systems. Pore structure of coals and carbonaceous material are classified according to IUPAC classification [44, 45] as: micropores ($d_p \leq 20 \text{ \AA}$); mesopores or transitional pores ($20 \text{ \AA} \leq d_p \leq 500 \text{ \AA}$); and macropores ($d_p > 500 \text{ \AA}$). It is widely, though not universally, accepted that the pores in coals have a broad size distribution and form a constricted, interconnected network [45-54]. Experimental evidence shows that coal porosity and pore size distribution varies with the degree of maturity of coal, termed rank and measured by the proxy indicators: carbon content and mean maximum reflectance of vitrinite. Both Rodrigues and Lemos de Sousa [51] and Gan and co-workers [46] found that, for lower-ranked lignites and sub-bituminous coals- (elemental carbon $< 75 \text{ wt.}\%$, dafb), porosity is primarily in the form of macropores (primary porosity). For intermediate-ranked bituminous coals ($76 \text{ wt.}\% \leq \text{elemental carbon} \leq 84 \text{ wt.}\%$, dafb), loss of primary porosity sets in and the evolution of secondary porosity (micro- and meso-porosity) starts, such that about 80% of the accessible porosity is contributed by micro- and meso-pores. In higher-rank coals (elemental carbon $> 85\%$, dafb), microporosity predominates [46, 51, 55]. Thus, as the rank of the coal increases, the importance of macroporosity decreases and microporosity becomes increasingly significant.

Low pressure gas adsorption (LPGA) of gaseous adsorptives (Ar, CO₂, C₂H₆, He, CH₄, Kr, N₂, Xe, water vapour, etc.) on coal (adsorbent) has been widely used to determine the surface area, pore structure (sizes and distribution) and porosity of coal and other carbonaceous materials. This is because gas adsorption methods are less costly and are more convenient to use than some of the other more advanced techniques [56]. CO₂ and N₂ are the most commonly used gases. Other widely used methods used to probe surface areas and porosity properties of solids are: wide angle x-ray diffraction (WAXRD), small angle x-ray and neutron scattering (SAXS and SANS), mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermoporometry, and NMR methods.

Although Marsh [57] has noted that it is difficult to model the mechanism of gaseous adsorptive-solid adsorbent adsorption process using LPGA, attempts had been made to use LPGA results to obtain information on microporous and mesoporous materials and describe the mechanism of adsorption [46, 50, 53, 54, 56-63]. Adsorption in microporous materials

(pore width $< 20 \text{ \AA}$) is dominated by the physical interactions (van der Waals dispersive forces) between adsorptive molecules and the pore walls of the solid adsorbent [46, 50, 53, 54, 58-63] which is complicated by the fact that some pores are small enough for the adsorption potentials of the opposite pore walls to overlap [56, 59, 62]. As a result, micropores fill through a continuous process-without phase transition- in supercritical gases. The filling of the narrowest micropores of width equivalent to not more than two or three molecular diameters is claimed to take place at very low relative pressures ($P/P_0 < 0.01$). This process is referred to as “primary micropore filling” [56, 62]. The filling of the wider micropores may occur over a much wider range of relative pressure ($0.01 \geq P/P_0 \geq 0.2$). In this mechanism, adsorbent-adsorbate interaction energy in the pore center is relatively very small and the increased adsorption with respect to increasing P/P_0 , is mainly due to the co-operative adsorbate-adsorbate interactions.

In gas sorption measurements at subcritical conditions, sorption in mesopores plays a vital role in the determination of porosity and surface areas. The sorption characteristics of mesoporous solids depends not only on the gaseous adsorbate and solid adsorbent pore wall attraction (as in microporous solids), but also on the attractive interactions between the gaseous adsorbate molecules (more significant for mesoporous solids). In sub-critical low pressure gas adsorption, this leads to the occurrence of mono- to multi-layer adsorption and capillary or pore condensation at $P/P_0 \geq 0.2$. At the onset of pore condensation, the pore walls are already covered by a multilayer of adsorbed film. The stability of the adsorbed multilayer film in the pores is dependent on van der Waals interactions, the surface tension and curvature of the liquid-vapour interface [56, 64-66]. When the adsorbed film thickness is small, adsorption is by dispersive forces. However, when the adsorbed film becomes thicker, the adsorption potential arising from the surface becomes less important, and the surface tension and curvature effects (adsorbate-adsorbate interaction) become more significant. Capillary or pore condensation may occur in the core of the pore, if the fluid film thickness grows beyond a certain critical thickness, when the multilayer film can no longer be stabilised by the intermolecular forces in the core fluid. This is a phenomenon where gaseous adsorbate condenses to a liquid-like phase in pores at a pressure less than the saturation pressure (P_0) of the bulk fluid. This marks a shift in phase transition under the influence of the attractive and dispersive adsorbate-pore wall interactions. The occurrence of pore condensation in mesoporous solid adsorbents is expected as long as the contact angle is below 90° . For N_2 adsorption at 77 K, a contact angle of 0° (complete wetting) is usually assumed [56]. Thus, adsorption in mesoporous material involves fluid phase transition and pore condensation,

which may give rise to hysteresis. Hysteresis occurs when the vapour-liquid transition (pore condensation) is delayed due to the existence of metastable adsorption film and hindered nucleation of liquid bridges [56, 64-72].

Generally, some pores are not reachable by the adsorbate gas, because the pore throat that connects them to the outside may be too narrow for easy penetration. If the throat diameter is only slightly greater than the size of the gas molecule, physical interactions between the throat wall and adsorbate modify the rates of penetration. This phenomenon is referred to as molecular sieving effect [47-50, 53, 57]. Small differences in the sizes of adsorbate gas molecules can lead to significant differences in the mechanisms or processes necessary for diffusion through a given pore opening to occur. The diffusion rate and the activation energy of the process is strongly dependent on the temperature of the system [47-49, 53, 57, 60, 63].

Surface area and porosity values obtained from CO₂ adsorption have been found to be much greater than the values from N₂ adsorption on coal [47, 48, 54]. This has been attributed to activated diffusion; the low thermal energy associated with N₂ at the analysis temperature during N₂ adsorption at -196 °C means that gas penetration is slow, whereas the thermal energy associated with carbon dioxide at 0 °C [47-50, 52, 53, 57, 60] is much greater: the rate of diffusion of CO₂ through cylindrical pores of molecular dimension at 0 °C has been found to be 10⁵ times higher than that of N₂ at -196 °C [53].

The low pressure gas adsorption of CO₂ on coal usually takes place at pressures < 1 atm and the shorter analysis time (< 10 hours) usually exhibited by CO₂ adsorption analysis make coal swelling an insignificant contributor to the final results obtained [48, 53, 57].

Mercury Intrusion Porosimetry (MIP) is another standard method of determining the porosity and surface areas of coals, but is limited only to meso- and macro-porosity [73-76]. Although the application of the macroporosity of bituminous coals to most of its utilisation processes is still very limited, as noted by Ross and Bustin [77], the understanding of this property is relevant in predicting total gas capacities of coals when used for CO₂ sequestration.

Each of these conventional methods only probe specific pore size ranges and thus cannot be used independently to describe the overall porosity or pore size distribution of the sample. Standard measurements from CO₂ low pressure gas adsorption technique can only probe pores in the range: $3 \text{ \AA} \leq dp \leq 5 \text{ \AA}$ (lower micropore range); while pores accessible to N₂ low pressure gas adsorption analysis are claimed to cover the range: $17 \leq dp \leq 3000 \text{ \AA}$ (higher micropore and entire mesopore range). Effective pore size distribution (PSD) analysed using MIP is in

the range: $30 \leq dp \leq 600000 \text{ \AA}$ ($60 \text{ }\mu\text{m}$) (meso- and macro-pore range). This means that a more complete description of the pore structure, surface area and porosity of coals has to combine results obtained from these three techniques. Unfortunately, properties of micropores in the size range: $5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$ are not readily picked up by any of these three widely used standard methods.

In recent times, Small Angle X-ray (SAXS) has gained popularity as a coal characterisation tool. SAXS has the advantage of probing a wider range of pore sizes in a single experiment than MIP or gas adsorption [47, 52, 78-82]. When X-rays penetrate materials, they are scattered off density contrasts within the material at a range of angles. The resulting scattering pattern, which is specific to the structure of the material, can be analysed to estimate surface areas and porosity features of the sample. Because SAXS scatters off density contrasts, in coals it not only scatters off density differences between the material and empty pores, but also off density differences between their organic and inorganic components. Thus, results from SAXS need to be corrected for the influence of coals' mineral matter. One way to correct for this is to assume that the mineral matter size distribution is the same as that of the empty pores [82].

2.2.3.2 *Density of coal*

The density of coal is an important physical property of coals that has been well studied by various investigators using widely accepted techniques including: helium pycnometry (HP), mercury intrusion porosimetry (MIP) and other fluid displacement methods [75]. [46, 47, 52, 57, 75, 76, 83-92]. The widely accepted techniques used to access the density of coals were summarised by Senel et al. [52] and include helium pycnometry, mercury intrusion porosimetry and other fluid displacement methods [75]. Two forms of density have been reported to exist in coals: the 'true' density, which is defined as the weight of a unit volume of pore-free solid, and the 'apparent' or skeletal density defined as the weight of a unit volume of solid including some pores. The 'true' density is generally measured by helium with the assumption that helium is a small molecule and able to access all of the pore volume with negligible adsorption, with the assumption that all pore voids are accessible [52]. Nevertheless, X-ray diffraction studies with a suite of American coals have shown that there is some pore voids in high-rank coals that are inaccessible to helium [46]. Hence, the helium density determined for such coals would apparently be lower than its 'true' density. It has been demonstrated that the helium density of coals decreases with increasing elemental carbon content up to 82 wt.%, daf, passes

through a minimum in the range of elemental carbon content 82 to 86 wt.%, dafb % and increases sharply with further increases in elemental carbon content [47, 83]. This U-shape trend was also observed for the variation of coal micropore surface area with elemental carbon content or rank of coals [46, 51].

The bulk density of coals, which includes micropores, macropores, and inter-particle voids, is obtained by fluid displacement methods including MIP [76, 86-93]. The bulk densities of 17 Asian coals of various ranks was measured in methanol, n-hexane, and mercury and compared with the helium density by Toda [90]. For all the fluids used, the density values obtained were higher for lower and higher rank coals and displayed a minimum at about 85 wt.%, dafb elemental carbon content. The densities and porosities of coal macerals were measured using helium, mercury, methanol, water, and CO₂ by Walker et al. [85]. They found that densities measured in methanol, water, and CO₂ were usually greater than those measured in helium, and attributed these discrepancies to the penetration of some solvents into pores inaccessible to helium, and probably uptake by and/or diffusion of these molecules into the polymer structure of organic matter of the coal structure, which results in swelling. However, they noted that CO₂ uptake by the macerals was primarily due to pore filling and not penetration into the coal structure [85]. Although MIP is widely used in the determination of the bulk density of coals, data from MIP measurements need to be corrected for coal compressibility at high pressures [76, 86-89, 91-94]. Toda and Toyoda [91] reported a sinusoidal trend of coal compressibility with elemental carbon content (a proxy of rank), but obtained a linear trend between coal compressibility and Knoop Hardness. This suggests that coal compressibility is more dependent on factors such as Knoop hardness [91], spot of sampling [94] and swelling properties of the sample, rather than rank.

2.2.3.3 Swelling of coal

It is generally known that coal swells to different extents during sorption of adsorbate (liquids or gases) [95-103]. Toda [90] measured the variation of the differences in the volume of coal estimated by CO₂ displacement and that estimated by He displacement for 17 coals of various rank. His reported data shows that the volume occupied by coal measured by CO₂ was always lower than that measured by He indicating that the CO₂ could penetrate into micropores which were inaccessible to He, which may be attributed to imbibition (Henry's law dissolution).

Reucroft and Patel [96] investigated the swelling and shrinkage of a Kentucky coal in different gases: CO₂, He, Xe, and N₂ using a dilatometric technique. They reported that He and N₂ did not cause any significant swelling or shrinkage of the samples. However, CO₂-induced expansion was significant. More so, considerable contraction was observed when CO₂ was evacuated from the sample. Very little swelling was observed for xenon [96], which has been disputed by Sakurovs et al. [104]. Assuming isotropic swelling, volumetric swelling in the range of 0.36% to 4.18% has been reported at pressures up to 15 bar, and the degree of swelling in CO₂ tends to decrease with increasing coal rank [95].

2.2.4 Chemical-structural properties of coal

The carbon crystallite structure of coal describes the microtextural and microstructural properties of the carbon contained in them. Evidence from atomic level characterisation using high-resolution transmission electron microscopy (HRTEM) [11, 39, 105-108] and wide-angle X-ray scattering - carbon fraction analysis (WAXRD-CFA) [11, 108-120] show that carbon crystallites in coal consist of a layered structure of covalently linked polycyclic aromatic units. Resulting data from WAXRD-CFA includes chemical-structural properties such as aromaticity, fraction of amorphous carbon, and the degree of disorder of the carbon crystallites in coal [10, 11, 22, 112, 116, 121]. The chemical-structural forms of carbon in coals have been studied extensively using ¹³C NMR spectroscopic techniques [22, 108, 122-125], which has enabled the quantification of aliphatic as well as aromatic carbon contents, and other carbon moieties in coal. Reports of similarities between chemical structural features of coals determined from WAXRD-CFA and ¹³C NMR do exist [11, 22]. Attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy has been successfully applied to study and elucidate the functional groups present in coals as a function of the type of hydrogen bonding present in coal [22, 126-128]. It is worthy to note that there has been some success in obtaining semi-quantitative and quantitative data from ATR-FTIR spectra [129-131], which is useful in describing, at a molecular level, some interactions in coal.

The molecular structural features of coals have been studied by image analysis of the high resolution fringe images usually acquired from HRTEM analytical technique. Sharma et al. [105, 106] have successfully studied the carbon crystallite and microstructure of coal through the lattice fringes of coals from HRTEM image analysis of the thin edges of the coal samples. HRTEM image analysis of coals show condensed aromatic units as forming stacks parallel to

each other. The results of Sharma and co-workers [105, 106] show significant differences between vitrinites and inertinites. They reported that coal vitrinite contained fewer stacked layers than coal inertinite, which is more oriented and contains more stacked layers. They also found that the inter-layer spacing between aromatic sheets in stacks is between 3.3 and 4.0 Å, similar to results obtained from WAXRD-CFA [11, 108, 112, 116]. The average crystallite diameter ranged from 10 – 13 Å, and was found to increase with increasing coal rank [106]. The chemical-structural properties of coal has also been found to correlate well with the physical-structural properties of coal, especially density and porosity properties [10, 11, 55].

In summary, data on the chemical-structural properties of coals obtained from these techniques have shown that the molecular skeleton of bituminous, and higher rank coals consist mainly of aromatic sheets or layers [15, 16, 22, 39, 105, 106, 109, 112, 113, 116, 132-134]. Detailed discussion on the chemical-structural properties of coals is presented in Chapter 4.

2.3 Carbon dioxide capture and sequestration (CCS)

Carbon dioxide (CO₂) capture and sequestration (CCS) is a process consisting of various technologies aimed at reducing anthropogenic CO₂ emissions from industrial and energy-related sources, as one of the options of mitigating global climate change. Thus, CCS is not a single technology [135-140], but an array of technology that can be synergised with the ultimate aim of reducing CO₂ emissions. CCS involves [141]:

- (i). The capture, separation and compression of anthropogenic CO₂ from large industrial point sources for example fossil fuel power generation facilities, coal to liquid (CTL) plants, metallurgical industries and other energy-related sources. Various anthropogenic CO₂ capture option are available as illustrated in Figure 2.2 [141-143]. These include:
 - Post-combustion capture from power plants,
 - Pre-combustion capture from integrated gasification combined cycle (IGCC) power utilities, CTL facilities (eg. Sasol) and other gasification systems,
 - Oxy-fuel (oxygen-rich) combustion system,
 - CO₂ capture from other fossil fuel industrial utilisation systems, eg. Metallurgical industries, paper production, etc.

- (ii). The transport of the captured, separated, and compressed CO₂ (usually in the liquid phase) to a candidate geological storage location using pipelines or trucks [144, 145].
- (iii). The safe and permanent long-term storage of the CO₂ in deep candidate geological storage sites, thus, isolating the CO₂ from the atmosphere.

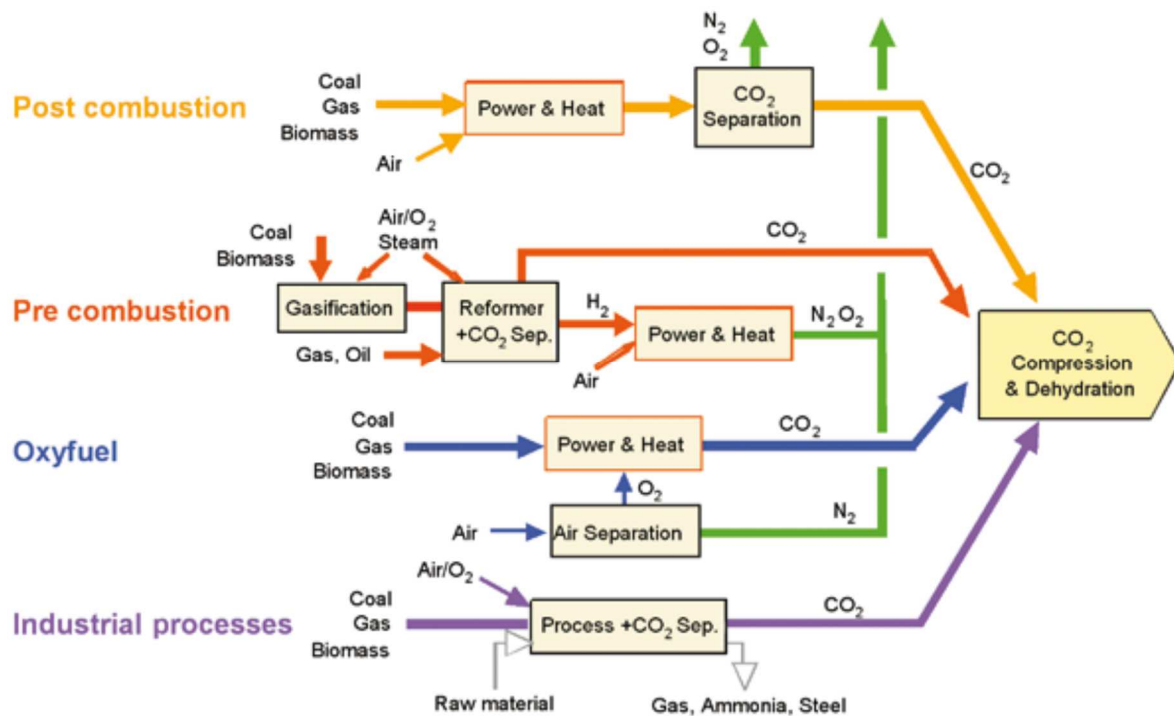


Figure 2.2: Visual overview of CO₂ capture processes and systems [141].

Geological locations for the storage of CO₂ include: ocean disposal of CO₂ [141, 143, 146-153], depleted oil and gas reservoirs with the synergy of enhanced oil and gas recovery (EOR & EGR) [139, 142, 152, 154-158], deep saline formations [152, 158-166], and “unmineable” coal seams with the synergy of enhanced coalbed methane (ECBM) recovery [11, 141, 142, 145, 152, 155, 167-170]. For a candidate geological location to be suitable for CO₂ storage, it must possess the following characteristics [171]:

- Capacity, to contain the projected volume of CO₂
- Injectivity, to take in the captured CO₂, and
- Confinement, to prevent the migration and seepage of the buoyant and mobile CO₂ from the storage spaces to other places in the subsurface, especially to shallow potable groundwater and or to the surface.

A conceptual overview of the geological storage option for CCS is shown in Figure 2.3.

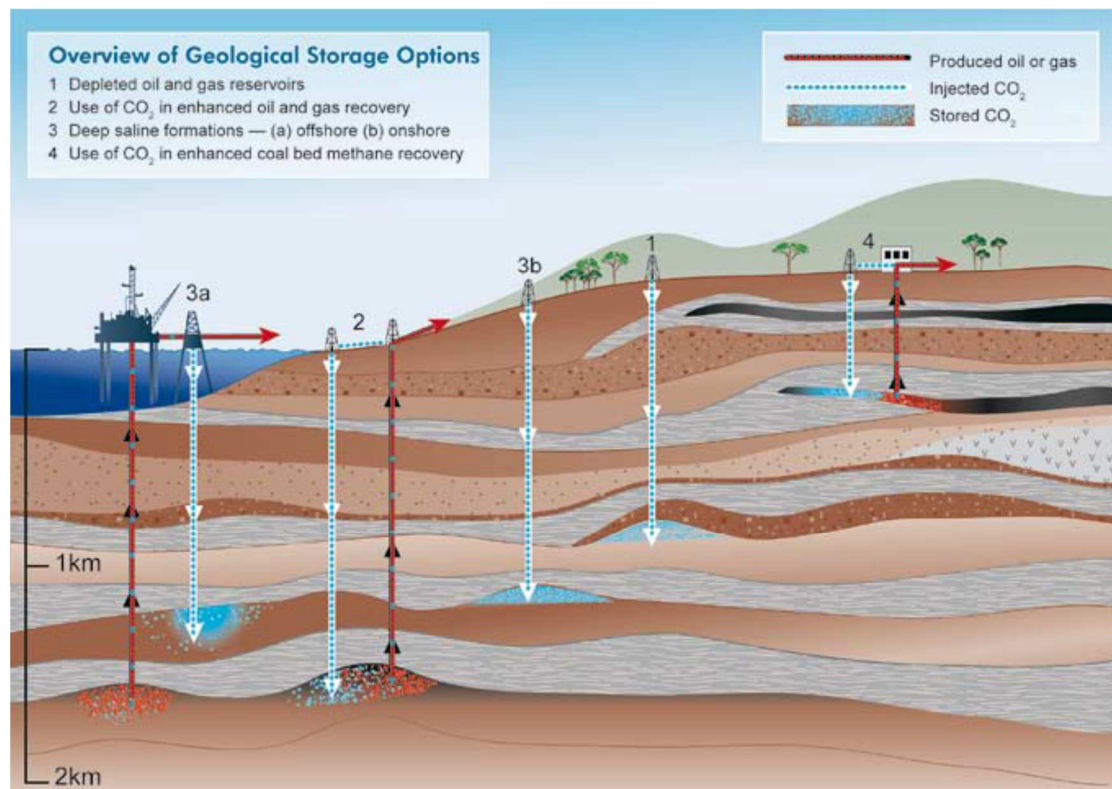


Figure 2.3: Visual overview of the geological storage options for CCS [141].

CCS is only one of the options in the portfolio of mitigation actions for the stabilisation of atmospheric greenhouse gas (GHG) concentrations. Other mitigation options include [141, 143]:

- (i). Improvement and optimisation of energy efficiency,
- (ii). Switching to less carbon-intensive fuels,
- (iii). Use of nuclear power,
- (iv). Use of renewable energy sources,
- (v). Enhancement of biological sinks, for example, CO₂ capture and storage by microalgae, and photosynthesis in plants,
- (vi). Ocean fertilisation with limiting nutrients,
- (vii). Non-biological capture of CO₂ from air
- (viii). Reduction of non-CO₂ greenhouse gas emissions.

CCS has the potential to reduce overall mitigation costs and increase flexibility in achieving greenhouse gas emission reductions. The widespread application of CCS would depend on technical maturity, costs, overall potential, diffusion and transfer of the technology to

developing countries and their capacity to apply the technology, regulatory aspects, environmental issues and public perception [141, 158, 171-179].

2.3.1 Storage mechanisms of CO₂ in geological formations

The overall effectiveness of storage of the captured CO₂ in geological formations largely depends on the CO₂ storage mechanism, which is a combination of geophysical and geochemical trapping. The most effective storage sites are those where stored CO₂ is immobilised as it is trapped permanently under a thick, low-permeability seal, converted to solid minerals, adsorbed on the surfaces of coal micropore structures or through a combination of physical and chemical trapping mechanisms [141, 142, 152, 159, 171, 172, 180].

Different geological trapping mechanisms have been identified that can contribute to immobilisation, isolation, and ultimate retention of the stored CO₂ over geological time [141, 145, 152, 171]. These are: structural trapping, capillary or residual-gas trapping, solubility trapping, and mineral trapping. While structural and capillary trapping are geophysical trapping mechanisms, solubility and mineral trapping are geochemical trapping mechanisms [171, 180]. The geo-physical trapping mechanisms are considered as primary CO₂ immobilisation processes; while the geochemical trapping mechanisms are regarded as secondary CO₂ immobilisation processes [152]. The relative significance of these processes is expected to change over time as CO₂ migrates and reacts with the geological media (rocks) and interacting fluids [142, 152, 159]. A conceptual illustration of the differences between various CO₂ trapping mechanisms in geological media through the CO₂ storage operating timeframe, and the evolution of trapping mechanisms over geological time with their contribution CO₂ storage security is presented in Figure 2.4. The reliance on the primary geological media seal or caprock to contain and retain the injected CO₂ decreases as the secondary CO₂ immobilisation processes begin to dominate [152], leading to a decrease in, or even complete loss of injectivity [169-171, 180]. It should be noted that actual trapping mechanisms and evolution will be expected to vary from one geological site to the other [152]. The geological storage security is highly dependent on a combination of geophysical and geochemical trapping. Over time, the geophysical process of residual CO₂ trapping and geochemical processes of solubility trapping and mineral trapping increase [141, 171].

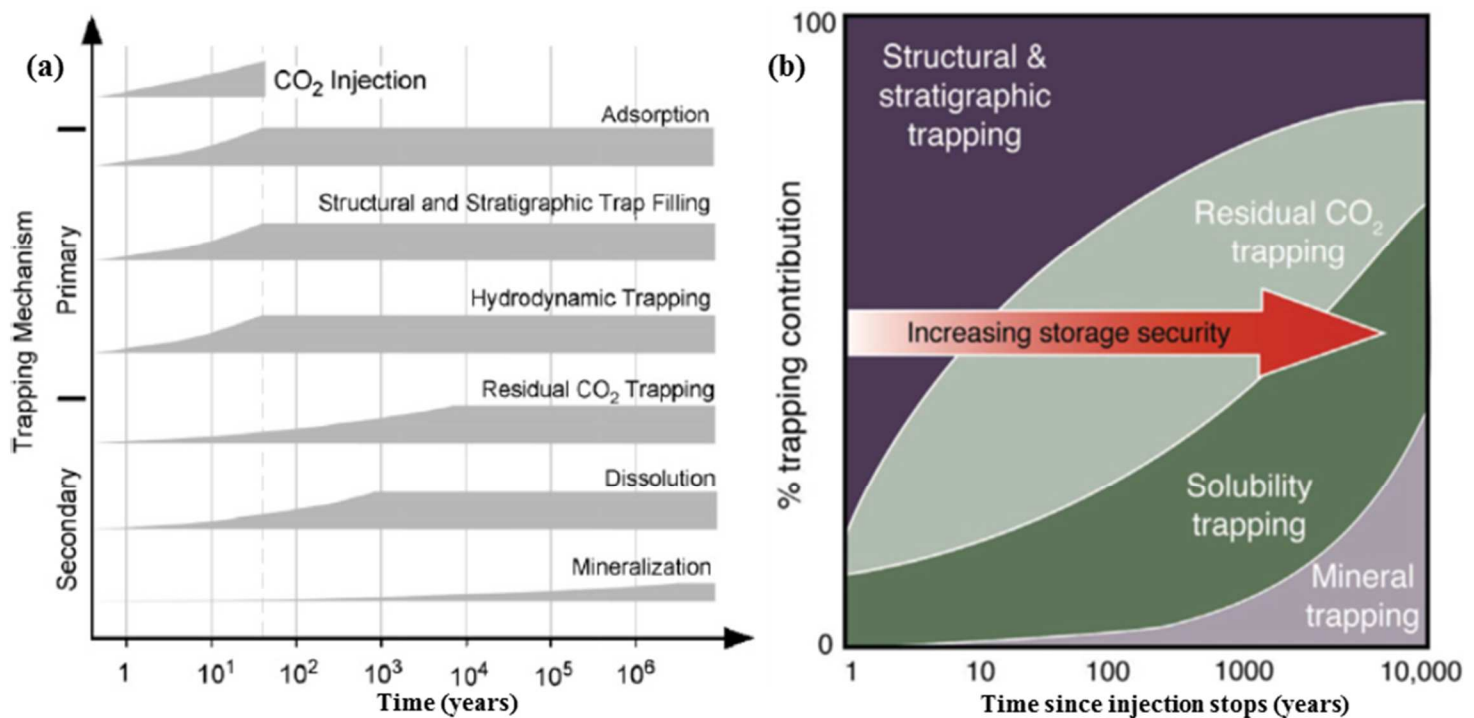


Figure 2.4: Differences between various CO₂ trapping mechanisms in geological media: (a) Operating timeframe, and (b) Conceptual illustration of the evolution of trapping mechanisms over time and their contribution to storage security [141, 152, 171]

2.3.1.1 Structural trapping

Structural trapping in stratigraphic and structural traps is the most important process in the early stages of CO₂ storage. The main prerequisite for securing mobile CO₂ is the presence of a thick and fine-textured rock of low permeability [152, 171] that serves as a seal above the sequestration reservoir. The seal should provide an effective permeability and capillary barrier to buoyancy-driven upward migration of CO₂. Structural trapping is also the most prevalent CO₂ trapping mechanism in coal seam storage of CO₂ [171, 180-182].

2.3.1.2 Capillary trapping

Capillary or residual-gas trapping occurs in the pore space of geological media at irreducible gas saturation. Thus the CO₂ is immobilised by the interfacial tension between CO₂ and geological formation water, and seepage of CO₂ is impossible even if a pathway is available

[171]. Capillary trapping primarily starts after the stop of CO₂ injection and formation water begins to imbibe or absorb into the CO₂ plume. The trailing edge of the CO₂ is immobilised, slowing up-dip migration. Capillary trapping is particularly important for sequestration in dipping aquifers that do not have structural closures [152].

2.3.1.3 Solubility trapping

Solubility trapping is a geochemical trapping process where the injected CO₂ dissolves into the pore water of the geological formation. The amount of gas that can dissolve into the geological media water depends on several factors including: pressure, temperature, and pH; and the salinity of the brine in place (especially for saline aquifers). At the in situ conditions expected for most geological formations (ambient to ≈ 150 °C and a few hundred bars total pressure), CO₂ solubility increases with increasing pressure (or depth) but decreases with increasing temperature and salinity [152]. Czernichowski-Lauriol et al. [183] demonstrated in laboratory experiments that CO₂ dissolution is rapid at high pressure in the presence of water in the pore spaces of geological media. However, in a real injection system, CO₂ dissolution may be rate-limited by the magnitude of the contact area between the CO₂ and the geological formation fluids. The main advantage of solubility trapping is that once the CO₂ is dissolved, there is less CO₂ subjected to the buoyant force that causes the upwards migration or seepage of CO₂ [152, 171].

2.3.1.4 Mineral trapping

This mechanism occurs when dissolved CO₂ reacts directly or indirectly with minerals in the geological formation, promoting precipitation of carbonate minerals [152, 164, 171, 184-187], especially in the presence of Ca and Mg rich minerals [164, 184-188]. Mineral trapping is attractive because it could immobilise the injected CO₂ for very long periods [152, 164, 184-186, 188]. However, the process is thought to be comparatively slow because it depends on dissolution of silicate minerals, so the overall impact may not be realised for tens to hundreds of years or longer [152]. However carbonate trapping by calcium species (Ca²⁺) may be relatively more rapid, which is more significant in saline aquifers or alkaline waters [164, 184].

2.4 Sequestration of CO₂ in coal seams

The CO₂ captive properties as well as its holding capacity in coal seams is an essential area of research both for an economic assessment of candidate coal seams and for a better understanding of the coal-CO₂ interactions. Due to the fact that CH₄ is the dominant gas in coal seams [3, 8, 13], the coalbed methane (CBM) reservoir capacity and the parameters that affect the adsorption capacity of CH₄ have been investigated extensively, aimed at the evaluation of the gas-in-place (GIP) and to enhance the safety of coal mining [8, 168, 189-192]. The CBM capacity of coal seams can be estimated by direct methods which measure the volume of CH₄ released from a coal sample sealed into a desorption canister first reported by Every & Dell'Oso [191] and others [8, 13, 190, 192-197]; or by indirect methods based on the adsorption-desorption isotherms data obtained from laboratory experiments [102, 104, 192, 195, 198-205]. The estimation of the CBM content of coals by different methods has been reviewed by several authors [8, 13, 145, 155, 190, 192]. However, data pertaining to the CO₂ storage capacity of coal seams at in situ (in-seam) conditions are limited. Unlike CH₄ content of coal seams that can be determined by direct methods, the CO₂ sorption and or storage capacity of coals is generally estimated indirectly from the adsorption isotherm data, usually by applying some empirical isotherm model expressions. The most widely used adsorption isotherm models, for the description of the adsorption isotherms of microporous adsorbents including coals are: the Langmuir monolayer model, the Brunauer-Emmet-Teller (BET) multilayer model, and the Dubinin-Radushkevich pore filling equation [52, 61, 206, 207], and modified variants of these models.

2.4.1 Gas Adsorption

Adsorption occurs when a gas or vapour (usually referred to as adsorbate) is brought into contact with a solid, part of the gas or vapour is taken up and remains on the outside attached to the surface. It is believed that the term adsorption was first used by Kayser [208-210] in 1881 to explain the condensation of gases on surfaces, in contrast to gas absorption in which gas molecules penetrate the bulk phase of the absorbing solid [209]. Adsorption is a complicated process and different expressions are used interchangeably to define it. While adsorption is simply used to imply the condensation of gases on free surfaces, the term, absorption and/or imbibition is used to describe the penetration of gas molecules into the mass of the absorbing solid. Hence the term, sorption, was proposed by McBain [211] in 1909 as a

complete description of mass transport into a solid, encompassing surface adsorption, absorption by penetration into the solid and condensation within pores [209, 210, 212]. However, the IUPAC definition of adsorption as the enrichment of one or more components gases or vapour in an interfacial solid layer is generally accepted [44, 45, 209]. Thus, in adsorption systems, an excess of the gas or vapour molecules exists at the adsorbate-adsorbent interface, resulting to a selective collection and concentration of the gas or vapour onto the solid surfaces.

Adsorption is divided into two sub-categories of physical adsorption (physisorption) or van der Waals adsorption and chemical adsorption (chemisorption), and the adsorption process can be classified depending on whether chemical bonds are formed during the process. Physisorption is applicable to all adsorbate-adsorbent systems provided the conditions of pressure and temperature are suitable, whereas chemisorption may only occur if the system is capable of making or creating chemical bonds. In an adsorption system, adsorbate molecules interact with the surfaces of the adsorbent with forces originating either from the “physical” van der Waals interaction or from the “chemical” hybridization of their orbitals with those of the atoms of the solid adsorbent [45]. Depending on which contribution dominates the adsorption process, adsorption is generally classified as chemical adsorption or chemisorption and physical adsorption or physisorption. Physisorption is applicable to all adsorbate-adsorbent systems as long as the conditions of pressure and temperature are suitable whereas chemisorption may only occur if the system is capable of breaking or forming a chemical bond.

2.4.1.1 Physisorption

Physisorption is a dynamic process where an equilibrium state exists with gas molecules and the interface between the adsorbate and adsorbent. No chemical bonds are formed during physisorption, and the attraction between the adsorbate and adsorbent occurs by the formation of inter-molecular electrostatic forces, such as van der Waals forces from induced dipole-dipole interactions [209, 213], or may be dependent on the physical configuration of the adsorbent [56]. Dispersion forces are the result of rapid fluctuations in the electronic density of one adsorbent molecule inducing an electrical moment in a second atom [209, 213]. Since there is no chemical bond between adsorbate molecules and the solid surface, physisorption is generally a reversible process, usually achieved by temperature or pressure swing, and the solid adsorbent can be regenerated. In addition, the energy associated with physisorption is usually

low compared to the product of the adsorption rate and absolute temperature (kT) at room temperature. How easy a reaction is to reverse depends significantly on the ratio of the absolute temperature to the heat of sorption. The process of physical adsorption into the microporous structure can be modelled using the theory of Dubinin [62]. Due to the energetic interactions between the adsorbate and the pores surfaces, the mechanism of physisorption is dependent upon the size of the adsorbate molecule in comparison with the pore width.

Table 2.1: Properties of physisorption and chemisorption

Properties	Physisorption	Chemisorption
Heat of adsorption (kJ/mol)	20 – 40 kJ/mol; equivalent to the heats of liquefaction or condensation of the gas.	60 – 4000 kJ/mol; equivalent to bulk-phase chemical reactions activation energy
Rate of adsorption (at 273 K)	Fast	Slow
Temperature dependence of uptake (with Increasing T)	Decreases	Increases
Desorption	Easy. Achieved by pressure or temperature swing	Difficult. High temperature required to break bonds or impossible
Desorbed specie(s)	Adsorbate unchanged	May be different to original adsorbate
Adsorbent regeneration	Adsorbent can be regenerated	Cannot be regenerated
Specificity	Non-specific	Very specific
Surface coverage	Mono- or multi-layer, pore-filling (dependent on operating conditions and sample pore surface physical properties)	Only monolayer

In physisorption, adsorbate molecules initially adsorb into the pores with the largest free energy of adsorption (which is negative), with negligible activated diffusion effects, then proceeds through filling of progressively larger pores, with decreasing energy and porosity [53, 56, 58, 65, 209]. Some pores are capable of accommodating two or three adsorbate molecules and, thus, may undergo co-operative adsorption effects by reducing the available pore volume for

subsequent adsorption (pore-filling), thus increasing the energy and the adsorption potential of the pore [56, 62, 209]. Physisorption is generally an exothermic process due to the increased ordering of the adsorbate on the adsorbent surface, leading to decreasing entropy of the system [44, 56, 57, 209, 214]. Thus, the amount of adsorbate adsorbed onto the adsorbent, is expected to decrease with increasing temperature as a reduction in the thermal energy supplied to the system favours the exothermic process of physisorption by increasing the equilibrium uptake, except in the case of activated diffusion [46, 68, 209]. It has been demonstrated from experimental data that physisorption is independent of the adsorbent's surface chemistry [214]. A comparison of physisorption and chemisorption is summarised in Table 2.1.

2.4.1.2 Chemisorption

During chemisorption, the adsorbate gas or vapour is bound to the solid adsorbent's surface by the formation and or breaking of chemical bond(s), by chemical reaction, resulting in the adhesion of the adsorbate molecules into the adsorbent. Chemisorption is far less common than physisorption. Due to the chemical bonds formed, during chemisorption, regeneration of the adsorbent is often difficult or impossible [44, 61], and the energy generated is the same order of magnitude as the heat of reaction [209, 212, 215]. Due to the fact that chemical bonds are formed during chemisorption, desorption of the adsorbed phase may yield products which are chemically different to the original adsorbate.

2.4.1.3 Adsorption isotherm

The quantity of gas adsorbed onto a solid sample, V , is a function of the mass of the sample, the temperature and pressure at which adsorption took place, and the nature of both the solid adsorbent and the adsorbate gas [44, 61, 209].

$$V = f(P, T, \text{adsorbate}, \text{adsorbent}) \quad (2.1)$$

For an isothermal adsorption system, Equation 2.1 simplifies to:

$$V = f(P)T, \text{adsorbate}, \text{adsorbent} \quad (2.2)$$

By introducing boundary conditions within the limits of vacuum and the saturation vapour pressure of the adsorbate gas, the pressure term may be expressed in terms of the relative vapour pressures, P/P_0 . Hence:

$$V = f\left(\frac{P}{P_0}\right)T, \text{adsorbate}, \text{adsorbent} \quad (2.3)$$

Equation 2.3 gives a universal basis upon which all isotherms may be displayed in order to make the comparison of results easier. The above relationship may be used to graphically represent different adsorbate uptake scenarios in the form of an adsorption isotherm. Adsorption isotherms are generally plotted on the basis of relative pressure, P/P_0 , versus adsorbed amount of adsorbate, to allow comparisons to be made. Adsorption data may alternatively be expressed in terms of an isobar, the variation in uptake with temperature at constant pressure, or an isostere, the change in temperature with pressure at a constant surface coverage. Isotherms provide a significant amount of information about the adsorbent used and the interaction with the adsorbate in the system, including:

- Assessment of the surface chemistry and fundamentals involved in the adsorption process;
- Estimation of the surface area, pore volume and pore size distribution;
- Determination of the efficiency profiles for carbons used in industrial processes.

The interpretation of adsorption isotherms can yield a large amount of information about the processes involved, as outlined above, but this is only possible upon careful analysis of the data obtained and this can often lead to confusion in the interpretations made. An understanding of the adsorption mechanisms involved in the different classes of porosity is essential to explain the shapes observed.

Based on the IUPAC [44, 155, 209, 215], adsorption isotherms can be classified into six significantly different scenarios as adsorption isotherm types I-VI, describing the physical

adsorption process. A visual illustration of adsorption isotherm classification is shown in Figure 2.5. Note that the two lines in adsorption isotherm types IV and V are hysteresis loops.

In **type I** adsorption isotherm, often referred to as Langmuir type isotherm, pores are typically microporous with the exposed surface residing almost exclusively inside the micropores, which once filled with adsorbate, leave little or no external surface for further adsorption. These are typical of adsorbents with a predominantly microporous structure, as micropore filling dominates the process. However, type I isotherm has been reported to also occur during the adsorption of gases onto non-porous solid, in which case the formation of a monolayer of adsorbate molecules on the adsorbent dominates [44, 45]. This type of isotherm is often called a Langmuir type isotherm.

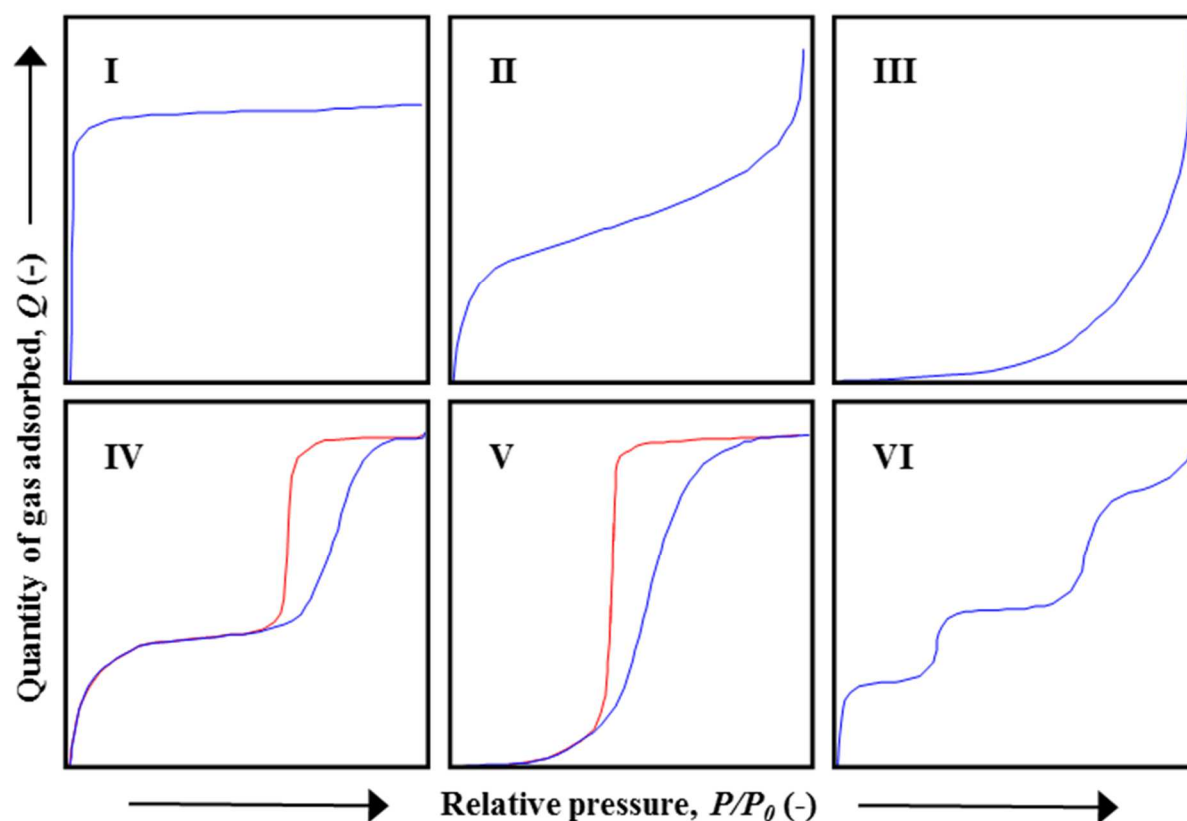


Figure 2.5: Visual illustration of adsorption isotherm classification: blue line- adsorption; red line- desorption. Adapted from [44, 58, 61, 209].

Type II adsorption isotherm, typically describes the physisorption of gases or vapours onto non-porous solids. Adsorption is firstly controlled by monolayer coverage, followed by multilayer coverage at higher relative pressures. This isotherm is characterised by an inflection point, which represents the completion of the monolayer coverage and the beginning of the formation of multilayers. Carbons with mixed micro- and meso-porosity usually gives type II isotherms.

Type III adsorption isotherm is typical of non-porous or macroporous adsorbent. This class of isotherm is characterised by weak adsorbate-adsorbent interactions [45, 56] and is most commonly associated with both non-porous and microporous adsorbents [55]. The weak interactions between the adsorbate and the adsorbent lead to low uptakes at low relative pressures. However, once a molecule has become adsorbed at a primary adsorption site, the adsorbate-adsorbate interaction, which is much stronger, dominates the adsorption process, resulting in accelerated uptakes at higher relative pressure.

Types IV isotherm, which is similar to the Type II, is typical for a mesoporous adsorbent. It displays a hysteresis loop (the shape of which is unique to each adsorption system) due to capillary condensation, with the significant presence of mesoporosity. Type IV isotherms usually show a limited adsorption at high relative pressures.

Type V adsorption is typical for non-porous or macroporous adsorbents and is observed for weak adsorbent-adsorbate interactions and are convex to the relative pressure axis [44, 209]. These isotherms are also indicative of microporous or mesoporous solids.

Although rarely observed, the **type VI** isotherm was primarily proposed as a hypothetical isotherm by Halsey [209, 216]. The stepped shape is due to the complete formation of monomolecular layers before progression to a subsequent layer, and may arise from adsorption onto extremely homogeneous, non-porous surfaces where the monolayer capacity corresponds to the step height. One example of type VI isotherm known to exist is the adsorption of krypton on annealed carbon black at 90 K [216].

It is well known that coal is a microporous solid, thus, the adsorption of gases such as CO₂, CH₄ and N₂ on coals generally exhibits a type I isotherm. However, various adsorption isotherm types have been reported for CO₂ [217, 218] and water vapour [219] adsorption onto coals.

2.4.1.4 Adsorption mechanisms of gases on coal

The adsorption mechanisms of gases and vapours in coals and other microporous and mesoporous carbonaceous materials have been reviewed by Marsh [57], and Thommes [56]. The widely accepted adsorption mechanisms are [57, 58, 61, 62, 220, 221]:

- (i). The Langmuir monolayer adsorption on the pore surface of the adsorbent [221],
- (ii). The BET multilayer adsorption mechanism, which is an extension of the Langmuir's monolayer adsorption mechanism [58, 61], and
- (iii). The Dubinin pore-filling mechanism [62, 220].

A visual illustration of these mechanisms, adapted from Ozdemir [222], is presented in Figure 2.6 (i-iii).

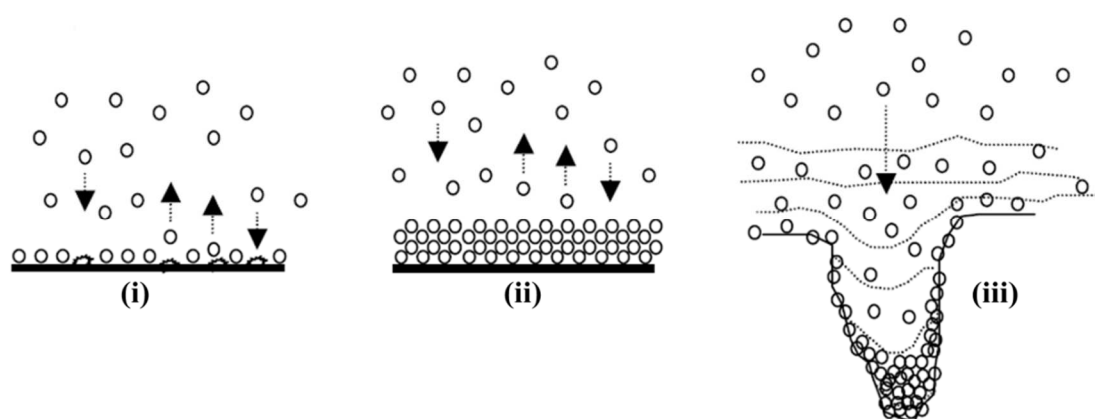


Figure 2.6: A visual illustration of adsorption mechanisms: (i) Langmuir's monolayer adsorption model, (ii) BET's multilayer adsorption model (iii) Dubinin's theory of volume filling of micropores (TVFM) pore-filling model [222].

The Langmuir monolayer adsorption model is a semi-empirical isotherm model, which was derived using the proposed kinetic mechanism from both kinetic and statistical mechanical theories [221]. Figure 2.6 (i) shows an illustrative schematic of the simplistic adsorption mechanism of the Langmuir isotherm model [222]. This isotherm was based on different assumptions, one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. It is based on four assumptions:

- The surface of the adsorbent is homogeneously uniform, that is, all the adsorption sites are energetically equivalent.
- Adsorbed molecules do not interact- no adsorbate-adsorbate interaction.
- All adsorption occurs through the same mechanism and each localised adsorption site on the adsorbent can only hold one adsorbate molecule.
- At the maximum adsorption, only a monolayer of the adsorbate is adsorbed onto the solid adsorbent's regular surface.

Langmuir suggested that adsorption takes place through this mechanism:



Where, $A_{(g)}$ is the concentration (or pressure) of unadsorbed gas molecules; $B_{(s)}$ is the concentration of unoccupied solid adsorbent surface sites, AB is the concentrations of surface sites occupied by adsorbed gas molecules. The adsorption and desorption rate constants are k and k^{-1} .

Based on his theory [221], Langmuir derived an equation, which explained the relationship between the number of active sites of the surface undergoing adsorption and pressure. This equation is called Langmuir equation and takes the form [207, 221, 223, 224]:

$$V = \frac{V_L P}{P + P_L} \quad (2.5)$$

Where, V is the volume of gas adsorbed at defined temperature and pressure; P is the instantaneous pressure of the system; V_L is the maximum sorption capacity of the coal, usually referred to as Langmuir volume; P_L is the Langmuir pressure parameter, which represents the pressure at half of the maximum sorption capacity of the coal.

In 1938, Brunauer, Emmett, and Teller (BET) [58] extended the Langmuir model by introducing a multilayer adsorption approach, whose mechanism is depicted in Figure 2.6 (ii) [222]. In addition to the already stated assumptions on which the Langmuir model is based, the BET isotherm model further assumes that:

- (i). Each adsorbate molecule in the first layer serves as an adsorption site for an adsorbate molecule into the second layer; the second layer into the third layer, and so on.
- (ii). The attractive forces between the adsorbate molecules are negligible.
- (iii). The heat of adsorption of the second and subsequent layers is assumed to be equal to the heat of condensation or liquefaction of the adsorbate and different from the heat of the adsorption of the first layer.

The general BET equation is expressed in the form:

$$V_{BET} = \frac{V_0 C (P/P_0)}{(1 - (P/P_0)) [1 + (C - 1)(P/P_0)]} \quad (2.6)$$

V_{BET} is the maximum sorption capacity at pressure, P ; V_0 is the monolayer capacity of the adsorbent; C is a constant related to heat of adsorption, P_0 is the saturation pressure of the adsorbate at adsorption temperature.

The Langmuir and BET models are generally used to describe adsorption on a homogeneous regular surface or on a pore surface when the radii of the pores are large ($\gg$ than the radius of the adsorbate molecule [56].

The applicability of both the Langmuir and the BET isotherm models is limited as they are not applicable to microporous adsorbents including coals with the pore sizes that are only few molecules wide [47, 57, 155]. The adsorption potentials associated with dispersion forces are strongly enhanced in micropores due to the overlapping of the adsorption fields from the opposite pore walls. Alternatively, the adsorption mechanism in microporous adsorbent can be described by a pore filling mechanism illustrated schematically in Figure 2.6 (iii). Polanyi [59] defined the adsorption potential, ε , of an adsorbate molecule within the attractive force field of an adsorbent as the work required to bring an adsorbate molecule from the gas phase to the adsorption space with the adsorption forces.

$$\varepsilon = \int_P^{P_0} V dP = RT \ln \left(\frac{P_0}{P} \right) \quad (2.7)$$

Applying the Polanyi theory, Dubinin and Radushkevich [62, 220, 225] postulated that the extent of micropore filling in micropore spaces could be expressed as a function of the

adsorption potential, ε , characteristic adsorption energy, E , and a constant, n , the structural heterogeneity parameter (related to the homogeneity of the micropore surfaces) (Equation 2.8) and additionally defined the characteristic adsorption energy as Equation 2.9.

$$\frac{V}{V_0} = \exp - \left[\frac{\varepsilon}{E} \right]^n \quad (2.8)$$

$$E = \beta E_0 \quad (2.9)$$

Where, β is affinity coefficient, and E_0 , is the characteristic heat of adsorption. Hence, the physisorption of adsorbate gases or vapours in coals and other microporous solids can be explained by the Dubinin-Radushkevich's (D-R) pore filling mechanism based on the theory of volume filling of micropores (TVFM) proposed by Dubinin [226]. The empirical DR isotherm equation takes the form:

$$V_{DR} = V_0 \exp \left[- \left(D \ln \left(\frac{P_s}{P} \right) \right)^2 \right] \quad (2.10)$$

Where, V , is the volume of adsorbed gas; V_0 , is the maximum sorption capacity; D , is the D-R affinity constant for a particular adsorbate-adsorbent system and is equal to $(RT / \beta E_s)^2$; E_s , is the characteristic energy of the adsorption system and, β , is the adsorbate affinity coefficient. If the power, 2, is replaced by n (the structural heterogeneity parameter), where, n , ranges from 1 to 4, then, Equation 2.10 becomes the Dubinin–Astakhov (DA) equation [220].

2.4.1.5 Adsorption measurement methods

Gravimetric and volumetric (also referred to as manometric) methods are two widely used techniques for the acquisition of adsorption data and the construction of adsorption isotherms. However, the use of a chromatographic method for adsorption measurements has been reported [227]. While the gravimetric technique is a direct measurement method, the volumetric technique is an indirect method for measuring gas sorption on solid adsorbents, including coals [228, 229]. Both techniques require an accurate assessment of the volume of the solid adsorbent [155, 228-230]. This is necessary in the gravimetric method to make buoyancy correction [155,

229, 230] and, in the volumetric system [155, 228], to determine the free gas space in the sample cell. In high pressure adsorption systems, using the volumetric method, the pressure-volume change (P-V) data, in conjunction with an appropriate real gas equation of state (EOS) are used to determine the sorption properties of the system.

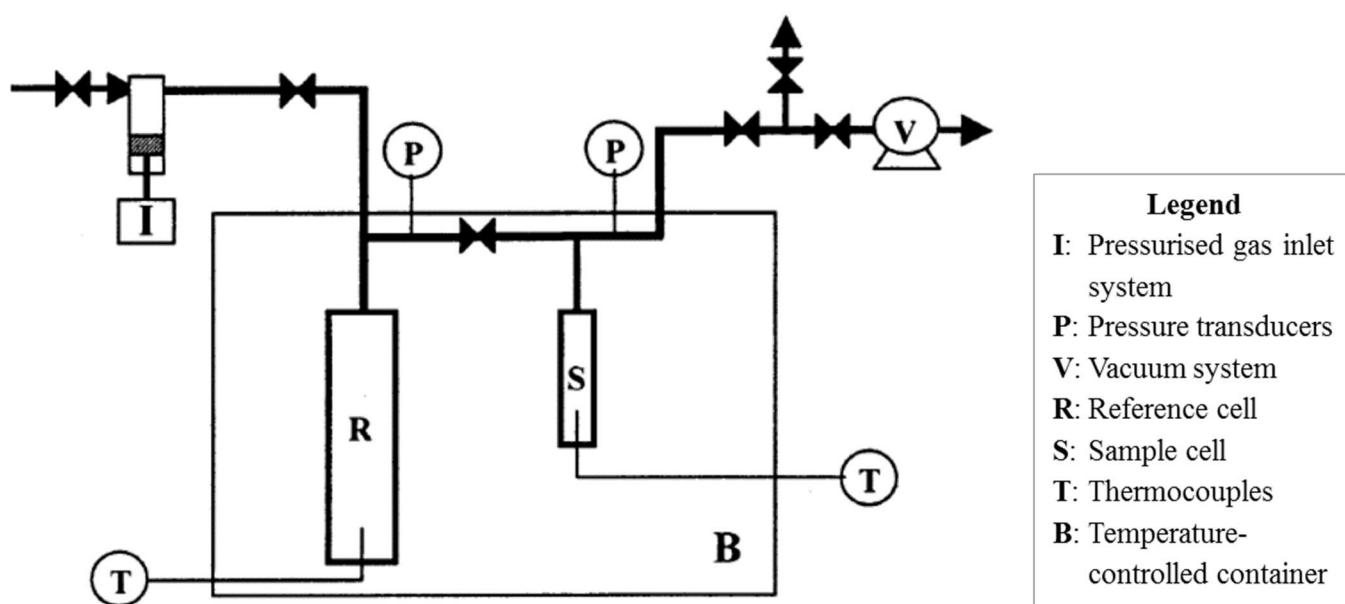


Figure 2.7: A typical volumetric adsorption system [100].

A typical volumetric adsorption system is illustrated in Figure 2.7 [100]. For gravimetric systems, the resulting mass gain data, gas density and density of the adsorbed phase (often referred to as van der Waal density) are important parameters for the generation of the adsorption isotherm of the system. One significant advantage of gravimetric adsorption systems over the volumetric method is that the density of the gas phase is determined directly using a reference cell, with an accurately known volume, connected to the sample cell [102, 229]. This removes the need for calculated real gas EOS necessary in volumetric systems [102, 228]. The schematic diagram of a gravimetric adsorption system is presented in Figure 2.8, after Day et al. [230].

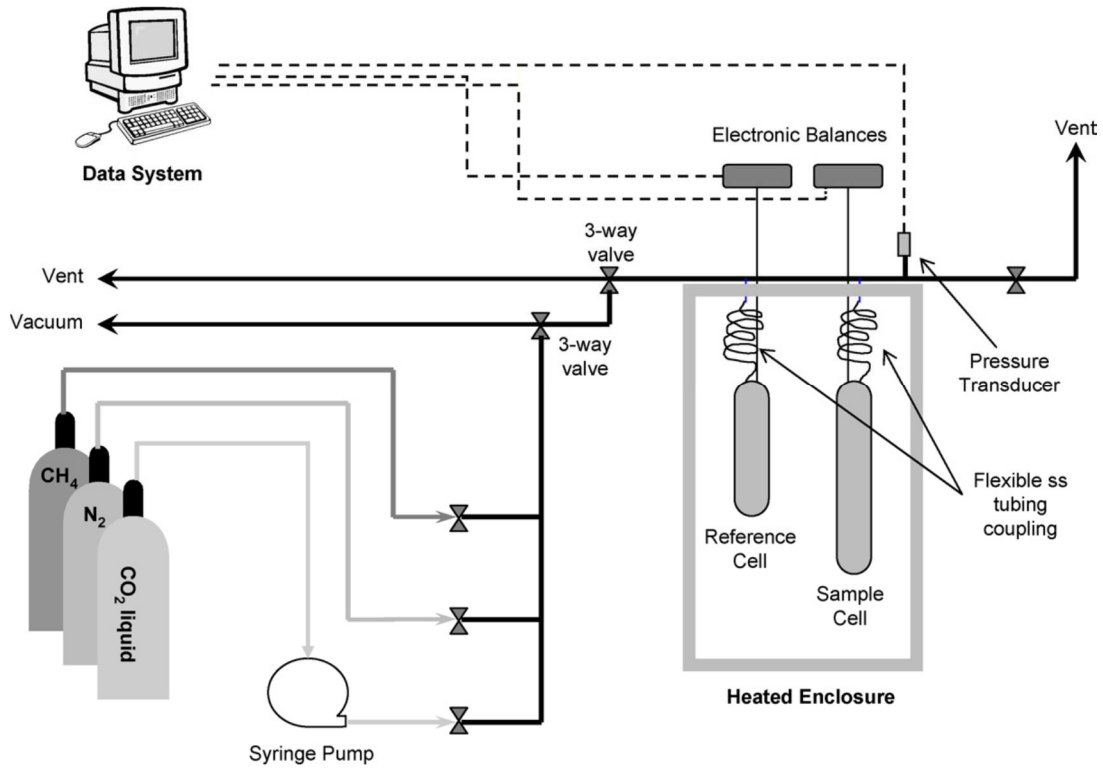


Figure 2.8: Schematic diagram of a high pressure gravimetric adsorption equipment [230].

2.4.1.6 Isotherm model equations at high pressure

In this section, the isotherm model equations applicable to high pressure gravimetric sorption systems is discussed in detail. The term “sorption” is used in this section to fully describe the adsorption phenomena observed for coals such as imbibition, Henry’s law dissolution and probably absorption [102, 231, 232]. Although, these are more significant for CO₂ sorption in coal.

In a gravimetric sorption system, the mass gain in the sample cell would be equal to the product of the gas density and void volume i.e. the difference between the skeletal volume of the cell and the volume of the sample. Since coal sorbs gases, the actual mass gain at any given pressure (pressure step) is greater than this calculated mass gain. The difference between the actual and the measured mass gain is called the Gibbs surface excess sorption or, more commonly the excess sorption. The excess sorption, Q_{exc} , can be expressed as [102]:

$$Q_{exc} = M_{mea} - (V_{cell} - V_{sample})\rho_g \quad (2.11)$$

where: M_{mea} is the mass of adsorbate sorbed at a given pressure; V_{cell} is the volume of the sample cell; V_{sample} is the skeletal volume of the sample; and ρ_g is the adsorbate gas density at the given pressure and temperature.

The sorption isotherm is usually plotted from the excess sorption data. Several sorption isotherm models have been proposed and used to describe the sorption characteristics of the coal-gas system, as well as to determine the sorption properties of the sample. The fit of the experimental sorption data provides important and meaningful parameters such as the maximum sorption capacity of the sample, the affinity coefficient, and the heterogeneity parameter, from which other sorption data such as the heat of sorption can be estimated. In the DR isotherm model equation, the heterogeneity parameter is equal to 2, while for the Dubinin-Astakhov (DA) isotherm model equation; the heterogeneity parameter can be a number between 1 and 4 [233]. The empirical DR excess sorption isotherm equation for a gravimetric system takes the form:

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{P_s}{P} \right)^2 \right] \quad (2.12)$$

$$D = \left[\frac{RT}{\beta E_s} \right]^2 \quad (2.13)$$

Where Q_0 is the maximum sorption capacity of the samples; ρ_g is the gas density; ρ_a is the density of the adsorbed phase; P_s is the saturation pressure (the pressure at which the gas condenses); and P is the instantaneous (step-wise) experimental pressure; D is the affinity constant (related to the heat of sorption) of the coals for the adsorbate gases defined by Equation 3 [155, 230, 234-236]; R is the universal gas constant; T the absolute temperature; β is the affinity coefficients between the adsorbate gas and the coal samples [101, 230, 234, 235]; and E_s is the characteristic heat of sorption of the coals [101, 230, 234, 236]. The term βE_s is the net heat of sorption [200, 230].

In the classical DR equation, the term $(1 - \rho_g / \rho_a)$ corrects for the volume occupied by the condensed phase on the surface of the sample, which displaces the gas phase of the adsorbate. Albeit, the classical DR equation is only valid when the instantaneous experimental pressure is less than the saturation pressure of the adsorbate gas, i.e. $P < P_s$. Thus, the DR cannot be

used to model gas sorption at or above supercritical conditions where the saturation pressure of the adsorbate gas, P_s , is undefined. In fact, some investigators [102, 231, 232, 237] have criticised the applicability of this important equation over a wide range of pressures and temperatures where $P \gg P_s$, including at and above supercritical conditions of most gases. To assuage this discrepancy in the use of the DR model at supercritical conditions, Sakurovs et al. [102] proposed a modification to classical DR equation by replacing the P_s term by the adsorbed phase density, ρ_a , and the pressure term by gas density. This modified DR (M-DR) isotherm equation is shown in Equation 2.14 and can be applied over a wider pressure and temperature ranges, including supercritical conditions.

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{\rho_a}{\rho_g} \right)^2 \right] \quad (2.14)$$

To further account for some observations [95, 98-103, 238] such as imbibition (Henry's law dissolution) especially for coal-CO₂ interactions at high pressures, differences in accessibility between helium and the other gaseous adsorbates to coal pore network, and errors and uncertainties in measured helium density and cell volume; a proportionality term [102] was added to the M-DR equation to improve applicability especially for coals at supercritical conditions. The hybrid equation hereinafter referred to as Dubinin-Radushkevich/Henry law hybrid (DR-HH) takes the form (Equation 2.15):

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{\rho_a}{\rho_g} \right)^2 \right] + k \rho_g \quad (2.15)$$

Where, k , is the proportionality constant.

Various modifications of the different isotherm equations has been applied in the study of sorption properties of different adsorbate gases on coal at both sub- and super-critical conditions using volumetric [101, 239, 240] and gravimetric [102, 202, 230, 241] systems. A summary of the isotherm models used in describing high pressure sorption of gases on dry coals is presented in Table 2.2.

Table 2.2: Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Refs).
[1] Brunauer- Emmet-Teller (BET)	$V = \frac{V_0 C (P/P_0)}{(1 - (P/P_0)) [1 + (C - 1)(P/P_0)]}$	(2.6)	Rarely describes experimental isotherm at higher pressure (higher P/P_0). Clarkson et al. [207] demonstrated the inadequacy of the BET equation in describing high pressure sorption of gases, especially CO₂ in the supercritical region. However, it is qualitatively useful in differentiating isotherm types. Range of validity for the BET model is usually $0.05 \leq P/P_0 \leq 0.35$. Basic features of the BET isotherm model are presented in Section 2.4.1.4. [58, 207, 209, 223]
[2] Modified Brunauer- Emmet-Teller (M-BET)	$V = \frac{V_0 C x}{(1 - x)} \left[\frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (C - 1)x - Cx^{n+1}} \right]; \quad x = \frac{P}{P_s}$ Where, n, is the number of adsorption layers. The supercritical saturated vapour pressure, P_s, of the 3-P BET equation was evaluated from the supercritical properties of the adsorbate gas using the relation [62, 200, 207, 233]: $P_s = P_c \left[\frac{T}{T_c} \right]^2$	(2.16)	Usually referred to as the 3-parameter BET equation. n is limited by the pore diameter of the adsorbent. At very low pressures ($P \ll P_0$), the 3-P BET equation approaches the Langmuir adsorption isotherm equation. When $n = 1$, the equation also converges to Langmuir equation. The 3-P BET has been used to evaluate sorption properties and theoretical CBM contents of coal seams. [240]
[3] Langmuir (L)	$V = \frac{V_L P}{P + P_L}$	(2.5)	The original Langmuir isotherm model equation is a monolayer adsorption model, based Langmuir's theory and dynamic equilibrium. Features of the model are given in Section 2.4.1.4. V_L and P_L are parameters determined by fitting the model equation to experimental data. Determination of V by the volumetric method requires appropriate equations of state (EOS). [207, 209, 221, 223, 224, 242, 243]

Table 2.2 (contd): Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Ref(s).
[4] Modified Langmuir (M-L)	$V = V_0 \left(1 - \frac{\rho_g(P, T)}{\rho_a} \right) \frac{P}{P + P_L} \quad (2.18)$ Where, V_0 is the maximum sorption capacity and P_L is the Langmuir pressure. ρ_g is the density of the gas in the free phase. ρ_a is the density of the adsorbed phase.	Modified by introducing the term, $(1 - \rho_g / \rho_a)$, which corrects for the volume occupied by the adsorbed phase of the adsorbate gas. Fitted parameters are V_0 , P_L , and ρ_a . For CO ₂ , ρ_g can be determined using the Span and Wagner EOS [244].	[245]
[5] Modified Langmuir (M-L)	$W_{total} = W_a + W_s = \frac{W_a^{\max} b_a \rho_g}{1 + b_a \rho_g} + \frac{W_s^{\max} b_s \rho_g}{1 + b_s \rho_g} \quad (2.19)$ where $W_a^{\max}$ and b_a, are the maximum sorption capacity per unit mass of coal and the Langmuir equilibrium constant of the adsorption term; $W_s^{\max}$ and b_s, are the corresponding constants for the absorption term. ρ_g, is the density of the gas in the free phase.	Equation 2.19 describes maximum sorption capacity as the sum of sorptions due to adsorption and absorption. The pressure term was replaced by a density term for applicability at high pressures (super-critical conditions). ρ_g was measured in situ by a calibrated titanium sinker coupled to gravimetric system, utilising a magnetic suspension balance. Takes into account absorption and swelling of coal in the presence of gases under pressure. Assumes that absorption and swelling are related.	[202]
[6] Modified Langmuir (M-L)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a} \right) \left(\frac{\rho_g}{\rho_g + \rho_L} \right) \quad (2.20)$ Where, ρ_L, is the Langmuir density constant.	Modified by introducing the term, $(1 - \rho_g / \rho_a)$, which corrects for the volume occupied by the adsorbed phase on the surface of the sample, that displaces the gas in the free phase. The pressure terms were also replaced by density terms. ρ_g can be determined experimentally [246] or calculated [62, 200, 207, 233]. ρ_a was adapted from published data of Sudibandriyo et al. [246]. Fitted parameters are V_0 and ρ_L . Use of EOS can be avoided depending on measurement technique used.	[102]

Table 2.2 (contd): Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Ref(s).
[7] Modified Langmuir (M-L+k)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a} \right) \left(\frac{\rho_g}{\rho_g + \rho_L} \right) + k \rho_g \quad (2.21)$ Where, k, is the Langmuir proportionality constant.	Modified following the 2-component sorption process proposed by Larsen [37] the equation is a Langmuir/Henry law hybrid, where the adsorption component is described by the Langmuir component of Equation 2.20, and the absorption (imbibition) component by a constant, k , proportional to pressure, following Henry's law. ρ_a was inferred from published data [246]. Fitted parameters are V_0 , ρ_L , and k . Depending on the measurement technique, the use of EOS may be avoided.	[102]
[8] Dubinin- Astakhov (DA)	$V = V_0 \exp \left[- \left(D \ln \frac{P_s}{P} \right)^n \right]; \quad D = \left(\frac{RT}{\beta E} \right)^n \quad (2.22)$ Where, V, is the volume gas adsorbed; V_0 is the maximum sorption capacity of the coal; n, is the DA structural heterogeneity parameter, and ranges from 1 to 4. D, is the affinity constant, related to adsorbent-adsorbate interactions.	Original DA isotherm model equation based on Polanyi's potential theory of heterogeneously energetic surfaces [59] and Dubinin's theory of volume filling of micropores (TVFM) [226]. At supercritical conditions, P_s can be evaluated using Equation 2.17 [62, 200, 207, 233]. If $n = 2$, the DA equation transforms to the DR equation. Fitted parameters are V_0 , D , and n . EOS may not be needed depending on the experimental procedure.	[200, 207, 209, 223]
[9] Modified Dubinin- Astakhov (M-DA)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a} \right) \exp \left[- \left(D \ln \frac{P_s}{P} \right)^n \right] + \rho_g \Delta V \quad (2.23)$ Where, ΔV, is the change in volume of the coal from both the Henry's law dissolution of gases, especially CO₂, and the swelling of the coal at higher pressures, leading to decreased void volumes in the sample cell.	Modified to account for the volume of the adsorbed phase by introducing the term, $(1 - \rho_g / \rho_a)$. Also accounts for Henry law dissolution and swelling by adding the term, ΔV_H , similar to the modifications of Sakurovs et al. [102]. The saturation vapour pressure, P_s , and the density of the adsorbed phase, ρ_a , were calculated using the methods of Reid et al. [247] and Dubinin [62] respectively. V_0 , D , n , and ΔV_H are fitted parameters.	[101]

Table 2.2 (contd): Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Ref(s).
[10] Dubinin-Radushkevich (DR)	$V = V_0 \exp \left[- \left(D \ln \left(\frac{P_s}{P} \right) \right)^2 \right]; D = \left[\frac{RT}{\beta E_s} \right]^2 \quad (2.10)$	Similar to the DA isotherm model equation, the original DR isotherm model equation is also based on Polanyi's potential theory of heterogeneously energetic surfaces [59] and Dubinin's TVFM [226]. At supercritical conditions, P_s can be evaluated using Equation 2.17 [62, 200, 207, 233]. In the DR isotherm equation, the structural heterogeneity parameter, $n = 2$. Fitted parameters are V_0 , and D .	[209, 223, 225, 242]
[11] Dubinin-Radushkevich (M-DR)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a} \right) \exp \left[- \left(D \ln \left(\frac{P_s}{P} \right) \right)^2 \right] \quad (2.12)$	Often referred to as the classical DR isotherm model equation, the original DR model equation was modified to more correctly account for the volume of the adsorbed phase by introducing the term, $(1 - \rho_g / \rho_a)$. P_s can be estimated from Equation 2.17 [62, 200, 207, 233]. ρ_a was adapted from published data [246]. Fitted parameters are V_0 , and D .	[102]
[12] Dubinin-Radushkevich (M-DR)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a} \right) \exp \left[- \left(D \ln \left(\frac{\rho_a}{\rho_g} \right) \right)^2 \right] \quad (2.14)$	Following the findings of Freeman [232] and Cerofolini [237] and the critical review of Cerofolini [231] that demonstrated that the P_s term of the DR isotherm equation may not essentially be the saturation vapour pressure of the adsorbate gas, but may be associated with the energy required to compress the gas to the adsorbed phase density at the adsorbent surface, Sakurovs et al. [102] modified the classical DR equation by replacing all the pressure terms with density term to allow for its applicability at supercritical conditions. ρ_g can be determined experimentally [246] or calculated [62, 200, 207, 233]. ρ_a was adapted from published data [246]. V_0 , and D are the regressed parameters.	[102]

Table 2.2 (contd): Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Ref(s).
[13] Dubinin-Radushkevich (M-DR+k)	$V = V_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \left(\frac{\rho_a}{\rho_g} \right) \right)^2 \right] + k \rho_g \quad (2.15)$ Where, k, is the DR proportionality constant.	To further account for Henry's law dissolution, and probable imbibition and swelling by gases, especially for CO ₂ and CH ₄ , at higher pressures, a term proportional to pressure based on Henry's law was added to the equation. ρ_a was adapted from the reported results [246]. Regressed parameters are V_0 , D , and k .	[102]
[14] Simplified local density (SLD)	$V_{ads} = \frac{SA}{2} \left(L_s - \frac{3}{4} \sigma_{ff} \right) \quad (2.24)$ Where, V_{ads}, is the volume of adsorbed phase of gas; SA, is the surface area (maximum sorption capacity); L_s, is the slit length; and σ_{ff}, is the molecular diameter of the adsorbate.	The SLD model assumes that the adsorbent surface is composed of rectangular-shaped 2-surface slits and the adsorbate molecules reside within these slits. A molecule inside a slit interacts with both walls of the slit. The SLD model accounts for both adsorbate-adsorbate and adsorbate-adsorbent interactions within the pore geometry. Peng-Robinson EOS was used to evaluate V_{ads} [248]. Maximum sorption capacity returned as surface area of the adsorbate on a particular solid. Fitted parameters are SA , L_s , and the adsorbent-adsorbent interaction energy, ϵ_{ss}/k_b , where k_b , is the Boltzmann constant.	[249, 250]
[15] Modified simplified local density (M-SLD)	$V_{ads} = V_{ads,0} \exp(-\delta(T - T_0)) \quad (2.25)$ Where $V_{ads,0}$, is equivalent to V_{ads} of Equation 2.24, determined at a reference temperature, T_0; δ, is the thermal expansion coefficient of the adsorbate; and T, is experimental temperature.	The M-SLD was modified to account for the changes in the volume of the adsorbed phase in the SLD model by introducing the term, δ , that incorporates the thermal expansion of the adsorbate into the model. Regressed parameters are SA , L_s , ϵ_{ss}/k_b , and δ .	[250]

Table 2.2 (contd): Sorption isotherm models used to describe gas sorption on dry coals.

Isotherm model	Model equation	Remarks	Reference(s)
[16] Kim isotherm model (KM)	$V = \left[\frac{(100 - M - A)}{100} \right] \frac{V_m}{V_d} [K(P)^N - bT] \tag{2.26}$	The KM considers many in-seam coal properties influencing gas sorption in coal, especially with regards to gas-in-place (GIP) in coal seams.	[224, 251]
	$\frac{V_m}{V_d} = (0.25M)^{-1}; T = 2.5 \cdot \left(\frac{h}{100} \right) + T_0 \tag{2.27}$	Developed from correlations of sorption properties of CH ₄ in US coals with the coal properties.	
	$K = 0.8 \cdot \left(\frac{FC}{VM} \right) + 5.6; N = 0.39 - 0.013K \tag{2.28}$	The KM has been applied and used to estimate the sorption properties of coal from 18 US coal seams of various ranks, ranging from sub-bituminous to anthracite.	
	Where, V, is the volume of gas adsorbed; M, is the moisture content of the coal; A, is the ash content of the coal; T and T_0, are the experimental or injection temperature and initial temperature of coal seam respectively; V_d and V_m, are the volumes of gas adsorbed in dry and wet coal; h is the depth of coal seam; P, is the pressure; FC, is the fixed carbon content; and VM, is the volatile matter content.		

2.5 High pressure sorption properties of gases on coals

A substantial number of reports and reviews are available on the high pressure sorption of gases and vapours on coals, especially for Northern hemisphere's coals of various ranks and types [52, 97, 101-104, 139, 155, 192, 197, 199, 224, 234, 242, 252-261]. Several investigator have studied simultaneously and compared the high pressure sorption properties of CO₂, CH₄, and N₂ [102, 104, 202, 234, 239, 242, 253, 257, 262-267], CO₂ and CH₄ [80, 245, 268-276], other gases and vapours [104, 257], and their binary and ternary mixtures [199, 262, 265, 267, 276-282]. These studies were conducted at temperatures and pressures usually encountered in deep- and shallow-seated coal seams, often considered as candidate geological site for the storage of CO₂. At depths > 750 m, Mazzotti et al. [199] reported temperatures of up to 40 °C and pressures > 7 MPa for various coal seams in Europe, Australia, and US; while Mastalerz et al. [275] reported a temperature range of 12 – 16 °C for Illinois deep-seated coal seams with temperature gradients of up to 0.54 °C/m. However, high pressures (up to 30 MPa) and high temperatures (up to 55 °C or higher) have been found for some coal seam sequestration processes [155, 283]. Under these conditions, CO₂ may be in gas, liquid, densified or supercritical phase, depending on the change in pressure during the adsorption-desorption processes within the coal seam.

Chaback and co-workers [265] investigated the sorption properties of 3 US bituminous coals from the widely studied San Juan Basin, using a volumetric sorption system at 46.1 °C and up to 10 MPa pressure. They analysed their resulting data using the Langmuir isotherm model and its extended form and found that these isotherm models adequately described the sorption isotherms of both the pure and multicomponent component gas mixtures; and reported that the maximum sorption capacities of the samples was higher for CO₂, compared with that of CH₄ and N₂ with relative maximum sorption capacities ratios of 4:2:1. They attributed the variations in the sorption capacities of the samples to differences in coal rank and the molecular properties of the samples, and noted that these variances in sorption capacities of the samples with respect to the different adsorbate gases follows the Gurvitsch rule [209, 235] of constancy of maximum volume sorbed [257], which has since been disputed [104, 257]. Pure and multicomponent high pressure sorption properties of CH₄, N₂ and CO₂ on Fruitland coal sample from US has been studied by DeGance et al. [267], applying an extended Langmuir isotherm model, a two-dimensional equation of state, (2-D EOS), and the ideal adsorbed solution theory, (IAS), to their resulting data. They demonstrated that although the EOS approach had some difficulty

matching the experimental data, especially for wet coals, the simplicity of the virial EOS made it useful for their modelling effort.

Clarkson et al. [207] studied the applicability and suitability of three empirical sorption models: the monolayer Langmuir model, the multilayer BET model, and the Dubinin-Astakhov (DA) model based on Polanyi's potential theory and Dubinin's TVFM to their high-pressure (up to 10 MPa) CH₄ sorption isotherms at a temperature range of 25 – 50 °C and low-pressure CO₂ isotherms. They demonstrated that the three-parameter DA isotherm model best described their high-pressure CH₄ isotherms. They noted that the assumption of the energetically homogenous adsorption surface by the Langmuir theory does not apply to coal, concluding that, although the adsorption potential theory and the TVFM applies to low-pressure CO₂ isotherms, high pressure sorption isotherms of CO₂ needs further evaluation. Clarkson and Bustin [274] further investigated the high pressure (up to 8 MPa) CO₂ and CH₄ sorption isotherms on 4 dried and moisture-equilibrated British Columbia bituminous coals at 30 °C, and found that, for both the dried and moisture-equilibrated samples, the 3-parameter DA isotherm model comparatively provided a better fit to their experimental data, which was more significantly for CO₂, than the widely used empirical Langmuir isotherm model. They also found linear correlations between the CO₂ and CH₄ maximum sorption capacities of the samples with the DR micropore volumes and DR micropore surface areas of the samples (determined from CO₂ LPGA), suggesting that the micropore structural properties of coals are primary limiting controls to high pressure gas sorption of coal seams as candidate geological storage site for CO₂.

Sakurovs and co-workers [102] also examined the adaptability, applicability and quality of fit (QOF) of both the classical and modified versions of the Langmuir and the Dubinin-Radushkevich isotherm models to CO₂, CH₄, and N₂ excess sorption data of 3 Australian bituminous coals under supercritical conditions (53 °C and up to 20 MPa) using a high pressure gravimetric sorption system (HPGSS). They modified the classical models by replacing the pressure term of the original equations by the gas density, and the saturation vapour pressure term by the adsorbed phase density following the findings detailed elsewhere [231, 232, 237]. Both parameters can be determined experimentally [102, 246], calculated or inferred from previous data [62, 200, 207, 233]. They also added a proportionality constant, k , to further account for Henry's law dissolution, and probable imbibition and swelling by gases, especially for CO₂ and CH₄, at higher pressures [37], which can also provide insights on the extent of coal volume penetrated by the adsorbate gases [104, 257]. They found that for the three gases investigated, the modified DR equation + k function best described their high pressure excess

sorption data with higher QOF metrics. They reported positive k values indicating that the gases can penetrate more coal volume than that expected from helium density (or that the free space volume may be in error [229], which has been demonstrated to be very small [102, 104, 257], from which it may be deduced that imbibition and swelling may only have small effects on the sorption properties of the samples studied. The k values can also be indicative of the differences in accessibility of the coal pore voids between the adsorbate gases [104, 257].

Sakurovs and his team [104, 230, 234, 238, 241, 257, 266] further investigated at supercritical conditions the relationship between sorption properties of gases on coals with coal properties [230], the critical properties of different adsorbate gases [104], and even impurities relevant to emitted flue gases and CO₂ capture process systems [241]. Their reported findings show that the maximum sorption capacities of the coals under supercritical conditions correlated well with the critical properties of the gases [99, 104]. With regards to coal properties, they reported (based on their limited characterisation data) that only coal rank, elemental hydrogen contents and the DR affinity constant gave a systematic trend with the obtained sorption capacities of their samples [230], and argued that evaluation of CO₂ storage potential of coal seams cannot be reliably inferred from the coal properties. However, other equally important characterisation data such as micropore structural properties and coal microlithotype abundance were not reported for the coals. Only the mercury intrusion data that only gives information on the macropore properties of the samples were presented [230].

Pini et al. [202] investigated the CO₂, CH₄, and N₂ sorption capacities of bituminous coals from Europe at up to 20 MPa, within the temperature range of 33 – 60 °C, using a gravimetric sorption system with a magnetic suspension balance, and found that the maximum sorption capacities of the dry coals fall within the range: 5 - 14 wt.% for CO₂, and 1 - 3 wt.% for both CH₄ and N₂. They also reported that the sorption capacities of the coal samples for the three studied gases decreased with increasing vitrinite reflectance. Morse et al. [264] examined the sorption behaviour of 16 coal samples from the Tanquary injection site in Illinois, USA under sub- and super critical conditions. They reported that the microlithotype compositions and abundances of the samples in combination with their mineral matter content impacts the micro- and meso-pore properties of the coals, which in turn, significantly influences the sorption capacities of the samples.

Cui and co-workers [262] have demonstrated experimentally and by numerical simulations (using a slit-shaped pore and bi-disperse model) that selective transport of CO₂, CH₄, and N₂

through the coal matrix is highly dependent on the micro- and meso-pore structures of the coals. They also found that the apparent diffusivity of the adsorptive gases through the pore structures (especially the micropores), which is a function of the adsorption kinetics, is highly dependent on the kinetic diameter of the gases [262].

Reported maximum sorption capacities of dry coals of various ranks, up to anthracite, by weight vary in the range: 20.7 – 151.4 kg/t, db for CO₂ [101, 102, 104, 202, 230, 236, 262, 264, 284], 7.4 - 29.0 kg/t, db for CH₄ [102, 104, 200, 202, 236, 262, 264, 266, 285], and 3.4 - 35.9 kg/t, db for N₂ [102, 104, 202, 262, 264]. These translates to sorption capacities of 2.1 to 15.1 wt.% of dry coal for CO₂, 0.7 - 2.9 wt.% of dry coal for CH₄, and 0.3 - 3.6 wt.% of dry coal for N₂.

From Tables 2.3 – 2.5, it was generally observed that on weight basis, the CO₂ sorption capacities were significantly higher than both the CH₄ and N₂ sorption capacities for the same coal [102, 104, 202, 239, 242, 262, 264, 265]. Data from these tables also show that, in most cases, the CH₄ sorption capacities on weight basis are less than the N₂ data [104, 202, 239, 242, 262, 264, 265] or approximately similar [102, 104]. Thus, the sorption capacities of these adsorptive gases on coals by weight decrease in magnitude in the order: CO₂ > N₂ $\approx$ CH₄. However, on volume [264, 265] or mole basis [104, 202, 239, 242, 262], the sorption capacities of coals with respect to these three gases decreases in the order: CO₂ > CH₄ > N₂ [104, 202], due to the lower molar mass of CH₄ (16 g/mol) compared to that of N₂ (28 g/mol). The determined net heats of sorption, βE_s , of coals of different ranks vary in the range: 8.2 – 13.5 kJ/mol for CO₂ [101, 102, 104, 230, 266], 8.8 – 11.8 kJ/mol for CH₄ [104, 200, 266], and 8.6 - 10.4 kJ/mol for N₂ [104]; and seem to decrease in the order: CO₂ > CH₄ > N₂.

The high pressure CO₂, CH₄, and N₂ sorption properties of coals of various ranks from different locations and countries, summarised from published reports, are presented in Tables 2.3 – 2.5. It should be noted that, for effective comparison, the data were normalised or recalculated to weight basis. For all three gases, higher sorption capacities were reported for higher ranked coals (Rr.% > 2.5) [245, 270, 271]. Although the South African coal samples studied by Saghafi et al. were igneous-intruded samples that are significantly affected by heat, which may have enhanced the micropore properties and bulk fluid transport of the coals [286]. However, Pini et al. [202] reported significantly higher CO₂, CH₄ and N₂ sorption capacities for Italian bituminous coals (0.70 – 0.74 Rr.%) with high volatile matter content (31.0 – 40.3 wt.%, adb) and the experiments were conducted at a lower temperature of 33 °C.

Table 2.3: Summary of CO₂ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Coal rank(s)	Vitrinite reflectance, Rr. %	Sorption system	Max. pressure, MPa	Temp., °C	Isotherm model used	Carbon dioxide, CO ₂				Reference
								Q_0 (kg/t, db)	D (-)	E_s (kg/mol)	k (m ³ /t)	
Australia	A, B, C	Bituminous	-	GAS	20.0	53.0 ± 1	Various	53.0 - 82.0	0.051 - 0.061		0.011 - 0.022	[102]
Australia	NSW1 - 10	Various	0.70 - 1.34	GAS	16.0	53.0	M-DR	52.0 - 82.0	0.043 - 0.052	11.9 - 13.2	0.014 - 0.037	[230]
Australia	QLD1 - 10	Various	0.62 - 1.63	GAS	16.0	53.0	M-DR	62.5 - 109.5	0.044 - 0.059	11.2 - 13.0	0.017 - 0.035	[230]
Australia	Hunter Valley	Bituminous	0.81	GAS	20.0	55.0 ± 1	M-DR	80.8	0.044	13.0	0.024	[266]
Australia	Illawarra	Bituminous	1.40	GAS	20.0	55.0 ± 1	M-DR	53.6	0.042	13.3	0.012	[266]
Australia	Coal 1 - 6 (6 coals)	Bituminous	0.62 - 1.40	GAS	20.0	55.0	M-DR	45.4 - 81.0	-	12.9 - 13.5	-0.001 - 0.007	[104]
Australia	A1, A2, A3	Bituminous	0.80 - 1.34	GAS	20.0	45.0 - 55.0	M-L	54.1 - 77.0	-	-	-	[202]
Australia	Various (27 samples)	Various	0.66 - 11.64	GAS	6.0	20.0 - 39.0	L	59.5 - 126.7	-	-	-	[287]
Australia	Various (41 samples)	Bituminous	0.6 - 1.7	GAS	6.1	27.0 - 39.0	L	59.5 - 154.2	-	-	-	[268]
Australia	Untreated coal	Bituminous	-	GAS	20.0	55.0	M-DR	77.9	-	12.8	-0.007	[241]
Brazil	Rio Bonito (4 coals)	Bituminous	0.82 - 1.62	VAS	17.0 - 25.0	35.0 - 45.0	L	39.6 - 84.1	-	-	-	[269]
Canada	1 sample	Bituminous	-	VAS	7	30.0	L	81.7	-	-	-	[262]
China	Tashan	Bituminous	0.81	GAS	20.0	55.0 ± 1	M-DR	45.3	0.045	12.8	0.016	[266]
China	Duanshi	-	-	VAS	6.0	25.0	L	102.5	-	-	-	[242]
China	Duanshi	-	-	VAS	6.0	25.0	D-R	106.1	0.037	-	-	[242]
China	3 Chinese coals	Various	0.53 - 3.86	VAS	25.0	35.0 - 55	M-L	74.8 - 191.9	-	-	-	[245]
France	Various (11 coals)	Various	0.49 - 3.65	GAS	5.0	25.0	Various	22.0 - 92.5	-	-	-	[270]
India	Various (14 coals)	Bituminous	0.61 - 1.94	VAS	4.6 - 5.9	30.0	L	27.4 - 146.6	-	-	-	[288]
Italy	I1, I2	Bituminous	0.70 - 0.74	GAS	20.0	33.0 - 60.0	M-L	118.8 - 151.4	0.045	-	0.028	[202]
Japan	J1	Bituminous	0.78	GAS	20.0	45.0	M-L	81.4	-	-	-	[202]
New Zealand	NZ	Bituminous	1.11	GAS	16.0	53.0	M-DR	50.5	0.054	11.7	0.015	[230]
New Zealand	Various (11 coals)	Sub-bituminous	0.34 - 0.53	VAS	5.0 - 8.0	31.5 - 35.1	L	43.2 - 46.6	-	-	-	[80]
Poland	Poland 1 - 2	Various	1.22 - 1.34	GAS	16.0	53.0	M-DR	55.8 - 58.3	0.046 - 0.047	12.5 - 12.8	0.021 - 0.027	[230]
Poland	Brzeszcze	Bituminous	0.78	Various	16.0 - 25.0	45.1 - 45.8	L	82.3	-	-	-	[284]
Switzerland	S1, S2, S3	Bituminous	0.85 - 0.90	GAS	20.0	45.0	M-L	33.0 - 57.7	-	-	-	[202]

Table 2.3 (contd.): Summary of CO₂ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Coal rank(s)	Vitrinite reflectance, Rr. %	Sorption system	Max. pressure, MPa	Temp., °C	Isotherm model used	Carbon dioxide, CO ₂				Reference
								<i>Q₀</i> (kg/t, db)	<i>D</i> (-)	<i>E_s</i> (kg/mol)	<i>k</i> (m ³ /t)	
Slovenia	Velenje	Lignite	0.41	Various	16.0 - 25.0	45.0 - 45.8	L	123.6	-	-	-	[284]
South Africa	MDT1 - 15	Various (15 coals)	0.79 - 4.31	GAS	6.0	27.0	L	53.0 - 102.8	-	-	-	[271]
South Africa	Various (8 coals)	Bituminous	-	VAS	8.5	35.0	L	48.4 - 95.5	-	-	-	[289]
South Korea	Kyungdong coal	Anthracite	5.07	VAS	15.2	45.0	L	95.8 - 98.9	0.077	-	0.025	[272]
South Korea	Kyungdong coal	Anthracite	5.07	VAS	15.2	65.0	L	70.7 - 74.3	0.065	-	0.015	[272]
UK	Selar Cornish	Semi-anthracite	2.41	Various	16.0 - 25.0	45.1 - 45.8	L	84.5	-	-	-	[284]
UK	Selar Cornish	Semi-anthracite	2.41	VAS	16.0	45.0 - 65.0	M-L	71.7	-	-	-	[239]
USA	USA1 - 3	Various	0.90 - 1.68	GAS	16.0	53.0	M-DR	50.7 - 64.1	0.043 - 0.048	12.4 - 13.1	0.014 - 0.032	[230]
USA	Beulah Zap	Lignite	0.25	GAS	16.0	53.0	M-DR	88.6	0.046	12.6	0.032	[230]
USA	Illinois #6	Bituminous	0.46	GAS	16.0	53.0	M-DR	95.7	0.065	10.6	0.017	[230]
USA	Pocahontas #3	Bituminous	1.68	GAS	16.0	53.0	M-DR	67.5	0.044	12.9	0.014	[230]
USA	Pocahontas #3	Bituminous	-	VAS	4.0	22.0	M-DA	55.0	-	9.9	0.17	[101]
USA	Upper Freeport	Bituminous	-	VAS	4.0	22.0	M-DA	47.1	-	8.9	0.18	[101]
USA	Pittsburgh #8	Bituminous	-	VAS	4.0	22.0	M-DA	51.5	-	8.4	0.16	[101]
USA	Lewiston–Stockton	Bituminous	-	VAS	4.0	22.0	M-DA	57.2	-	8.7	0.18	[101]
USA	Blind canyon	Bituminous	-	VAS	4.0	22.0	M-DA	72.6	-	8.2	0.19	[101]
USA	Illinois #6	Bituminous	-	VAS	4.0	22.0	M-DA	66.9	-	9.5	0.49	[101]
USA	Wyodak–Anderson	Sub-bituminous	-	VAS	4.0	22.0	M-DA	86.7	-	8.9	0.34	[101]
USA	Beulah–Zap	Lignite	-	VAS	4.0	22.0	M-DA	75.7	-	10.1	0.40	[101]
USA	Seelyville	Bituminous	-	VAS	5.0 - 7.0	28.6	Various	38.1 - 53.2	0.440 - 0.458	-	-	[243]
USA	Herrin	Bituminous	-	VAS	5.0 - 7.0	28.6	Various	33.7 - 59.2	0.416 - 0.484	-	-	[243]
USA	Danville	Bituminous	-	VAS	5.0 - 7.0	28.6	Various	35.9 - 61.4	0.336 - 0.408	-	-	[243]
USA	San Juan	Bituminous	-	VAS	5.6	45.0	Various	79.4	0.355	-	-	[223]
USA	Herrin	Bituminous	-	VAS	5.3	23.5	Various	69.2	0.357	-	-	[223]
USA	Davis	Bituminous	-	VAS	5.2	23.5	Various	35.6	0.172	-	-	[223]

Table 2.3 (contd.): Summary of CO₂ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Coal rank(s)	Vitrinite reflectance, Rr. %	Sorption system	Max. pressure, MPa	Temp., °C	Isotherm model used	Carbon dioxide, CO ₂				Reference
								Q_0 (kg/t, db)	D (-)	E_s (kg/mol)	k (m ³ /t)	
USA	Seelyville	Bituminous	-	VAS	5.0	23.5	Various	60.1	0.272	-	-	[223]
USA	8 Indiana coals	Bituminous	0.48 - 0.62	VAS	2.1	17.0	VAS	32.1 - 43.9	-	-	-	[273]
USA	8 Indiana coals	Bituminous	0.48 - 0.62	VAS	2.8	17.0	VAS	34.4 - 48.4	-	-	-	[273]
USA	Various (3 samples)	Bituminous	-	GAS	1.8	30.0	GAS	20.7 - 63.8	-	-	-	[263]
USA	Various (16 samples)	Various	-	VAS	4.8 - 17.2	20.6 - 22.8	L	52.7 - 72.1	-	-	-	[264]
USA	4 B. Columbia coals	Bituminous	-	VAS	5.0 - 8.0	30.0	L	28.7 - 66.8	-	-	-	[274]
USA	3 Illinois coal	Bituminous	-	VAS	5.0	28.6	D-A	35.1 - 44.7	0.40 - 0.48	-	-	[243]
USA	4 Illinois coal	Bituminous	-	VAS	5.0	28.6	L	45.7 - 52.1	-	-	-	[243]
USA	3 USA coals	Bituminous	-	VAS	10.0	46.1	L	12.1 - 48.8	-	-	-	[265]
USA	3 USA coals	Bituminous	0.72 - 1.56	VAS	20.0	40.0 - 80.0	VAS	39.5 - 103.0	-	-	-	[275]

Table 2.4: Summary of CH₄ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Rank of coal(s)	Vitrinite reflectance, Rr. %	Sorption system	Maximum pressure, MPa	Temp., °C	Isotherm model used	Methane, CH ₄				Reference
								<i>Q₀</i> (kg/t, db)	<i>D</i> (-)	<i>E_s</i> (kg/mol)	<i>k</i> (m ³ /t)	
Australia	A, B, C	Bituminous	-	GAS	20.0	53.0 ± 1	Various	17.0 - 18.0	0.068 - 0.074		0.012 - 0.018	[102]
Australia	Hunter Valley	Bituminous	0.81	GAS	20.0	55.0 ± 1	M-DR	18.0	0.054	11.8	0.006	[266]
Australia	Illawarra	Bituminous	1.40	GAS	20.0	55.0 ± 1	M-DR	13.9	0.057	11.4	-0.006	[266]
Australia	Coal 1 - 6 (6 coals)	Bituminous	0.62 - 1.40	GAS	20.0	55.0	M-DR	9.5 - 17.5	-	10.0 - 11.6	-0.001 - 0.013	[104]
Australia	A1, A2, A3	Bituminous	0.80 - 1.34	GAS	20.0	45.0 - 55.0	M-L	15.1 - 19.3	-	-	-	[202]
Australia	16 Bowen basin coals	Bituminous	0.81 - 1.66	VAS	5.0	30.0	L	20.3 - 31.1	-	-	-	[290]
Australia	Various (41 samples)	Bituminous	0.6 - 1.7	GAS	6.1	27.0 - 39.0	L	15.4 - 55.7	-	-	-	[268]
Brazil	Rio Bonito (4 samples)	Bituminous	0.82 - 1.62	VAS	17.0 - 25.0	35.0 - 45.0	L	2.9 - 9.1	-	-	-	[269]
Canada	1 sample	Bituminous	-	VAS	7	30.0	L	15.8	-	-	-	[262]
China	Tashan	Bituminous	0.81	GAS	20.0	55.0 ± 1	M-DR	9.9	0.072	10.2	-0.006	[266]
China	Fenghuangshan	Anthracite	-	VAS	4.5	30.0	D-A	23.5	0.262	9.6	-	[200]
China	Changcun	Bituminous	-	VAS	4.5	30.0	D-A	17.6	0.287	8.8	-	[200]
China	Malan	Bituminous	-	VAS	4.5	30.0	D-A	11.8	0.264	9.6	-	[200]
China	Xin'an	Bituminous	-	VAS	4.5	30.0	D-A	14.7	0.252	10.0	-	[200]
China	Various (9 coals)	Various	0.50 - 3.45	VAS	12.0	27.0	L	15.8 - 24.7	-	-	-	[285]
China	Variuos (12 samples)	Sub- & bituminous	0.46 - 0.73	VAS	10.0	30.0	L	2.2 - 8.3	-	-	-	[291]
China	Duanshi	-	-	VAS	6.0	25.0	L	26.8	-	-	-	[242]
China	Duanshi	-	-	VAS	6.0	25.0	D-R	26.5	0.062	-	-	[242]
China	12 Haizi coals	Semi-anthracite	2.30 - 2.78	VAS	5.0	30.0	L	17.6 - 26.5	-	-	-	[292]
China	Variuos (11 samples)	Various	0.82 - 4.06	VAS	5.0	30.0	L	11.3 - 40.5	-	-	-	[293]
China	3 Xutong coals	Bituminous	0.88 - 0.96	VAS	10.0	30.0 - 70.0	L	3.4 - 9.6	-	-	-	[294]
China	3 Chinese coals	Various	0.53 - 3.86	VAS	25.0	35.0 - 55	M-L	12.8 - 25.7	-	-	-	[245]
China	Heilongjiang (6 samples)	Bituminous	-	VAS	20.0	20.0 - 70.0	M-BET	8.7 - 11.1	-	-	-	[240]
China	Sihe	Anthracite	-	VAS	10.0	20.0 - 40.0	L	15.7 - 21.4	-	23.3	-	[295]
France	Various (11 samples)	Various	0.49 - 3.65	GAS	5.0	25.0	Various	4.6 - 23.4	-	-	-	[270]

Table 2.4 (contd.): Summary of CH₄ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Rank of coal(s)	Vitrinite reflectance, Rr. %	Sorption system	Maximum pressure, MPa	Temp., °C	Isotherm model used	Methane, CH ₄				Reference
								<i>Q₀</i> (kg/t, db)	<i>D</i> (-)	<i>E_s</i> (kg/mol)	<i>k</i> (m ³ /t)	
India	Various (14 coals)	Bituminous	0.61 - 1.94	VAS	4.6 - 5.9	30.0	L	6.7 - 21.6	-	-	-	[288]
India	5 Sawang coals	Bituminous	0.94 - 1.21	VAS	5.9	30.0	L	7.9 - 15.6	-	-	-	[296]
Italy	I1, I2	Bituminous	0.70 - 0.74	GAS	20.0	33.0 - 60.0	M-L	26.2 - 29.0	-	-	-	[202]
New Zealand	Various (11 samples)	Sub-bituminous	0.34 - 0.53	VAS	5.0 - 8.0	31.5 - 35.1	L	1.9 - 3.0	-	-	-	[80]
Switzerland	S1, S2, S3	Bituminous	0.85 - 0.90	GAS	20.0	45.0	M-L	13.2 - 14.6	-	-	-	[202]
South Africa	MDT1 - 15	Various (15 coals)	0.79 - 4.31	GAS	6.0	27.0	L	5.9 - 16.5	-	-	-	[271]
South Korea	Kyungdong coal	Anthracite	5.07	VAS	15.2	45.0	L	9.5 - 10.5	0.042	-	0.0057	[272]
South Korea	Kyungdong coal	Anthracite	5.07	VAS	15.2	65.0	L	10.1 - 10.2	0.068	-	0.0035	[272]
UK	Selar Cornish	Semi-anthracite	2.41	VAS	16.0	45.0 - 65.0	M-L	15.6	-	-	-	[239]
USA	San Juan	Bituminous	-	VAS	9.9	45.0	Various	12.1	0.308	-	-	[223]
USA	Herrin	Bituminous	-	VAS	9.6	23.5	Various	17.7	0.490	-	-	[223]
USA	Davis	Bituminous	-	VAS	9.1	23.5	Various	7.4	0.0804	-	-	[223]
USA	Seelyville	Bituminous	-	VAS	8.7	23.5	Various	13.5	0.263	-	-	[223]
USA	8 Indiana coals	Bituminous	0.48 - 0.62	VAS	2.1	17.0	VAS	2.3 - 3.8	-	-	-	[273]
USA	8 Indiana coals	Bituminous	0.48 - 0.62	VAS	2.8	17.0	VAS	2.9 - 3.9	-	-	-	[273]
USA	Various (3 samples)	Bituminous	-	GAS	1.8	30.0	GAS	4.2 - 10.7	-	-	-	[263]
USA	Various (16 samples)	Various	-	VAS	4.8 - 17.2	20.6 - 22.8	L	7.7 - 9.5	-	-	-	[264]
USA	4 British Columbia coals	Bituminous	-	VAS	5.0 - 8.0	30.0	L	6.5 - 14.7	-	-	-	[274]
USA	3 USA coals	Bituminous	-	VAS	10.0	46.1	L	1.7 - 14.2	-	-	-	[265]
USA	3 USA coals	Bituminous	0.72 - 1.56	VAS	20.0	40.0 - 80.0	VAS	5.9 - 54.5	-	-	-	[275]

Table 2.5: Summary of N₂ high pressure sorption properties of coals of various ranks and diverse origins.

Origin of coal	Sample ID	Rank of coal(s)	Vitrinite reflectance, Rr.%	Sorption system	Maximum pressure, MPa	Temp., °C	Isotherm model used	Nitrogen, N ₂				Reference
								Q_0 (kg/t, db)	D (-)	E_s (kg/mol)	k (m ³ /t)	
Australia	A, B, C	Bituminous	-	GAS	20.0	53.0 ± 1	Various	17.0 - 19.0	0.012 - 0.018	-	0.093 - 0.010	[102]
Australia	Coal 1 - 6 (6 coals)	Bituminous	0.62 - 1.40	GAS	20.0	55.0	M-DR	9.4 - 19.2	-	8.6 - 10.4	-0.001 - 0.018	[104]
Australia	A1, A2, A3	Bituminous	0.80 - 1.34	GAS	20.0	45.0 - 55.0	M-L	20.1 - 26.3	-	-	-	[202]
Canada	1 sample	Bituminous	-	VAS	7	30.0	L	13.5	-	-	-	[262]
China	Duanshi	-	-	VAS	6.0	25.0	L	32.8	-	-	-	[242]
China	Duanshi	-	-	VAS	6.0	25.0	D-R	28.6	0.11	-	-	[242]
Italy	I1, I2	Bituminous	0.70 - 0.74	GAS	20.0	33.0 - 60.0	M-L	28.0 - 35.9	-	-	-	[202]
Switzerland	S1, S2, S3	Bituminous	0.85 - 0.90	GAS	20.0	45.0	M-L	18.5 - 18.8	-	-	-	[202]
UK	Selar Cornish	Semi-anthracite	2.41	VAS	16.0	45.0 - 65.0	M-L	20.5	-	-	-	[239]
USA	Various (3 samples)	Bituminous	-	GAS	1.8	30.0	GAS	3.4 - 9.2	-	-	-	[263]
USA	Various (16 samples)	Various	-	VAS	4.8 - 17.2	20.6 - 22.8	L	7.3 - 7.4	-	-	-	[264]
USA	3 USA coals	Bituminous	-	VAS	10.0	46.1	L	1.1 - 12.0	-	-	-	[265]

2.6 Factors affecting high pressure sorption properties of gases in coals

The sorption properties, including sorption capacities of coals and the stability of the adsorbed gases can be affected by a number of factors. These factors include those related to coal properties and composition (petrography, rank, physical- and chemical-structural properties, moisture content of the coal, etc.), and the environmental or operational variables as temperature and pressure. In a practical coal seam storage, variables such as: change in pH, underground water floods through the coal seam, temperature and pressure gradient through the depth of the seam, and mineral composition becomes significant [155, 185, 199, 236, 275, 297, 298]. Some of the parameters that can affect the sorption properties and the stability of the adsorbed gases are summarised in this section.

2.6.1 Influence of coal properties on the sorption capacities of the samples

2.6.1.1 Influence of coal rank and petrography

Coal is highly heterogeneous and contains a wide variety of organic and mineral matter in a complex, porous, three-dimensional network, which varies from one coal deposit to another and from one location to another within the same seam. Petrographic properties such as rank has been severally reported as having considerable influence in the sorption capacities of gases in coals [199, 205, 230, 255, 271, 275, 285, 289, 299-301]. This can be attributed to the micropore structural evolution during coalification [55], with the simultaneous improvement in the micropore volume, microporosity, micropore surface area with decreasing rank. However, this trend tend to reverse after vitrinite reflectance of 1.2 – 1.3 Rr.% and higher, especially for CO₂ and CH₄. Day et al. [230] and Zhang et al. [255] have reported a U-shaped trend with rank, where the CO₂ and CH₄ maximum sorption capacities of coals of various ranks decreased with increasing Rr.% until a point of inflection at around 1.3 Rr.%, after which sorption capacities increased, which has been corroborated by other investigators for coals of varying ranks [236, 289].

It has been reported by several authors that maceral composition (inertinite, vitrinite, and liptinite) and abundance does not significantly influence the sorption properties of gases on coals [230, 236, 289]. The correlation of the sorption properties of coals by these investigators have yielded a wide scatter without any systematic trend. In fact, Weishauptová, et al. [236]

described the influence of maceral compositions of some European bituminous coals from the Upper Silesian basin on the CO₂ and CH₄ sorption capacities of the samples as ambiguous. However, maceral composition has been reported to impact on the evolution and development of porosity during coalification in coal [46-48, 54, 55, 60, 85, 302, 303].

Petrographic properties such as microlithotype abundance has been found to influence the sorption capacities of gases on coal [286, 302-304]. It is well known that coal microlithotype which is a reflection of the variety of combination(s) of maceral groups is not evenly distributed in coal; but tend to occur in band or layers, which gives coal its layered luster. Banding in coal develops or rather becomes more apparent with the increased compaction during rank advance from lignite to bituminous coal [302]. Thus, microlithotypes becomes less observable with increasing rank as the more reactive macerals (vitrinites and liptinites) lose their volatile components with concomitant increase in elemental carbon content, and thus appear more comparable to inertinites under the petrographic microscope, in terms of shade and gray [9]. However, it is still possible to distinguish between vitrinites and inertinites in anthracites, and thus possible to distinguish the different microlithotypes in anthracites, although significantly less in volume compared to microlithotypes in bituminous coals [302]. Cleats and often fractures in coal matrices follow these bands; they are the conduits and principal pathways for the migration of fluids in coal seams [286, 302-305], which may enhance the accessibility of remote pores [55, 304], and thus the pore volume of the geological storage media [304]. Furthermore, the abundance of these intermediate macerals (microlithotype) decreases with increasing rank [10, 302].

2.6.1.2 *Influence of pore and porosity properties of coal*

It has been demonstrated by several investigators that the physical-structural properties of coal including: surface area, porosity, pore size distribution, and pore structure, significantly influences gas sorption on coal [60, 155, 199, 230, 236, 255, 275, 289, 302]. The sorption capacities of gases on coals has been found to increase with increasing micropore surface area, microporosity and micropore volume; and decreasing average micropore diameter [223, 255, 289, 306, 307]. These show that the micropore properties of coals largely determine the high pressure sorption capacity of coal to various gaseous adsorbates, and that detailed characterisation of the micropore properties of coal seams can give useful insights into their gas storage capabilities, if they are intended to be used as a geological sinks for CO₂. However,

knowledge of the meso- and macro-pore properties is still important as they are the channels for fluid transport in coal seams, and thus may influence the kinetics of sorption [77, 264, 300]. Storage of gases, especially CO₂ and CH₄ in coal seams, is widely known to occur via physisorption and pore filling of micropores and held in place by capillary and structural trapping [152, 171, 180-182, 308, 309] (see Section 2.3.1).

2.6.1.3 *Influence of operational and environmental parameters*

In a typical coal seam designated for use as a geological sink for CO₂, several operational and or environmental variables influence the sorption capacity of the coal seams. These include: temperature, pressure, coal moisture (water flood), and minerals. Underground seam pressure and temperature increases with depth, but tends to be constant at the same depth on a regional scale. Mazzotti et al. [199] reported temperatures of up to 40 °C and pressures > 7 MPa for various coal seams, while Mastalerz et al. [275] reported a temperature gradients of up to 0.54 °C/m. However, high pressures, up to 30 MPa and high temperatures, ≥ 55 °C, have been found for some deep seated coal seams [155, 283].

2.6.1.3.1 *Operational temperature*

Sakurovs et al. [234] investigated the influence of temperature on the high pressure (up to 15 MPa) CO₂, CH₄ and N₂ sorption capacities of the well-studied Argonne premium coals at a temperature range of 25 to 55 °C, and found for the three gases studied, that the sorption capacity of the coals decreased inversely with increasing absolute temperature. They noted that this is inconsistent with expectations from Langmuir isotherm model of coal sorption, which predict a temperature-invariant sorption capacity, and further discarded activated diffusion as possible cause of differences in sorption capacity. If activated diffusion occurs during the sorption processes, then the sorption capacity of the coals should be expected to increase with increasing temperature. Ruppel et al. [310] reported significant decrease in the CH₄ and C₂H₆ sorption with increasing temperature (0 – 50 °C) on dry coals.

Levy et al. [189] showed a linear decrease in CH₄ sorption capacity on moisture-equilibrated Bowen basin Australian coal with increasing temperature. Due to the fact that sorption of gases

such as CO₂ and CH₄ on coal is exothermic [97, 102, 104, 234, 311], the sorption process will provide a heat source, at least during the active pumping phase of sequestration. Furthermore, some sequestration scenarios would provide additional heating mechanisms, such as heat production by the dissolution of co-sequestered acid gases (SO_x, NO_x) or by reaction of CO₂ with residual oxygen in the flue gas. Thus, temperature consideration is an important factor during storage of gases in coal seams.

2.6.1.3.2 Operational pressure

It is well known from both laboratory and field experiments that, while the density of the adsorbed phase increases, the volume of adsorbed phase of sequestered gases decreases with increasing pressure [97, 199, 275, 285, 287, 305, 309, 312]. In a practical storage scenario, this observation will further be compounded (or enhanced) by increasing pressure and temperature gradient with depth, and the evolving hydraulic pressure resulting from the injection of the gases [309, 312].

2.6.1.3.3 Moisture content

Coal seams are naturally wet and will undergo recharge from surface water more rapidly during storage processes as a result of drilling operations, fracturing of the coal bed and over-lying strata, and the injection of gases which may contain residual water. Thus, an aqueous phase will be present during sequestration and will vary in composition according to its source and the nature of the coal bed and the surrounding minerals with which it is in contact. From laboratory experiments, it has been shown that moisture in coal reduces the sorption capacity of gases on coal [97, 230, 267, 313]. Krooss et al. [97] studied the influence of moisture on the CO₂ and CH₄ sorption capacity of both dry and moisture-equilibrated Pennsylvanian coals of different ranks (0.72 - 1.56% Rr.%) at different temperatures and up to 20 MPa pressure. Their results show that, for both gases, the sorption capacities of the samples were reduced by 20 – 25% in the moisture-equilibrated compared to the dry coals, which has been attributed to competition for adsorption sites by water molecules and the molecules of the gases. Joubert et al. [314] studied the effect of varying moisture contents on the CH₄ sorption capacities of US bituminous coals at a temperature of 30 °C and pressures up to 6.1 MPa, and found that for all

coals studied, the CH₄ sorption capacity decreased with increasing moisture content up to a critical value which is characteristics of the coal type. Moisture contents above the critical moisture value seem to have no effect on the CH₄ sorption capacity [314]. However, the presence of water in coal seams may, in practical sequestration systems, provide some additional storage capacity through dissolution of CO₂, beyond that afforded by sorption alone. Busch et al. [315] estimated for some low rank coals, that the dissolution of CO₂ into coal seam moisture may account for up to 50% of the total sorption capacity of the coals, and highlighted the need to measure sorption properties under actual seam conditions for accurate sequestration potential to be established.

2.6.1.3.4 Changes in pH of coal seam moisture

Although changes in pH will be difficult to measure during laboratory experimentations of high pressure sorption processes, changes in pH during practical storage processes in coal seams is a real possibility [275]. Changes in pH can affect the coal and CO₂ sequestration process in coal seams in various ways. A decrease in pH can dissolve and extract minerals associated with the coal [11, 55, 316-318]. Changes in pH can also alter the surface charge of the coal [318] which, can affect the intermolecular interactions responsible for the 3-dimensional structure of coal macromolecular network [317]. Due to the significance of the aperture size of pores in coal as fluid transport channels and because the maximum adsorbed amount is related to the pore volume [47, 54], the resulting impact of changes in pH may affect the storage capacity of the coal and the stability of the adsorbed gases, especially the reactive CO₂.

2.6.1.3.5 Influence of mineral matter in coal

It is generally accepted that dissolved gases especially CO₂, SO_x and NO_x during sequestration of gases in coal seams may directly or indirectly react with minerals in and around the coal seam, promoting precipitation of carbonate minerals [152, 171, 184-187]. These reactions are more significant in the presence of Ca and Mg rich minerals [184-188]. Mineralisation during CO₂ sequestration in coal seams is attractive due to its immobilisation effect on the injected CO₂ for long geological periods [152, 184-186, 188]. However, Benson & Cole [152] have noted that the mineralisation process is comparatively slow and may only be realised in tens to hundreds of years.

2.6.1.4 *Influence of critical properties of the gases*

It has been demonstrated by several investigator that the sorption capacities (by volume) of CO₂, CH₄, and N₂ on coals of various rank and types, generally decreased in the order: CO₂ < CH₄, < N₂ [102, 104, 202, 234, 239, 242, 253, 257, 262-267]. This widely accepted order is definitely not due to the coals' properties, but due to the properties of the adsorbates, especially the critical properties of the gases [104, 235, 257, 267]. Sakurovs and co-workers [104] investigated the relationship between the critical properties of different adsorptive gases on their supercritical sorption behaviour on Australian bituminous coals, and reported that the maximum sorption capacities of the coals under supercritical conditions correlated well with the critical properties of the gases. Critical properties of gases such as van der Waals' attractive constants and the polarizabilities, have been reported to significantly influence the sorption properties of gases on coals and other carbonaceous adsorbents [104, 235, 257]. It has been demonstrated that the easier a gas is to polarise, the stronger the interaction with the adsorbent surface, as well as neighbouring adsorbate molecules [104, 235, 257, 319, 320]. This may explain the greater affinity exhibited by coal pore surfaces to CO₂ compared with coal pore surfaces' affinity to CH₄ and N₂ [102, 210, 235, 257, 267, 321].

2.7 Summary

A detailed literature review of research conducted in the area of coal properties and sorption properties of coals relevant for CO₂ sequestration in coal seams has been conducted. A summary of major findings are presented below:

- It has been shown from scientific evidence that anthropogenic greenhouse gas emissions emanating from fossil fuel utilisation, largely contributed to global climate change. Although unit CO₂ concentration possesses lower greenhouse warming potential (GWP), relative to unit concentrations of the other GHGs, its higher abundance in emitted anthropogenic GHGs means that it exhibits higher effective radiative forcing (RF), global temperature change potential (GTP) and GWP, compared to the total effects of the other GHGs.

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- Carbon capture and storage (CCS) has been identified as one of the options to mitigate global climate change. CCS is an array of value-added technologies that can be synergised with the ultimate aim of reducing anthropogenic CO₂ emissions from industrial point sources. CCS value-chain include:
 - (i). CO₂ capture and separation via:
 - Post-combustion capture from power plants,
 - Pre-combustion capture from IGCC power utilities, and other gasification systems,
 - Oxy-fuel (oxygen-rich) combustion system,
 - CO₂ capture from other fossil fuel industrial utilisation systems, eg. Metallurgical industries, paper production, etc.
 - (ii). The transport of the captured, separated, and compressed CO₂ (usually in the liquid phase) to a candidate geological storage location using pipelines or trucks.
 - (iii). The safe and permanent long-term storage of the CO₂ in deep candidate geological storage sites, thus, isolating the CO₂ from the atmosphere.
 - Geological locations for the storage of CO₂ include: ocean disposal, depleted oil and gas reservoirs with the synergy of enhanced oil and gas recovery (EOR & EGR), deep saline formations, and “unmineable” coal seams with the synergy of enhanced coalbed methane (ECBM) recovery.
 - For a candidate geological location to be suitable for CO₂ storage, it must have:
 - (i). Capacity, to contain the projected volume of CO₂
 - (ii). Injectivity, to take in the captured CO₂, and,
 - (iii). Confinement, to prevent the migration and seepage of the buoyant and mobile CO₂ from the storage spaces to other places in the subsurface, especially to shallow potable groundwater and or to the surface.
 - Structural trapping is the dominant initial storage mechanism for storage of gases (CO₂, CH₄, N₂, etc.) in coal seams, through physisorption. This is followed further by capillary trapping, solubility trapping and finally, mineralisation depending on the mineralogy of the coal seams and the surrounding media.
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- Various isotherm models have been used to describe and determine the sorption properties of coals. Sixteen (16) different isotherm models have been highlighted and discussed in this review. The applicabilities and limitations of these isotherms models in high pressure sorption systems, similar to operational conditions during coal seam sequestration of CO₂ has been discussed in detail.
 - The empirical and classical isotherm models: the Brunauer-Emmet-Teller (BET)-, the Langmuir-, the Dubinin-Astakhov-, and the Dubinin-Radushkevich- isotherm models were found to be applicable only for low pressure sorption systems. Only modified versions of these models can be applied to high pressure sorption processes.
 - The modified Dubinin-Radushkevich isotherm model and its Henry's law hybrid (Dr-HH) isotherm model has been variously reported to fit high pressure sorption isotherm data of different adsorptive gases on coals better than the other modified isotherm models. In the DR-HH isotherm model, a proportionality constant, k , was incorporated into the isotherm model equation to account for Henry's law dissolution, and probable imbibition and swelling by gases, especially for CO₂ and CH₄, at higher pressures. This proportionality constant can also provide insights on the extent of coal volume penetrated by the adsorptive gases.
 - Data on maximum sorption capacities of dry coals of various ranks, up to anthracite from 16 different countries (Australia, Brazil, Canada, China, France, India, Italy, Japan, New Zealand, Poland, Switzerland, Slovenia, South Africa, South Korea, UK, and USA), vary on weight basis in the range: 20.7 – 151.4 kg/t for CO₂, 7.4 – 29.0 kg/t for CH₄, and 3.4 – 35.9 kg/t for N₂. These translates to sorption capacities of 2.1 to 15.1 wt.% of dry coal for CO₂, 0.7 - 2.9 wt.% of dry coal for CH₄, and 0.3 - 3.6 wt.% of dry coal for N₂. Generally, sorption capacities of coals were found to decrease in the order: CO₂ > N₂ $\approx$ CH₄ by weight and CO₂ > CH₄ > N₂ on volume or mole basis.
 - The determined net heats of sorption, β Es, of coals of different ranks reported in open literature vary in the range: 8.2 – 13.5 kJ/mol for CO₂, 8.8 – 11.8 kJ/mol for CH₄, and 8.6 - 10.4 kJ/mol for N₂; and seem to decrease in the order: CO₂ > CH₄ > N₂.
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- Operational and environmental conditions such as temperature, pressure, moisture content of the geological site, pH and mineralogy of the geologic media, influences the sorption properties of coal seams as geological storage site.
 - The physical- and chemical-structural properties of coals impact their sorption properties, especially storage capacity and containment properties. Coal properties and / or characteristics can be studied by both conventional and advanced analytical techniques. Standard analytical techniques used include: proximate and ultimate analysis, petrography, helium pycnometry, surface area and pore properties analysis via CO₂- and N₂-low pressure gas adsorption (CO₂- and N₂-LPGA), mercury intrusion porosimetry (MIP), wide-angle X-ray diffraction (WAXRD) mineral analysis, X-ray florescence (XRF) inorganic components analysis, etc. Some of the advanced analytical techniques applied in coal characterisation include: small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction carbon fraction analysis (WAXRD-CFA), scanning electron microscopy (SEM), attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy, ¹³C nuclear magnetic resonance spectroscopy (¹³C NMR), high-resolution transmission electron microscopy (HRTEM), etc.
 - Some of the coal properties found to influence the sorption properties of coal as a geological sink include: coal rank, pore structural properties (micro-, meso- and macro-pore properties) of the coal, the mineralogy of the coal, and the in-situ chemical properties of the coal seam surroundings.
 - As the high pressure sorption of gases in coals as a storage option for anthropogenic GHGs occur at conditions usually above the critical properties of the gases (CO₂, CH₄, N₂, etc.), the critical properties of these gases also impact their sorption properties at the in-situ storage condition.

Nomenclature

<u>Symbol</u>	<u>Definition</u>
$A_{(g)}$	Unadsorbed gaseous molecule
AB	Adsorbed gaseous molecule
$B_{(s)}$	Unoccupied solid adsorbent surface
C	A BET isotherm model constant related to heat of adsorption
D	DR or DA affinity constant (-)
d_p	Pore diameter (Å)
E	Polanyi's characteristic adsorption energy (kJ/mol)
E_0	Characteristic heat of sorption (kJ/mol)
k	Proportionality constant (ml/g)
kg/t	Kilogram per tonne
M_{mea}	Mass of gas sorbed at a given pressure and temperature
n	Structural heterogeneity parameter (-)
P	Instantaneous experimental pressure (MPa)
P/P_0	Relative vapour pressure (-)
P/P_s	Relative vapour pressure (-)
P_0	Saturation vapour pressure (MPa)
P_L	Langmuir pressure (MPa)
P_s	Saturation vapour pressure (MPa)
Q_0	Maximum sorption capacity of sample(s) (kg/t _{coal})
Q_{exc}	Gibb's or excess sorption (kg/t _{coal})
R	Ideal gas constant (kJ/mol·K ⁻¹)
$Rr. \%$	Vitrinite reflectance (%)
T	Experimental absolute temperature (K)
V	Quantity of gas adsorbed onto a solid sample (kg/t _{coal} ; m ³ /t _{coal})
V_0	BET monolayer capacity of the adsorbent (coal) (kg/t _{coal})
V_{BET}	Maximum sorption capacity from BET isotherm model (m ³ /t _{coal})
V_{cell}	Volume of the sample cell (m ³)
V_{DR}	DR maximum sorption capacity (kg/t _{coal})
V_L	Langmuir volume (Maximum sorption capacity) (kg/t _{coal})
V_{sample}	Volume of sample (m ³)
wt. %	Weight percent (%)

Greek symbols

<u>Symbol</u>	<u>Definition</u>
ϵ	Polanyi adsorption potential (J)
β	Affinity coefficient (-)
ρ_g	Adsorptive gas density at a given pressure and temperature (kg/m ³)
ρ_a	Density of the adsorbed phase (kg/m ³)

Abbreviations

<u>Acronym</u>	<u>Definition</u>
adb	Air dry basis
ATR-FTIR	Attenuated total reflection Fourier transform infra-red spectroscopy
BET	Brunauer-Emmet-Teller isotherm model
CBM	Coal bed methane
CCS	Carbon dioxide capture and sequestration (or storage)
CH ₄	Methane
CO ₂	Carbon dioxide
CTL	Coal to liquid
DA	Dubinin–Astakhov isotherm model
dafb	Dry ash free basis
db	Dry basis
DR	Dubinin-Radushkevich isotherm model
DR-HH	Dubinin-Radushkevich/Henry law hybrid isotherm model
ECBM	Enhanced coal bed methane
EGR	Enhanced gas recovery
EOR	Enhanced oil recovery
EOS	Real gas equation of state
FTIR	Fourier transform infra-red spectroscopy
GAS	Gravimetric adsorption system
GHG	Greenhouse gas
HP	Helium pycnometry
HPGSS	High pressure gravimetric sorption system

HRTEM	High resolution transmission electron microscopy
IGCC	Integrated gasification combined cycle
IR	Infra-red spectroscopy
IUPAC	International Union of pure and applied Chemistry
L	Langmuir isotherm model
LPGA	Low pressure gas adsorption (LPGA)
M-DA	Modified Dubinin–Astakhov isotherm model
M-DR	Modified Dubinin-Radushkevich isotherm model
MIP	Mercury intrusion porosimetry
M-L	Modified Langmuir isotherm model
N ₂	Nitrogen
NMR	Nuclear magnetic resonance spectroscopy
NO _x	Oxides of nitrogen
P-V	Pressure-volume change
SANS	Small angle neutron scattering
SAXS	Small angle x-ray scattering
SEM	Scanning electron microscopy
SO _x	Oxides of sulphur
ss ¹³ C NMR	Solid state nuclear magnetic resonance spectroscopy
TEM	Transmission electron microscopy
TVFM	Theory of volume filling of micropores
USANS	Ultra small angle neutron scattering
USAXS	Ultra small angle x-ray scattering
VAS	Volumetric adsorption system
WAXRD	Wide angle X-ray diffraction
WAXRD-CFA	Wide-angle X-ray scattering - carbon fraction analysis

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Chapter 3

3.0 Sample characterisation I. Physical-structural properties of the coal samples

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Highlights

- ✓ Surface area and porosity of coal obtained using different analytical techniques.
 - ✓ Each technique probes different pore size ranges in coal.
 - ✓ Compressibility effect accounts for 20 – 25% of the obtained porosity and pore volume of coals from MIP.
 - ✓ SAXS technique returns higher values of surface area and porosity of coal.
 - ✓ SAXS technique covers pore sizes in the range: $5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$, not captured by the three other widely used methods.
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3.1 Abstract

In this paper, we compare the surface area, porosity and other physical-structural properties of four bituminous coals from three different coal fields of South Africa determined using carbon dioxide (CO₂) and nitrogen (N₂) low pressure gas adsorption (LPGA), mercury intrusion porosimetry (MIP), and advanced small angle x-ray scattering (SAXS) analytical techniques. Consistent with previous findings, N₂ adsorption underestimated the surface area and porosity of the samples compared to results obtained using the other techniques, but it provided a good insight into the pore size distribution of mesopores. The surface areas and porosities of the samples determined from SAXS were found to be larger than any of the values obtained using the other techniques. This is attributed to SAXS probing a wider range of pores, including pores that are closed to, or restricted in access by, gas adsorption or mercury intrusion and also capturing the properties of pores of diameters between 5 and 17 Å, which are not readily measured by any of the other techniques used in this investigation. However, we show here that because each technique probes different pore size ranges in coal, a combination of SAXS with other techniques (gas adsorption, MIP etc.) provides a richer picture of the nature of the porosity in coals.

Keywords: Surface area, porosity, pore sizes, PSD, SAXS, MIP, LPGA

3.2 Introduction

The porosity and surface area of coals are key elements in the study, determination and prediction of the behaviour of coals during their various preparation, beneficiation and utilisation processes [1-6]. Porosity and surface area are also leading factors when considering deep-seated coal seams as candidate site for geological sequestration of carbon dioxide, as an option for global climate change mitigation [6-13]. The sequestration of carbon dioxide in coal seams can be used to expel inherent methane in the process of Enhanced Coal Bed Methane (ECBM) production [5, 8, 14-17]. Moreover, understanding the nature of porosity in coals provides valuable information regarding the channels and pathways for fluids to move into and interact with the macromolecular structure of coals.

The pore structure of coals and other carbonaceous material are classified according to IUPAC classification [18, 19] as: micropores ($d_p \leq 20 \text{ \AA}$); mesopores or transitional pores ($20 \text{ \AA} \leq d_p \leq 500 \text{ \AA}$); and macropores ($d_p > 500 \text{ \AA}$), where d_p is the pore diameter. It is widely, though not universally, accepted that the pores in coals have a broad size distribution and form a constricted, interconnected network [1-4, 17, 19-23]. Experimental evidence shows that coal porosity and pore size distribution varies with the degree of maturity of coal as measured by the proxy indicators: carbon content and vitrinite reflectance. Both Rodrigues and Lemos de Sousa [22] and Gan and co-workers [20] found that, for lower-ranked lignites and sub-bituminous coals- (elemental carbon $< 75\%$, daf), porosity is primarily in the form of macropores (primary porosity). For intermediate-ranked bituminous coals ($76\% \leq$ elemental carbon $\leq 84\%$), loss of primary porosity sets in and the evolution of secondary porosity (micro- and meso-porosity) starts, such that about 80% of the accessible porosity is contributed by micro- and meso-pores. In higher-ranked coals (elemental carbon $> 85\%$, daf), microporosity predominates. Thus, as the rank of the coal increases, the importance of macroporosity decreases and microporosity becomes increasingly significant.

Adsorption of gaseous adsorbate (Ar, CO₂, C₂H₆, He, Kr, CH₄, N₂, Xe, water vapour, etc.) on coal (adsorbent) has been widely used to determine the surface area, pore structure (sizes and distribution) and porosity of coal and other carbonaceous materials. This is because gas adsorption methods are less costly and are more convenient to use than the other more advanced techniques. CO₂ and N₂ are the most commonly used adsorbate gases. Other methods widely used to probe surface areas and porosity properties of coals and other porous solids are: Wide angle x-ray diffraction (WAXRD), Ultra and Small angle x-ray and neutron scattering (SAXS,

SANS, USAXS and USANS), MIP, Helium pycnometry, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) [24, 25]. The adsorption mechanisms in microporous and mesoporous carbonaceous and other materials have been reviewed by Marsh [26], and Thommes [24].

For bituminous coals, surface area and porosity values obtained from CO₂ adsorption have been generally found to be much larger than the values from N₂ adsorption [1, 21, 23, 27]. This has been attributed to activated diffusion; the low thermal energy associated with N₂ at the analysis temperature during N₂ adsorption at -196 °C retards gas penetration, whereas the thermal energy associated with carbon dioxide at 0 °C [1-6, 17, 21, 26] is much larger (the rate of diffusion of CO₂ through cylindrical pores of molecular dimension at 0 °C has been found to be 10⁵ times higher than that of N₂ at -196 °C [4]). Measurement of low pressure gas adsorption of CO₂ on coal usually takes place at pressures < 1 atm and the shorter analysis time (< 10 hours) makes coal swelling an insignificant contributor to the obtained results [1, 4, 26].

MIP is another standard method of determining the porosity and surface areas of coals, but is limited only to meso- and macro-porosity [27-38]. Although the application of the macroporosity of coals to most of its utilisation processes is still very limited, the understanding of this property is relevant in predicting total gas capacities of coals when used for CO₂ sequestration [39].

Each of these widely used techniques only probe specific pore size ranges and thus cannot be used independently to describe the overall porosity or pore size distribution of the sample. Standard measurements from CO₂ low pressure gas adsorption techniques can only probe pores in the range: $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ (lower micropore range), determined using the Horvath-Kawazoe (H-K) method in this study. However, an upper limit of 8.5 Å has been reported by Mastalerz et al. utilising the DFT technique in their PSD analysis [6, 13]. N₂ analyses are claimed to cover pores in the range: $17 \text{ \AA} \leq d_p \leq 3000 \text{ \AA}$ (higher micropore and entire mesopore range). Effective pore size distribution (PSD) analysed using MIP is in the range: $30 \text{ \AA} \leq d_p \leq 600000 \text{ \AA}$ (60 µm) (meso- and macro-pore range). The lower and upper pore size limits from MIP was determined from the intrusion pressure of mercury using the empirical Washburn equation [25, 27-31, 34-37, 40]. This means that a more complete description of the pore structure, surface area and porosity of coals has to combine results obtained from these three techniques. Unfortunately, properties of micropores in the size range: $8.5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$ are not readily picked up by any of these three widely used standard methods.

In recent times, Small Angle X-ray (SAXS) has gained popularity as a coal characterisation tool. SAXS has the advantage of probing a wider range of pore sizes in a single experiment than MIP or gas adsorption (CO_2 and N_2) [3, 14, 21, 41-44]. When X-rays penetrate materials, they are scattered off density contrasts within the material at a range of scattering angles. The resulting scattering pattern, which is specific to the structure of the material, can be analysed to estimate surface areas and porosity features of the sample. Because SAXS scatters off density contrasts in coals, it not only scatters off density differences between the material and empty pores, but also scatters off the density differences between their organic and inorganic components [44]. Thus, results from SAXS need to be corrected for the influence of coals' mineral matter. One way to correct for this is to assume that the mineral matter size distribution is the same as that of the empty pores and subtracting the scattering length density (SLD) of the significant mineral phases from the overall SLD of the coal and using the corrected SLD for the necessary calculations [44]. In this paper, this assumption has been avoided by demineralising the four samples following a three step HCl-HF-HCl process reported elsewhere [45], with demineralisation efficiency $> 93\%$. Demineralisation will produce a material whose pore distribution as determined by SAXS is that of the organic component of the coal.

The objective of this paper is to show the relative significance of different techniques employed in probing the surface area and porosity properties of coals with regard to the effective pore size ranges analysed by these methods and the overall quality of fit. To achieve this, results obtained from four different techniques were methodically examined in detail and critically compared against each other. The findings from this paper give insights into the capabilities and limitations of techniques available for the determination of the surface area and porosity of coals; which are some of the major factors influencing the characteristic behaviour of coals during utilisation processes including CO_2 storage in coal seams, combustion, gasification, liquefaction, etc.

3.3 Experimental

3.3.1 Origin of coal samples

The four Run of Mine (ROM) coal samples investigated in this work were collected from actively mined underground coal seams within the Highveld, Witbank, and the Tshipise-Pafuri

coalfields of South Africa. The coal samples were selected from four different actively mined underground coal seams for the study of their sub- and super-critical CO₂, CH₄ and N₂ sorption capacities with a view to generating data that can be used to predict the CO₂ captive properties of deep seated unmineable or uneconomical coal seams of South Africa. The coal samples are code-named Coal DEN, Coal FOZ, Coal OGS and coal TKD. Coals DEN and OGS originated from the Highveld Coalfields, while coal FOZ and coal TKD are from Witbank and Tshipise-Pafuri coalfields respectively.

3.3.2 Sample preparation

The ROM coal samples were received in particle sizes ranging from fine powders to 50 mm particle diameter. Representative samples were obtained by cone and quartering; and crushing and screening was employed to obtain the required size ranges for analyses and experimentations. The samples were initially flushed with N₂ gas, stored in a vacuum-sealed thick polyethylene container and kept in a desiccator. All sample characterisation analyses and experiments were conducted on -75 µm size particles, except MIP and petrographic analysis that were carried out on 1 mm average size particles.

3.3.3 Sample Characterisation

3.3.3.1 Standard properties

Standard analyses used were the proximate, ultimate, and petrographic analysis, total sulphur content, free swelling index and calorific value. The petrographic analysis was conducted at Petrographics SA, Pretoria, and the rest of the standard analyses were carried out at the laboratory of Advanced Coal Technology (ACT), Pretoria.

3.3.4 Physical-structural properties of samples

3.3.4.1 Density measurement

The skeletal density of the samples was measured on a Micromeritics Accupyc II 1340 Gas Pycnometer, using helium gas at an outlet pressure of 1.34 bars in a 10 cm³ sample cell. The samples were initially dried under vacuum at 105 °C prior to the analysis. Dried samples

weighing 5-6 g (or about 75 vol. % of the sample cell) were placed in the sample compartment; flushed with helium gas and degassed automatically to a pressure of 10 μmHg . Helium skeletal density data were taken as average of three analysis results and the experimental error was calculated from this set of data at 95% confidence interval.

3.3.4.2 *CO₂ and N₂ low pressure gas adsorption*

The determination of the CO₂- and N₂- surface areas and porosity properties of the coals were conducted on a Micromeritics ASAP 2020 surface area and porosity analyser. The samples (about 0.20 g each) were degassed under vacuum (10 $\mu\text{m Hg}$) at 90 °C for 2880 minutes on the degassing port of the equipment prior to adsorption analysis (0 °C in an ice bath for CO₂ and at -196 °C (77 K) in liquid N₂ for N₂ adsorption measurements respectively) [46]. The adsorption data were automatically acquired by the ASAP 2020 v4.0 software in the relative pressure range: $0 < P/P_0 \leq 0.032$ for CO₂ and $0 < P/P_0 \leq 0.30$ for N₂ analyses respectively. For N₂ adsorption, especially for coals, P/P_0 is usually limited to ~ 0.3 as this relative pressure range corresponds to a multi-layer coverage of few layers of N₂, and the $1/[Q(P_0/P-1)]$ against (P/P_0) plot remains linear in this range. At higher P/P_0 values condensation of N₂ in the pores starts, leading to a wide scatter, a non-linear $1/[Q(P_0/P-1)]$ versus (P/P_0) plot and a significantly lower correlation coefficient and surface areas [4, 24, 38, 47]. Lower limit of P/P_0 (~ 0.03) is used for the evaluation of CO₂ adsorption surface areas in coal as micropores are filled at a much lower P/P_0 than mesopores [4, 5, 24, 26].

The micropore surface areas of the samples were determined from CO₂ adsorption data using the Dubinin-Radushkevich (D-R) method [3, 46]. The maximum micropore volume, the average micropore diameter, and the pore size distribution (PSD) of the samples were determined from the CO₂ adsorption results following the H-K method [46, 48-50]. The calculations were based on the entire isotherms within the reduced pressure ranges. The Horvath-Kawazoe method is a modification of the Kelvin equation, but differs from it, as pore filling by the liquid phase of adsorbate rather than gaseous phase adsorbate layer formation and slit shaped pore dimensions are considered [48, 50], giving a more realistic micropore PSD in the lower P/P_0 range ($0 \leq P/P_0 \leq 0.07$) than the Kelvin equation. However, the application of the H-K method is only suited for micropore PSD. Both Jaroniec et al. [49] and Kowalczyk and co-workers [50] have demonstrated the reliability of the H-K method experimentally and numerically for microporous carbons and other solid materials respectively. The surface areas

from the N₂ adsorption were evaluated from different methods including: BET, Langmuir and Barrett-Joyner-Halenda (BJH) methods. The pore volumes and average pore diameter from N₂ adsorption results were determined using the H-K, BET and BJH models. The PSD of the samples from N₂ adsorption were determined from the desorption isotherm using the BJH method [51]. The micro- and meso-porosity of the samples were determined from the CO₂ and N₂ adsorption data [46]. All the adsorption experiments were repeated three times and the final results are averages of three independent results from which experimental errors were calculated at 95% confidence interval.

3.3.4.3 *MIP measurements*

MIP measurements were obtained from Micromeritics AutoPore IV 9500. An average sample particle size of 1 mm (+850 -1140 µm) and a penetrometer with a stem volume of 0.392 cm³ were used for this analysis, while sample loading was done to achieve a used stem volume of 60-90% under high pressure intrusion. 1 mm particle size was used as it is difficult to analyse fine coal powders using MIP technique due to the problems associated with inter-particle voidage [34]. The samples were first degassed at the low pressure port at < 50 µmHg. After evacuation, the samples were pressurised in the high pressure port where mercury intrusion takes place. Both degassing and intrusion are automatically controlled by the AutoPore IV 9500 software. Samples can be pressurised from 0.51 psi (3.52 kPa) to 60000 psi (414 MPa) and the mercury contact angle and surface tension during intrusion were assumed to be 130° and 0.485 N.m⁻¹ respectively [30, 37]. Results obtained from the MIP measurements were corrected for coal compressibility, which is very significant, especially at higher pressures (>200 MPa) on the lower mesopore size ranges [27-29, 31-38, 52]. Reported results were average values from three independent experiments and error calculations were based on 95% confidence interval. Using the bulk density from MIP and the skeletal density from Helium pycnometry, the total porosity and the total pore volume of the samples can also be estimated [9, 25, 31, 37].

3.3.4.4 *Small Angle X-ray Scattering (SAXS) measurements*

SAXS data were collected from the SAXS facility at CSIR, Pretoria, at 25 °C and a pressure of 0-3 mbar. The SAXS facility consists of a 45 kV, 50 mA PANalytical PW 3830 X-ray generator with copper target ($\lambda=1.542$ Å) coupled to an Anton Paar SAXees Collimator.

Scanning angle was $0.1^\circ \leq 2\theta \leq 4^\circ$. X-ray data were collected stored on data imaging detector, read on a Perkin Elmer Phosphor System Cyclone Plus data reader, and processed with the PANalytical EasySAXS software using the advanced interactive mode. Both the raw and demineralised coal samples were subjected to SAXS analysis. Analysis on each sample was repeated thrice independently and reported results are average of the three results with experimental error based on 95% confidence interval.

The specific surface area per unit volume of the samples, S_v , was determined from the recorded intensity after normalising the total scattering intensity using Equation 3.1 [3, 41, 43, 53].

$$S_v = \frac{\pi \lim_{q \rightarrow \infty} q^4 I(q)}{Q} \quad (3.1)$$

where: Q is the Porod invariant and q is the scattering vector ($q = 4\pi \sin \theta / \lambda$; θ and λ are the scattering angle and the X-ray wavelength respectively).

The specific surface area per unit mass, S_g , was determined using the relative density of the samples with respect to the density of graphite (2.26 g/cm^3) [3, 41]. The porosity of the samples was determined using Porod Invariant equation (Equation 3.2) with defined q intervals to distinguish between the micro-, meso- and macro-porosities [14, 43, 44, 51].

$$Q = \int_0^\infty q^2 I(q) dq \quad (3.2)$$

The boundary conditions of q used for the different porosities in this study are: macroporosity ($4.17\text{E-}6 \leq 2.5/q \leq 5.00\text{E-}3$; $\{500 \text{ \AA} \leq d_p \leq 600,000 \text{ \AA}\}$); mesoporosity ($5.00\text{E-}3 \leq 2.5/q \leq 1.25\text{E-}1$; $\{20 \text{ \AA} \leq d_p \leq 500 \text{ \AA}\}$) and microporosity ($1.25\text{E-}1 \leq 2.5/q \leq 8.33\text{E-}1$; $\{3 \text{ \AA} \leq d_p \leq 20 \text{ \AA}\}$), corresponding relatively to the Guinier, Invariant and the Porod regions respectively [14, 43, 44, 51]. While the Invariant region was based strictly on experimental data, the Guinier region was extrapolated to capture the macropores and the Porod region was extrapolated to include pores $\geq 3 \text{ \AA}$. Pores $< 3 \text{ \AA}$ were not accounted for in this investigation.

3.4 Results and discussions

3.4.1 Standard properties of coal samples

The results of the standard tests on the coals (proximate, ultimate, petrographic, total sulphur content and calorific value analyses) are presented in Table 3.1. The samples exhibited relatively high ash yields (22 - 26 wt. %, adb) and lower fixed carbon content values ≤ 50 wt. %, adb, except for coal TKD; which was found to contain lower ash yield of 16.8 wt. %, adb and a higher fixed carbon content (60.5 wt.%, adb). Three of the four coals possessed low volatile matter yields (≤ 22 wt. %, adb); compared to coal FOZ (27 wt. %, adb). Petrographic analysis results show that, except for coal TKD that is vitrinite-rich (68 vol. % mmb); the other three coal samples are inertinite-rich. The vitrinite and total maceral reflectance of three of the samples were also found to be lower than the values for coal TKD (1.2 and 1.5 respectively). According to ISO-11760:2005, coals DEN, FOZ and OGS were classified as bituminous medium rank C; while coal TKD was classified as bituminous medium rank B [54]. The coal vitrinite and the maceral scan random reflectance histograms of the coal samples are given in Appendix A.

A good agreement in trend also exists between the ash yields determined from proximate analysis and the visible mineral matter contents observed from the petrographic analysis. All the four coals were found to contain very low volumes of liptinite (< 5 vol. %, mmb). The standard properties of these coals are quite similar to results reported elsewhere on South African coals [45, 55, 56].

Table 3.1: Conventional properties of coal samples.

Sample ID	Standard method	Coal DEN	Coal FOZ	Coal OGS	Coal TKD
Proximate Analysis (wt. %, adb)					
Inherent moisture	ISO 1171: 1997	4.0	3.3	2.7	0.7
Ash content	ISO 1171: 1997	25.9	22.0	24.5	16.8
Volatile Matter	ISO 562: 1998	21.5	26.6	22.4	22.0
Fixed carbon	By difference	48.6	48.1	50.4	60.5
Gross Calorific Value (MJ/kg) (adb)	ISO 1928: 1995	21.6	23.5	23.3	29.6
Ultimate Analysis (wt. %, dafb)					
Carbon	ISO 12902	78.7	78.5	81.3	86.9
Hydrogen	ISO 12902	4.4	4.9	4.7	5.1
Nitrogen	ISO 12902	2.2	2.0	2.0	2.1
Oxygen	By difference	13.0	13.2	10.6	4.8
Total sulphur content	ISO 19759	1.7	1.4	1.3	1.0
Free Swelling Index (FSI)	ISO 501: 2012	0.0	0.0	0.5	8.5
Calculated from Ultimate analysis					
H/C atomic ratio		0.663	0.741	0.699	0.710
O/C atomic ratio		0.124	0.126	0.098	0.042
Petrographic analysis (vol. %, mmb)					
Vitrinite	ISO 7404-3: 1994	20	36	21	68
Liptinite	ISO 7404-3: 1994	3	5	5	1
Inertinite	ISO 7404-3: 1994	59	45	57	23
Visible minerals	ISO 7404-3: 1994	18	14	17	8
Total reactive macerals (vol. %, mmb)		41	54	42	72
Reflectance properties (%)					
Mean vitrinite random reflectance (Rr, %)	ISO 11760: 2005	0.65	0.63	0.69	1.2
Mean total maceral reflectance (Rsc, %)	ISO 11760: 2005	1.24	1.05	1.19	1.5
Rank (Bituminous)	ISO 11760: 2005	Medium Rank C	Medium Rank C	Medium Rank C	Medium Rank B

3.4.2 Physical structural properties of samples

3.4.2.1 CO₂ low pressure gas adsorption (CO₂-LPGA)

Results from the CO₂ low pressure gas adsorption analyses are shown on Table 3.2. The CO₂ adsorption isotherms of the four coal samples are given in Figure 3.1. The D-R transformed isotherm plots used to calculate the D-R surface areas and the characteristic energy of adsorption of the samples are presented on Figure 3.2, with the corresponding correlation coefficients ($R^2 > 0.99$). Coals DEN and FOZ (0.63 and 0.65 Rr.% respectively) had near identical CO₂ sorption behaviour. The CO₂ BET surface area plot and the resulting BET surface areas of the samples are provided as a supplementary data in Appendix B.

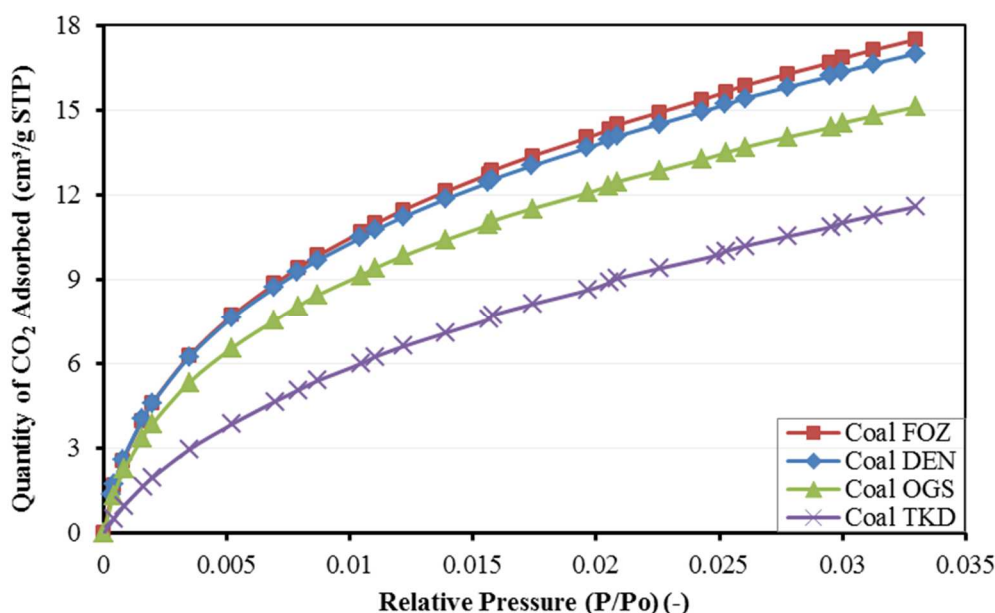


Figure 3.1: CO₂ adsorption isotherms of the coal samples from CO₂-LPGA.

The relationship between the characteristic energy of adsorption and the average micropore diameter (Figure 3.3) is consistent with the higher energy barrier needed to overcome the dispersive forces or potential between the adsorbate molecule and the adsorbent pore surfaces, when pores are smaller [24, 57]. The range of values of the characteristic energy of adsorption is comparable to published results [1, 2, 4, 58]. The D-R micropore surface area, D-R monolayer capacity, D-R micropore volume, H-K micropore volume, and microporosity of the samples were all found to decrease as the vitrinite reflectance of the coal samples increases; while the H-K average micropore diameter increased with increasing vitrinite reflectance. The

PSD in the range $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ obtained from the CO_2 adsorption results for the micropore ranges is presented in Figure 3.4. Coal TKD was found to exhibit the lowest volume of micropores among the four samples. This agrees well with published results on bituminous coals [1, 3-5].

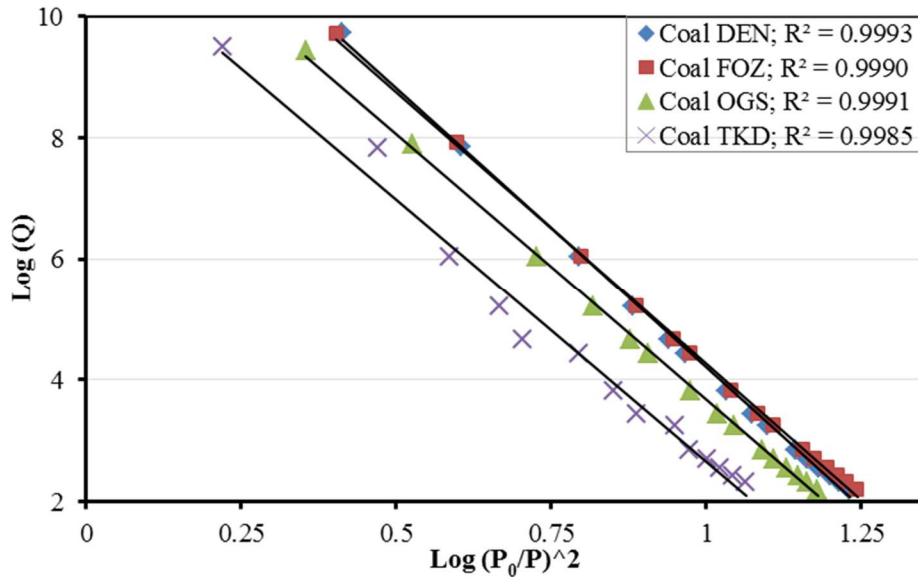


Figure 3.2: Dubinin-Radushkevich transformed isotherms used to calculate the D-R surface areas of the samples.

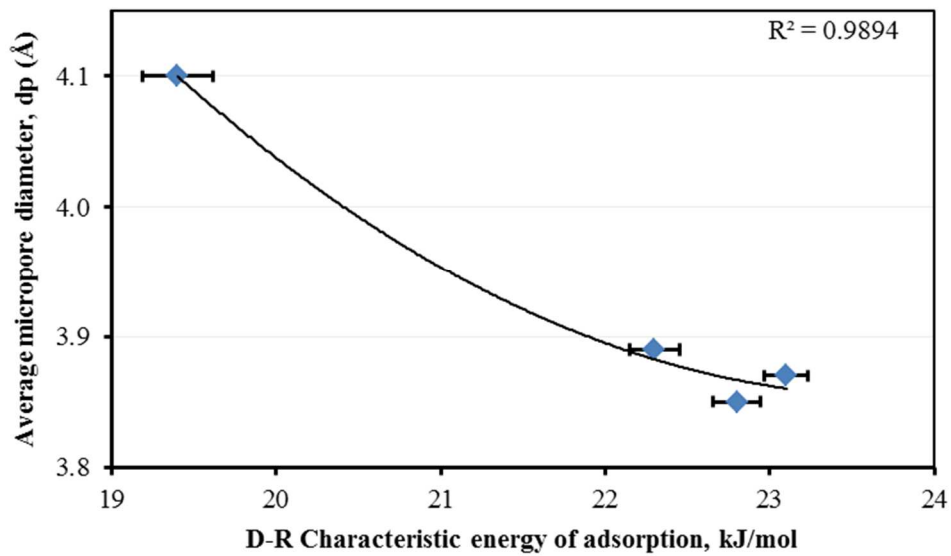


Figure 3.3: Relationship between the characteristic energy of adsorption and the average pore diameter.

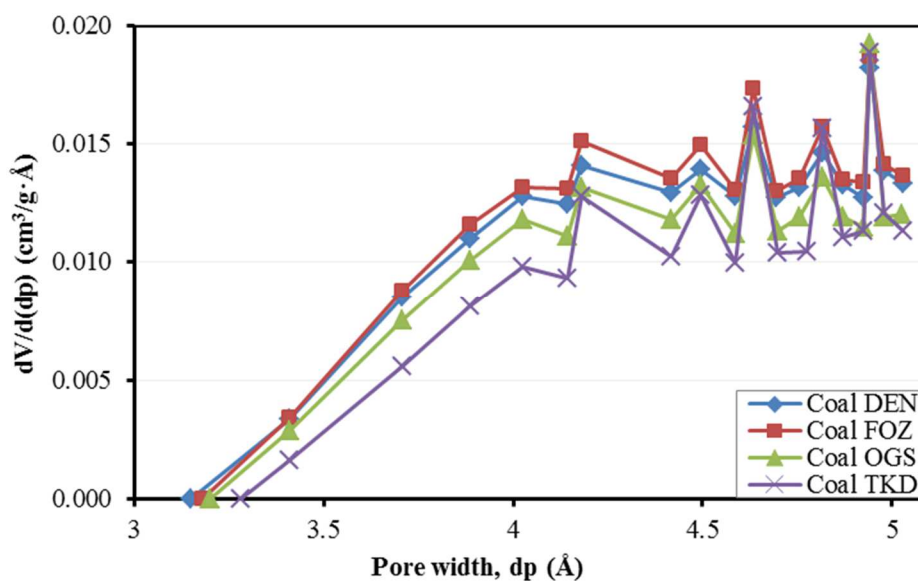


Figure 3.4: Micropore size distribution of the samples from CO₂ adsorption data.

3.4.2.2 N_2 low pressure gas adsorption (N_2 -LPGA)

The N_2 adsorption isotherms of the samples shown in Figure 3.5 were of Type IV [19, 59], which indicate that the samples are mesoporous solids [19, 24, 51], with an adsorption-desorption hysteresis loop indicative of delayed pore condensation during desorption [24, 60]. This may also be attributed to narrow pore throats. However, the hysteresis loop was lacking in coal TKD. This suggests that the coal TKD has a less constricted and more accessible pore network to N_2 than the other coals [3]. The N_2 BET surface area plots used to evaluate the N_2 BET surface areas of the samples are presented in Figure 3.6. The correlation coefficients of the 4 plots are > 0.99 . The determined properties from N_2 low pressure adsorption data are summarised on Table 3.2. Both the surface areas and pore volumes (determined from different methods: BET, Langmuir, BJH) were observed to increase from coal TKD to coal DEN. The average pore diameter calculated from both the N_2 adsorption and desorption results using the BET method showed that the pores in the coal samples as probed by N_2 were in the mesopore range ($339 \text{ Å} \geq d_p \geq 440 \text{ Å}$), but does not follow a particular sequence. The result from the BJH method for the average pore diameter (from N_2 adsorption and desorption) showed that the probed pores are within the mesopore range ($125 \text{ Å} \geq d_p \geq 307 \text{ Å}$) and increased from coal DEN to coal TKD; contrary in trend to the surface areas and pore volumes results. Differences were observed between some of the results determined from the N_2 adsorption and desorption isotherm data and had been explained by the fact that equilibrium may not be reached during

adsorption; but attained during desorption [3, 24, 60-63]. The N₂ mesoporosity was observed to be highest for coal TKD.

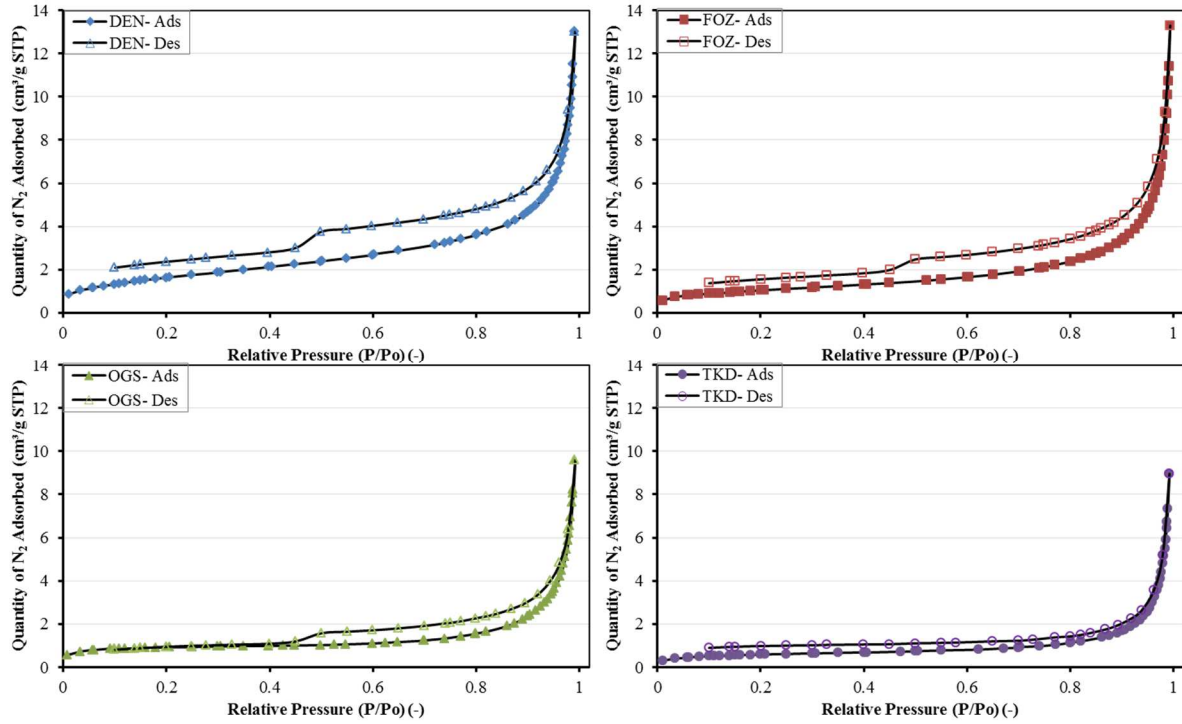


Figure 3.5: N₂ adsorption isotherms of the coal samples from N₂-LPGA.

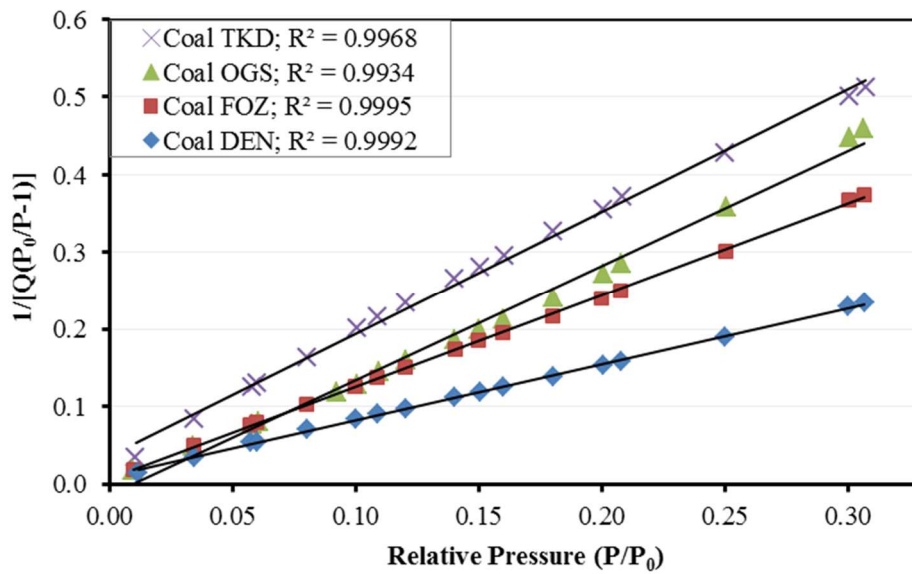


Figure 3.6: N₂ BET surface area plots of the sample.

Table 3.2: Physical-structural properties of samples from CO₂- and N₂-LPGA, MIP and HP.

Properties	Method used	Coal DEN	Coal FOZ	Coal OGS	Coal TKD
CO₂ Adsorption Results					
D-R micropore surface area (m ² /g)	D-R	129 ± 3	128 ± 3	118 ± 2	107 ± 3
Characteristic adsorption energy, kJ/mol	D-R	22.8 ± 0.2	23.1 ± 0.1	22.3 ± 0.2	19.4 ± 0.2
D-R limiting micropore capacity, cm ³ /g STP	D-R	28.3 ± 1	28.0 ± 1	25.8 ± 1	23.5 ± 1
D-R limiting micropore volume x10 ⁻² , cm ³ /g	D-R	5.2 ± 0.1	5.1 ± 0.1	4.7 ± 0.1	4.3 ± 0.1
Micropore volume x10 ⁻² , (cm ³ /g)	H-K	3.1 ± 0.1	3.2 ± 0.1	2.8 ± 0.1	2.1 ± 0.1
Average micropore diameter (Å)	H-K	3.85 ± 0.06	3.87 ± 0.06	3.89 ± 0.05	4.10 ± 0.06
Porosity (%) (3 Å ≤ d _p ≤ 5 Å)	CO ₂ Ads data	5.3 ± 0.2	5.4 ± 0.2	4.6 ± 0.1	2.9 ± 0.1
N₂ Adsorption Results					
BET surface area (m ² /g)	BET	5.7 ± 0.6	3.6 ± 0.4	2.9 ± 0.3	2.6 ± 0.3
Langmuir surface area (m ² /g)	L	8.8 ± 0.4	5.4 ± 0.2	4.3 ± 0.1	4.1 ± 0.3
BJH adsorption surface area (m ² /g)	BJH	5.1 ± 0.3	3.1 ± 0.2	1.5 ± 0.1	2.6 ± 0.2
BJH desorption surface area (m ² /g)	BJH	6.1 ± 0.2	4.3 ± 0.2	3.1 ± 0.1	3.1 ± 0.1
BET adsorption total pore volume x10 ⁻² (cm ³ /g)	BET	1.47 ± 0.05	1.32 ± 0.07	1.01 ± 0.03	1.02 ± 0.03
BET desorption total pore volume x10 ⁻² (cm ³ /g)	BET	1.46 ± 0.03	1.44 ± 0.05	0.99 ± 0.02	0.83 ± 0.01
BJH adsorption total volume of pores x10 ⁻² (cm ³ /g)	BJH	1.95 ± 0.05	2.01 ± 0.06	1.40 ± 0.03	2.03 ± 0.04
BJH adsorption total volume of pores x10 ⁻² (cm ³ /g)	BJH	1.89 ± 0.03	1.99 ± 0.03	1.46 ± 0.01	2.03 ± 0.02
H-K Maximum pore Volume x10 ⁻² (cm ³ /g)	H-K	0.29 ± 0.03	0.18 ± 0.02	0.15 ± 0.02	0.13 ± 0.04
H-K average pore diameter (Å)	H-K	10.7 ± 0.3	9.7 ± 0.3	9.4 ± 0.2	12.3 ± 0.3
BET adsorption average pore diameter (4V/A) (Å)	BET	341 ± 9	403 ± 11	423 ± 14	424 ± 12
BET desorption average pore diameter (4V/A) (Å)	BET	339 ± 4	440 ± 5	412 ± 6	346 ± 9
BJH Adsorption average pore diameter (4V/A) Å	BJH	153 ± 3	263 ± 5	281 ± 6	307 ± 6
BJH Desorption average pore diameter (4V/A) Å	BJH	125 ± 2	187 ± 3	196 ± 3	261 ± 4
Porosity (%) (17 Å ≤ d _p ≤ 500 Å)	N ₂ Ads data	1.60 ± 0.09	2.23 ± 0.10	1.32 ± 0.07	2.63 ± 0.14

Table 3.2 (contd.): Physical-structural properties of samples from CO₂- and N₂-LPGA, MIP and HP.

Properties	Method used	Coal DEN	Coal FOZ	Coal OGS	Coal TKD
MIP Measurements (corrected for coal compressibility)					
Coal compressibility factor, k_c , $\times 10^{-11}$ (Pa ⁻¹)	MIP	4.74 ± 0.08	5.02 ± 0.11	4.31 ± 0.10	4.01 ± 0.07
Total pore area (m ² /g)	MIP	14.1 ± 0.3	13.9 ± 0.4	12.5 ± 0.5	10.9 ± 0.3
Total intrusion pore volume $\times 10^{-2}$ (cm ³ /g)	MIP	3.9 ± 0.1	4.4 ± 0.2	5.2 ± 0.3	5.7 ± 0.2
Average pore diameter (4V/A) (Å)	MIP	111 ± 3	127 ± 5	168 ± 7	208 ± 6
Porosity (%) ($30 \text{ Å} \leq d_p \leq 600000 \text{ Å}$)	MIP	6.1 ± 0.1	6.2 ± 0.2	7.1 ± 0.1	7.6 ± 0.1
Bulk density (kg/m ³)	MIP	1455 ± 22	1295 ± 21	1367 ± 15	1206 ± 23
Skeletal (Apparent) density (kg/m ³)	MIP	1585 ± 20	1414 ± 19	1519 ± 21	1354 ± 28
Helium Pycnometer measurements					
Skeletal (Apparent) density (kg/m ³)	HP	1668 ± 18	1595 ± 24	1623 ± 19	1495 ± 31
Calculated from Hg bulk density and He skeletal density					
Pore Volume $\times 10^{-2}$ (cm ³ /g)	Calculated	8.8 ± 0.3	14.5 ± 0.5	11.5 ± 0.4	16.0 ± 0.4
Porosity (%)	Calculated	12.8 ± 0.5	18.8 ± 0.8	15.8 ± 0.6	19.3 ± 0.5

Nomenclature: BET- Brunauer-Emmet-Teller; BJH- Barrett-Joyner-Halenda; CO₂ Ads data- CO₂ Adsorption data; D-R- Dubinin-Radushkevich; H-K- Horvath-Kawazoe;

HP- Helium pycnometer; L- Langmuir; MIP- Mercury intrusion porosimetry; N₂ Ads data- N₂ Adsorption data

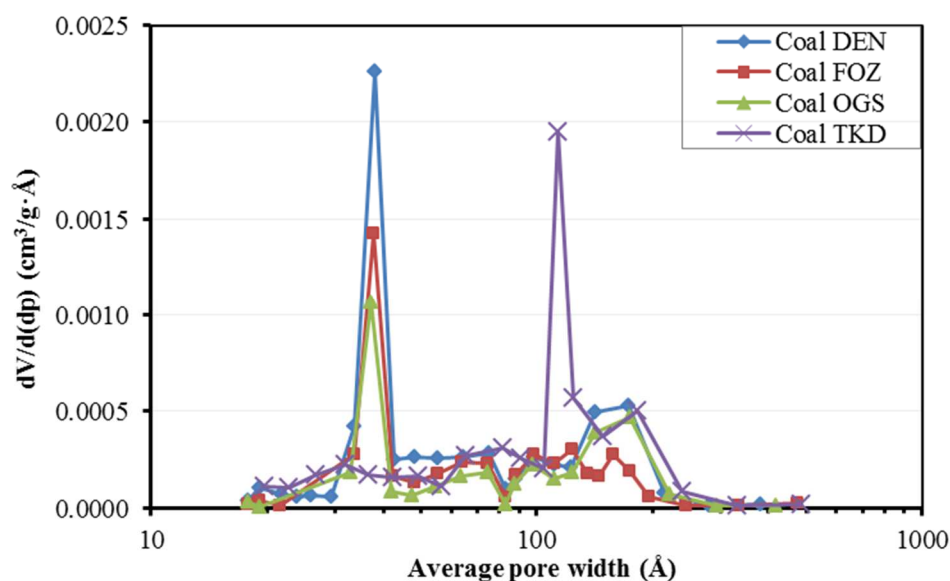


Figure 3.7: Mesopore size distribution of the samples from N₂ adsorption results.

The pore volumes and average pore diameter determined from the H-K method from the N₂ adsorption data were found to be considerably lower than those calculated by the other methods (CO₂ LPGA and MIP). Notably, the H-K average pore diameters ranged from 9.4 Å - 12.3 Å, implying that the probed pores are within the micropore range. This shows that the H-K method is more reliable for CO₂ adsorption analysis than for the analysis of N₂ adsorption data; as it based on a ‘pore filling’ mechanism, which is more suited to CO₂ adsorption on microporous solids. The experimental errors calculated for the N₂ adsorption derived results were well below 5%. The single axis logarithmic plot of the pore size distribution of the coal samples from the N₂ adsorption data is presented in Figure 3.7. This shows that the effective pore size measurable by N₂ in this study ranged from 17 Å to 500 Å. It can be observed from Figure 3.7 that coal TKD has a greater volume of pores on the higher mesopore size range than the other samples. The other three samples (coals DEN, FOZ and OGS) exhibited bi-modal PSD in the pore size ranges: 30 Å - 50 Å and 100 Å - 300 Å; while coal TKD only showed a mono-modal PSD in the 100 Å - 300 Å pore size range. However, the surface areas, porosities and pore volumes calculated from N₂ adsorption were much less than the corresponding properties’ results from CO₂ adsorption data. This differences are consistent with previous results [1, 3-5, 17, 21, 26, 58] and has been attributed to activated diffusion and kinetic restriction of N₂ molecules at 77 K, which is more pronounced in the lower size ranges of the mesopores often probed at lower relative pressures.

3.4.2.3 MIP and HP measurements

In order to avoid the problem associated with MIP measurements due to compression of coal at high pressures, the compressibility of the coal samples were determined from the mercury intrusion data following the procedure described by other investigators [27, 31-35, 37, 52]. The intrusion data was used in this study as the slope of the plot of the cumulative mercury intrusion versus pressure remained almost constant in the high pressure region for the coal samples as presented in Figure 3.8. The compressibility factors, k_c , of the coal samples were calculated from the slope ($R^2 \geq 0.99$) of the resulting plots at the higher pressure range of 300 - 414 MPa and the samples' helium density. The results obtained ranged from $4.01 \times 10^{-11} \text{ Pa}^{-1}$ for coal TKD to $5.02 \times 10^{-11} \text{ Pa}^{-1}$ for coal DEN (Table 3.2). This range of values are comparable to the range of values obtained by other investigators on a suite of coal of various rank [31, 32]. Toda and Toyoda [32] had reported a sinusoidal trend of coal compressibility with carbon content (a proxy of rank); but obtained a linear trend between coal compressibility and Knoop Hardness. This suggests that coal compressibility is more dependent on factors which may include Knoop hardness [32], spot of sampling [36] and swelling properties of the sample, rather than rank.

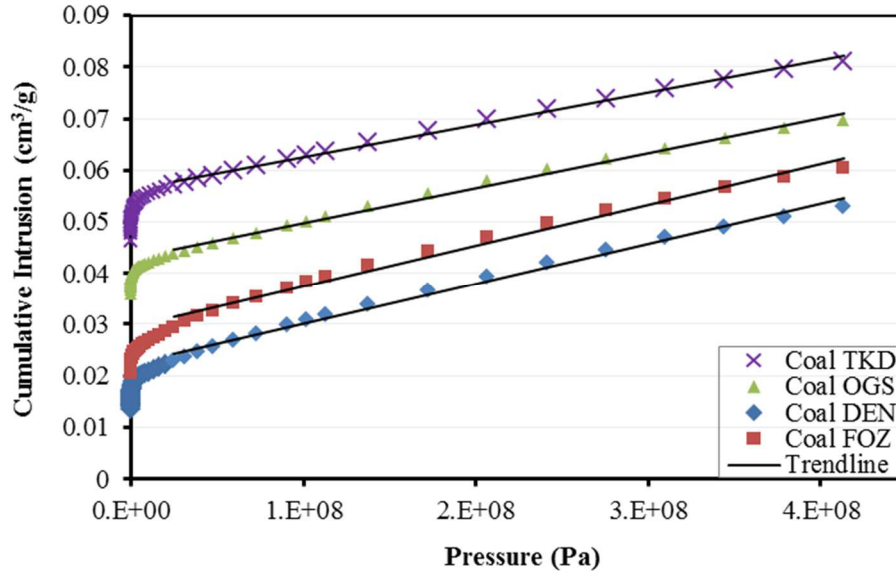


Figure 3.8: Cumulative mercury intrusion vs pressure.

It can be seen from Figure 3.9 that the effect of coal compressibility was more significant on coal TKD than the other samples. Interestingly, coal TKD also had the greatest propensity to swell ($\text{FSI} \approx 8.5$). It should be noted that coal compressibility factor is a multiplicative

numerator; its effect on the corrected result increases as its value decreases. MIP pore size distributions were determined from the compressibility corrected intrusion data as logarithmic differential intrusions. The comparison of the raw and corrected pore size distribution of the samples is given in Figures 3.10 and 3.11. It was found that correction for coal compression only affected the values obtained in the mesopore range of the MIP PSD; after correction for compression, pore volumes were reduced by 20-25%.

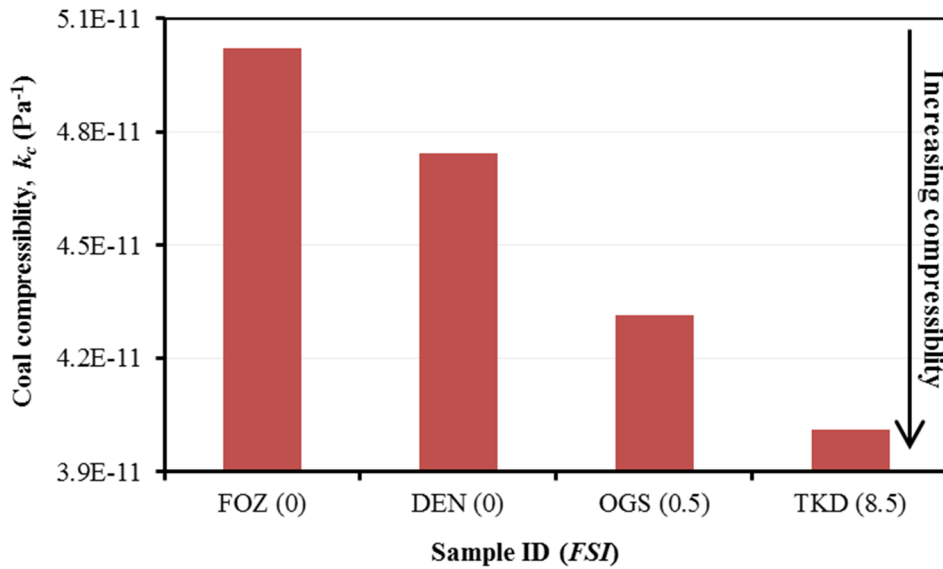


Figure 3.9: Relationship between coal compressibility, k_c , and free swelling index, FSI .

Results from the compressibility-corrected MIP measurements are summarised in Table 3.2. It was observed that the total intrusion pore volume, average pore diameter and porosity increased from coal DEN to coal TKD, while the total pore areas showed the opposite trend, increasing from Coal TKD to coal DEN. The total pore area ranged from 10.9 m²/g for coal TKD to 14.1 m²/g for coal FOZ. The pore size distribution obtained from all four coals from the corrected MIP data as given Figure 3.11 shows that coal TKD has greater volume of macropores < 10⁵ Å; while coal DEN has the lowest volume of pores in that range. From Table 3.2, coal TKD also had larger MIP porosity (7.6%) than the other three samples (6.1% - 7.1%). However, the total pore volume and the total porosity calculated from the MIP bulk density and the skeletal density from HP (Table 3.2) were significantly higher than the corresponding properties determined from compressibility-corrected MIP data, and were higher for coal TKD (with

higher vitrinite reflectance) compared with the other three coal samples. This shows that coal TKD is more meso- and macro-porous than the other samples.

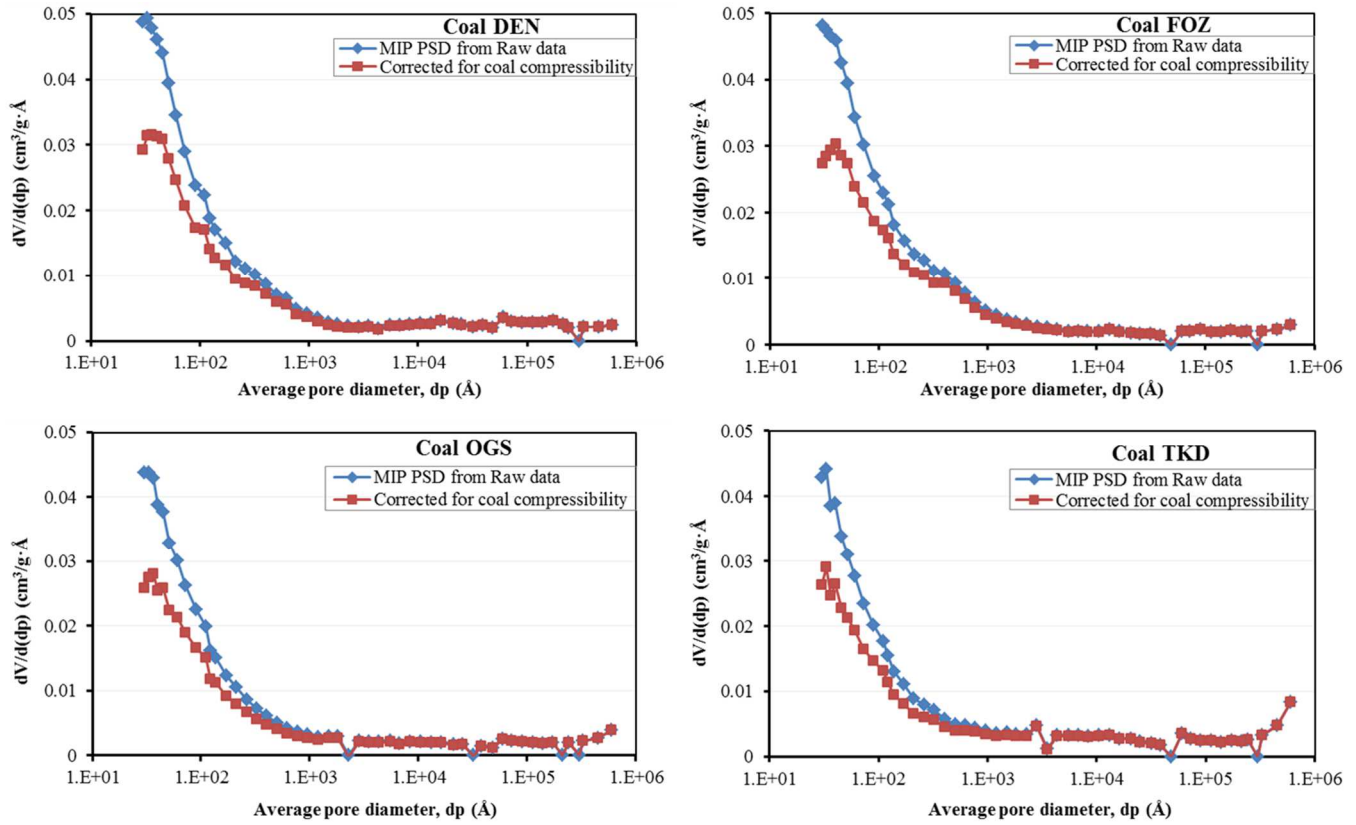


Figure 3.10: Effect of coal compressibility on the PSD from MIP.

A comparison was made of the pore size distributions (PSD) resulting from N₂ adsorption analysis and MIP measurements to qualitatively identify regions of overlap, when these techniques are used together. This comparison is inserted in Figure 3.11 and shows that an overlap region does exist in the mesopore region ($30 \text{ Å} \leq d_p \leq 500 \text{ Å}$). However, the area under the curve of N₂ adsorption PSD data is very small when compared to the broader area occupied by the MIP PSD. Coals DEN and FOZ were found to exhibit much the same value with respect to surface area and porosity from both the MIP and CO₂ adsorption analysis. Thomas and Damberger [4] and Spitzer [29] reported similar range of porosity values from MIP measurement on a suite of bituminous coals from different coal fields in the former

Czechoslovak republic and Illinois respectively. However, the average pore diameter, intrusion pore volume, and the porosity from MIP were found to increase from coal DEN to coal TKD, opposite to the trends with regard to similar properties determined from the CO₂ adsorption results.

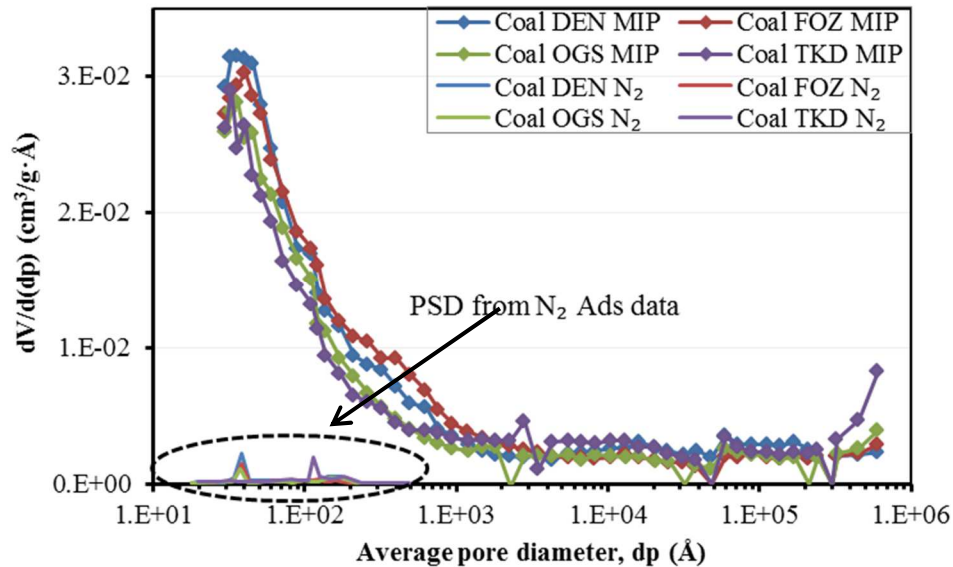


Figure 3.11: Meso- and macro-pore size distribution of the samples from MIP results (PSD from N₂ adsorption inserted for comparison of the PSD from N₂ adsorption and MIP data and identification of the overlap region).

There is a good agreement in trend between the skeletal densities determined from MIP and Helium Pycnometry (HP) data (Table 3.2), although results from helium intrusion were relatively higher than mercury intrusion results, due to helium being able to penetrate into smaller and finer pores in coals that remain inaccessible to mercury. Both the bulk and skeletal density of the samples determined from HP and MIP were observed to increase with increasing inertinite contents and ash yields. These values and trends are similar to reported results from our other studies on some South African coals [45], and coals from other countries [3, 4, 64, 65].

Table 3.3: Physical structural properties of samples determined using extrapolated S

SAXS Analysis Results						
Properties / Sample ID	Coal DEN	Demin Coal DEN	Coal FOZ	Demin Coal FOZ	Coal OGS	Demin Coal OGS
Specific Surface Area						
S_{SAXSm} per unit mass (m^2/g)	172 ± 8	166 ± 6	163 ± 7	159 ± 6	158 ± 6	157 ± 6
S_{SAXSv} per unit volume (m^2/cm^3)	109 ± 6	91 ± 4	99 ± 6	85 ± 3	99 ± 4	83 ± 3
Porosity						
Microporosity (%)	10.1 ± 0.6	9.2 ± 0.5	10.3 ± 0.8	9.6 ± 0.7	9.5 ± 0.5	8.9 ± 0.4
Mesoporosity (%)	7.7 ± 0.05	6.0 ± 0.03	8.6 ± 0.06	7.1 ± 0.04	8.6 ± 0.04	7.5 ± 0.03
Macroporosity (%)	9.9 ± 0.3	10.0 ± 0.2	11.0 ± 0.3	9.7 ± 0.2	10.5 ± 0.2	10.3 ± 0.2
Total Porosity (%)	27.7 ± 1.0	25.2 ± 0.7	29.9 ± 1.2	26.5 ± 0.9	28.6 ± 0.7	26.7 ± 0.6

3.4.2.4 SAXS Analysis

The SAXS-determined physical structural properties of the coal and demineralised coal samples are summarised in Table 3.3. Generally, the magnitude of values obtained from the SAXS measurements on the raw coals were comparatively greater ($1.4\% \leq \% \Delta \leq 3.6\%$) than corresponding results from the demineralised samples. This is due to the additional x-ray scattering from the mineral matter of the raw coal samples that were almost eliminated by demineralisation. These changes were found to increase with increasing ash yield of the coals. This clearly demonstrates the influence of mineral matter content on SAXS derived results for coals. Comparisons of the porosity results from the three other used techniques were thus based on the SAXS results from the demineralised coals. While a similar trend was observed for the surface areas determined from SAXS as for the other three techniques, results from SAXS were generally greater than the sum of the results from the other three techniques (CO_2 and N_2 adsorption and MIP). This is probably due to the fact that SAXS probes a wider range of pores and even closed pores [3, 14, 21, 41-44]; coupled with its ability to probe pore sizes in the range of $5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$, not analysed by any of the three other techniques used. The total porosity of the samples determined from SAXS data was also found to be generally higher than the sum of the porosities returned by the combined techniques of N_2 and CO_2 gas adsorption and compressibility corrected MIP. Part of these greater values could be due to fact that SAXS results on the demineralised coals included pores that were generated on removal of the mineral matter; while excluding the additional x-ray scattering resulting from the minerals.

Note that the double logarithmic SAXS diffractograms of the raw coal and demineralised coal samples, and the graphical comparison of the surface areas and porosity properties of the coals from different techniques are presented in Appendix B (Figures B-2 – B-4).

$$QOF(\%) = 100 \times \left[1 - \frac{\sum_{i=1}^N \left| \frac{V_{Expt.} - V_{Trend}}{V_{Expt.}} \right|}{N} \right] \quad (3.3)$$

where: $V_{Expt.}$ is the experimentally determined values of the properties; V_{Trend} is the value of the properties determined from 2nd order polynomial trend line fitting to the observed experimental trend; and N is the number of data points and / or number of samples in this case ($N = 4$).

A general comparison of the observed trends from the correlation of the major results (surface area, porosity and average pore diameter) obtained from the four analytical techniques with the vitrinite reflectance (Rr.%) of the coal samples is presented in Figure 3.12. To qualitatively compare the efficiency of the techniques, the quality of fit (QOF) parameter defined by Equation 3.3 was determined for the observed trends and summarised in Table 3.4.

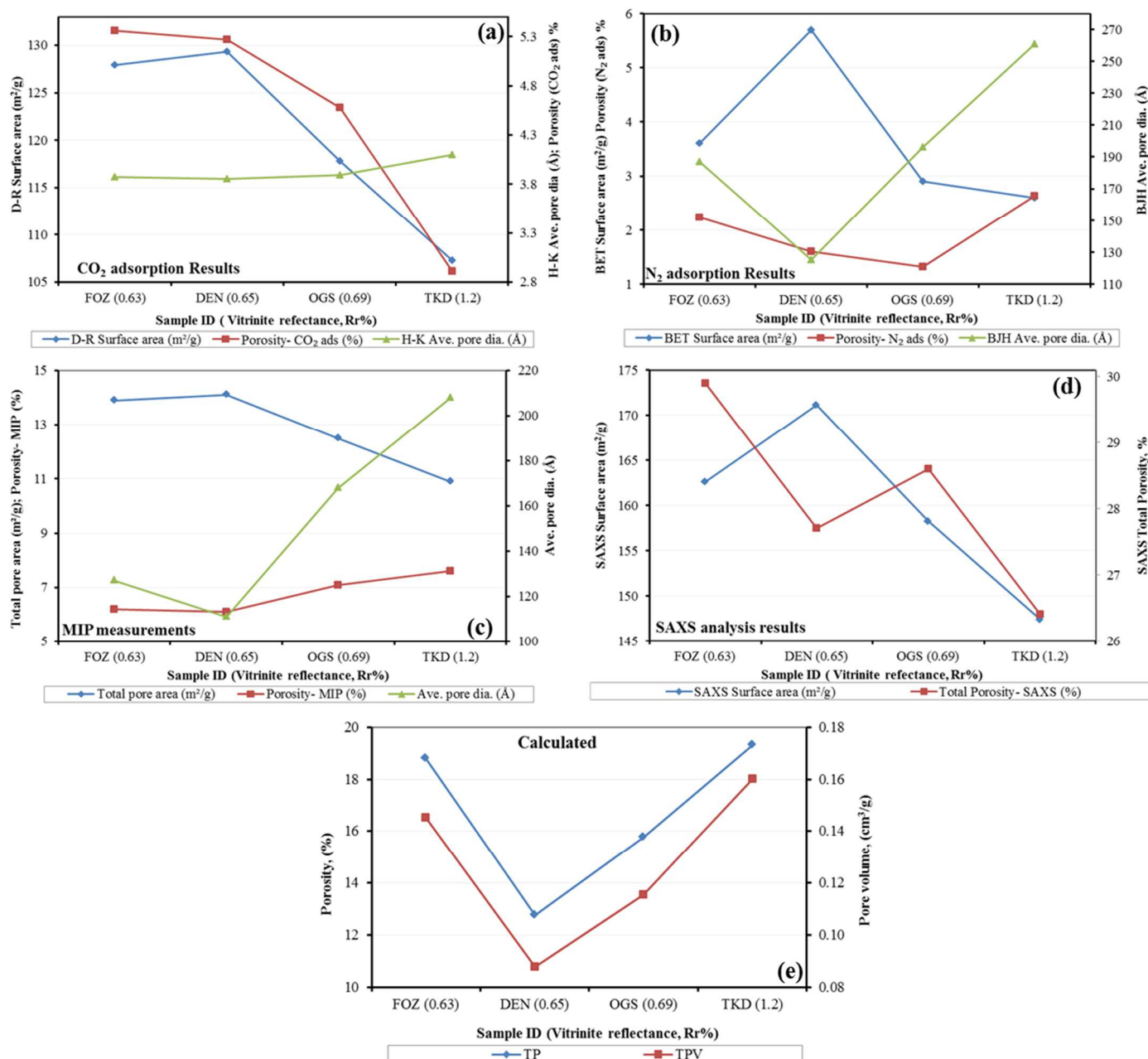


Figure 3.12: Comparisons and correlations of the surface area, porosity and average pore diameter determined from all four techniques used. (Note: Average pore diameter was not determined for SAXS analysis).

Table 3.4: Correlation coefficients and quality of fit (QOF) of trends of determined properties with respect to the four investigated samples

Properties	R ²	Fitting equation ^a	QOF (%)
CO₂ Adsorption			
D-R Surface area	0.9692	$y = -2.975x^2 + 7.545x + 124.03$	92.5
Porosity	0.9981	$y = -0.395x^2 + 1.171x + 4.565$	73.8
H-K Average pore diameter	0.9851	$y = 0.0575x^2 - 0.2145x + 4.0325$	97.6
N₂ Adsorption			
BET Surface area	0.5328	$y = -0.6x^2 + 2.42x + 2.15$	68.3
Porosity	0.9275	$y = 0.485x^2 - 2.333x + 4.14$	40.8
BJH Average pore diameter	0.8960	$y = 31.75x^2 - 129.45x + 277.75$	70.8
MIP			
Total pore area	0.9275	$y = -0.45x^2 + 1.19x + 13.25$	89.5
Porosity	0.9185	$y = 0.15x^2 - 0.23x + 6.2$	91.3
Average pore diameter	0.9288	$y = 14x^2 - 40x + 148.5$	69.4
SAXS			
Surface area per unit mass	0.9054	$y = -4.825x^2 + 18.275x + 150.33$	94.6
Total Porosity	0.7057	$y = -9E-14x^2 - 0.96x + 30.55$	94.0
Calculated from Hg bulk density and He skeletal density			
Porosity	0.8698	$y = 2.3992x^2 - 11.539x + 27.524$	71.1
Pore Volume	0.9262	$y = 0.0256x^2 - 0.1207x + 0.237$	59.9

^a- x is the vitrinite reflectance of the coal samples; and y is the examined physical-structural property of the sample (See Figure 3.12)

It is obvious from Figure 3.12 and Table 3.4 that with respect to the correlation trends observed for the four samples investigated in this study, CO₂ adsorption results showed the best consistency in trend with higher QOF and correlation coefficients. N₂ adsorption results exhibited the least consistency in trend with significantly lower QOF and correlation coefficients. The trend observed for the SAXS derived results exhibited good QOFs, notwithstanding the fact the correlation coefficients were not as good as those from CO₂

adsorption results. The trends observed for MIP measurements were fairly consistent and better than the trends from N₂ adsorption results.

The very low values obtained from N₂ LPGA compared to MIP and SAXS confirm that most pores are inaccessible to N₂ at 77 K. MIP result shows a decreasing contribution of pores in the size range 30 to 300 Å as pore size increases, but N₂ PSD shows an increasing contribution in this size range. This probably reflects increasing accessibility of pores to N₂ at 77 K as pore size increases, rather than a real increase in pore numbers or pore volume with increasing pore size, since even at the largest pores sizes measureable by N₂ LPGA, the fraction of pores penetrable by N₂ is still small (Figure 3.11). Even at 200 Å diameter, most pores are largely impenetrable by N₂ at 77 K. This inaccessibility is not due to narrow pore throats restricting N₂ access, since MIP results would also be affected. If activated diffusion is responsible for this inaccessibility, then it must occur even at pores of this size, which would indicate a longer long-range interaction with the coal surface than is typically considered for van der Waals forces.

3.5 Conclusions

Standard and advanced techniques were effectively used to characterise the surface area, pore size distribution and porosity of four bituminous South African coal samples.

- The similarities in the physical-structural properties of three of the four coal samples shows that the Permian-aged coal deposit of the Highveld and Witbank coalfields of South Africa are comparatively of similar maturity with a very close range of vitrinite reflectance (0.63 – 0.69).
- Compressibility effect due to mercury intrusion at high pressures in coal accounted for about 20-25% of the recorded porosity and pore volume of coals.
- Small Angle X-ray Scattering (SAXS) analysis was found to return higher values of surface area and porosity than any of the three other methods used in this study. SAXS technique probes a wider pore size distribution (PSD) range in coal and covers PSD in the range: $5 \text{ Å} \leq d_p \leq 17 \text{ Å}$, not captured by the other three standard methods.

- SAXS derived-results obtained for the raw coals were greater ($1.4\% \leq \% \Delta \leq 3.6\%$) than for the demineralised coal samples, and this difference increases with increasing ash yield of the coals. This is due to the contribution of the coals' mineral matter content to the total scattering of the raw coals which are very minimal in the demineralised samples.
- The ranges of pores sizes analysed significantly depend on the equipment and technique used. The effective PSD analysable by gas adsorption (CO_2 and N_2) and MIP with regard to this study are: $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ for CO_2 adsorption; $17 \text{ \AA} \leq d_p \leq 500 \text{ \AA}$ for N_2 adsorption; and $30 \text{ \AA} \leq d_p \leq 600,000 \text{ \AA}$ for MIP.
- Results obtained from SAXS in combination with data from the other three techniques provide more information about the nature of the pores and porosities in coals.

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Chapter 4

4.0 Sample characterisation II. Chemical-structural properties of the coal samples

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Highlights

- ✓ Chemical-structural properties of coal investigated using various techniques.
 - ✓ Crystallite height, L_c , increases with increasing coalification.
 - ✓ Intact bridges and cross-links increase with increasing rank.
 - ✓ Greater preferential alignment of fringes was observed for the higher ranked coal.
 - ✓ Agreement and consistency was found between different techniques.
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4.1 Abstract

The chemical-structural properties of four South African bituminous coals were investigated using wide angle X-ray diffraction-carbon fraction analysis (WAXRD-CFA), attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR), solid state ^{13}C nuclear magnetic resonance spectroscopy (ss ^{13}C NMR), and high resolution transmission electron microscopy (HRTEM). The aromaticity of the samples determined by solid state ^{13}C NMR ranged from 0.74 to 0.87 and compared well with the WAXRD-CFA results (0.73-0.86). WAXRD-CFA, ATR-FTIR and ^{13}C NMR data showed that the lower iso-rank coal samples contained more aliphatic moieties; while the higher rank sample contained higher fractions of polyaromatic moieties and saturated long chain hydrocarbons. The lattice parameters determined from WAXRD-CFA show that lower rank coals investigated are structurally less well-ordered than the higher rank coal. Also, its fringes were quantified as having the greatest preferential alignment of the coals examined. HRTEM aromatic fringe image analysis revealed that the carbon lattice of the samples consist of aromatic fringes of varying lengths, L ($3\text{\AA} \leq L \leq 95\text{\AA}$), which corresponded to a molecular weight distribution ranging from 75 to 1925 amu, assuming circular catenation. The coal with the highest volatile matter yield was found to exhibit a higher frequency of lower molecular weight fringes; while the higher rank coal possessed the most higher molecular weight fringes. The average molecular weights determined for the samples from ^{13}C NMR varied between 504 to 544 amu; and compared well with the values from HRTEM aromatic fringe image analysis data. Thus, there was good

agreement and consistency between the different techniques. It was demonstrated that, for the characterisation methods used in this study; that vitrinite reflectance impacts more on the chemical-structural properties of these coals than maceral composition does.

Keywords: *Chemical-structural properties, WAXRD-CFA, ATR-FTIR, solid state ^{13}C NMR, HRTEM*

4.2 Introduction

Coal has a highly complex chemical structure, consisting of macerals and minerals that reflect the depositional environment and the nature of the organic precursors [1]. The resulting heterogeneity complicates the characterisation of coal samples, and thus a wider variety of techniques is necessary to provide the greatest insight into the structure of coal. Conventional analytical methods that give the bulk properties of the samples, often give poor predictions of coal behaviour for most of its utilisation processes [1-3]. Moreover, outliers that do not conform to the prediction equations are common [4]. It is well known that these processes follow different reaction routes or reaction mechanisms, whose study is further compounded due to the heterogeneity of coal. While coal utilisation processes such as combustion and gasification require chemical bond breaking and bond formation, other utilisation systems such as liquefaction and solvent extraction may require that the coals swell and or solubilise in a solvent, either in part or in whole.

In response to global climate change mitigation, carbon dioxide sequestration and or storage in “unmineable” or unprofitable deep-seated coal seams, has further emerged as an utility of coal resources [5-7]. This coal utilisation process may involve: physical adsorption, where no chemical bond breaking and bond formation is envisaged; chemical adsorption and absorption; mineralisation, where the super-critical liquid CO_2 reacts with the inorganic chemical species within the coal matrix; swelling; and solubilisation; or a combination of these processes. Carbon dioxide sequestration in deep unmineable coal seams has been identified as one of the geological storage options for captured CO_2 and has been found to be an attractive CO_2 storage sink as the CO_2 can be stored in the adsorbed super-critical fluid state, which is expected to be

stable for a geologically significant period [5, 7]. This may also enable the synergy of enhanced coal bed methane production that will add to the energy resource and generate income to offset some of the capital expenditure of the sequestration infrastructure [5].

In coal utilisation processes, the fundamental understanding of the coal's chemical, physical, and structural properties remains paramount and often challenging to coal scientists and engineers [1-3]. However, the variety of analytical techniques employed by researchers is greatly dependent on problem description, intended coal use or motive, and availability of the desired technique. The recent increase in software development and technical advances has allowed a number of new analytical techniques to proliferate. These include: solid state ^{13}C nuclear magnetic resonance spectroscopy (ss ^{13}C NMR), attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR), wide angle X-ray diffraction-carbon fraction analysis (WAXRD-CFA), high resolution transmission electron microscopy (HRTEM), matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF) and computer controlled scanning electron microscopy (CCSEM). These techniques have been used to examine coals with varying degrees of success [3, 8-29], but, overall, have enabled a better understanding of coal molecular chemical structure. Some of these methods provide average values, while others provide vital distribution data. Hence, when used in combination, these can be more informative and can also be used as a means of checking consistency to some degree. Results from these techniques have shown that the molecular skeleton of bituminous, and higher rank coals consist mainly of aromatic sheets or layers [9-14, 17-19, 24, 27, 30, 31].

The improved understanding of the chemical structure of coal at the molecular level that has resulted from these new investigations has led to the development of refined coal molecular structures, so that they could be more effectively used in the prediction of coal behaviour (reactivity and reaction mechanisms) in its various utilisation processes [27, 32-40]. Understanding the structural properties of coal is necessary in identifying the chemical and physical interactions between coal and various reactants during its utilisation [33]. For CO_2 storage in coal seams, this is necessary to determine the suitability of the coal seams and the stability of the adsorbed CO_2 in the geological disposal site.

In this paper, the chemical-structural properties of four South African bituminous coals determined from WAXRD-CFA, ATR-FTIR, solid state ^{13}C NMR, and HRTEM techniques are reported. Results obtained from these techniques were compared to validate their consistency. These data will be used for the development of the molecular models of these

South African coals, which will be utilised for further studies, including numerical and molecular modelling of various coal utilisation systems.

4.3 Experimental

4.3.1 Origin of coal samples

The four run-of-mine bituminous coal samples examined in this investigation were collected from actively mined underground coal seams within the Highveld, Witbank, and Tshipise-Pafuri coalfields of South Africa. The coal samples are identified henceforth as coals: DEN, FOZ, OGS and TKD. DEN and OGS originate from the Highveld coalfields, while FOZ and TKD are from the Witbank and Tshipise-Pafuri coalfields respectively.

4.3.2 Sample preparation

The coal samples were received as -50 mm particles. Representative samples were obtained by cone and quartering and packed in units of 1 kg in polyethylene plastic bags, flushed with N₂, vacuum-sealed; and stored in a climate controlled coal storage chamber. To obtain the size ranges for characterisation purposes and analyses, the whole 1 kg bag of sample was crushed and screened to required size; either as -75 µm or 1 mm size; and further processed if necessary. Samples were screened as necessary to remove the required size fraction and crushing continued until the whole 1 kg unit of sample has been crushed to the needed size. For the 1 mm size fraction, the samples were crushed in a jaw-crusher (Samuel Osborne (SA) LTD, Model: 66YROLL) set at a jaw opening of 1.12 mm and screened with 850 µm and 1180 µm screens to the size: 0.85 mm < dp < 1.18 mm (dp is the particle size). In this case, the small amount of fines generated (< 10 wt.%) were discarded. For the -75 µm size fraction, crushing was initially carried out on the jaw-crusher at a jaw opening of 1.0 mm and further crushed on a Fritsch P-14 rotary mill (R-mill) with a mounted 280x230 mm ceramic macro crusher (Model No. 46-126) containing 10 mm ceramic balls and screened with a 75 µm screen. The speed setting of 600 revolutions per minute (rpm) was used and allowed to run for 30 minutes. It should be noted that the mills were cleaned properly with compressed air prior to use to avoid any contamination with previously crushed samples. As South African coals can be relatively high in mineral matter (> 20%), the -75 µm (200 mesh) [41] size fractions of the coals were

further demineralised to reduce the influence of the inorganic mineral matter content of the coals on the analyses. This was accomplished using a three step HCl-HF-HCl demineralisation procedure detailed elsewhere [19, 27, 42]. After demineralisation, the samples were further washed in excess distilled water until the pH of the filtrate was neutral. The effectiveness of demineralisation, E_d (Equation 4.1), was introduced to quantify the extent of demineralisation; described as the ratio of the mineral matter removed or ‘demineralised’ to the original ash yield of the sample on air dry basis, expressed as a percentage [2].

$$E_d = \left(\frac{A_i - A_d}{A_i} \right) \cdot 100 \quad (\%) \quad (4.1)$$

where A_i is original ash yield of the sample (wt. %, adb) and A_d is the ash yield of the demineralised sample.

Solid state ^{13}C NMR signals are influenced by paramagnetic organic free radical and residual paramagnetic mineral matter [43, 44]; to reduce this effect the samples were further treated with 0.1M samarium (II) iodide (SmI_2) in tetrahydrofuran (THF), following the method adapted from other investigators [17, 27, 43-45]. SmI_2 is a powerful one-electron reducing agent for organic radicals with high chemo-selectivity amongst organic functional groups [45]. About 10 g of demineralised coal was added to 50 ml of 0.1M SmI_2 in THF and stirred in a glass beaker, agitated with a polyethylene coated magnetic stirrer at a mild rotational speed of 200 rpm for 24 hours in an inert atmosphere glove box assembly. The reaction was quenched with distilled water and then, the THF was evaporated off. The coal samples were washed with 2M HCl to leach out the remaining lanthanide ions, and further washed and filtered with excess distilled water to remove the HCl, until the pH was neutral. The residual demineralised and SmI_2 -treated coal samples were dried in a vacuum oven at 60 °C until constant mass.

Petrographic analysis was conducted on the raw coals of 1 mm average particle size (-1170 +850 μm); proximate and ultimate analyses were conducted on both raw and demineralised samples (-75 μm particle size). The 1 mm average particle size fraction of the samples was used for petrographic analysis as it is difficult to distinguish visualised maceral entities and lithotypes under the petrographic microscope, when fines (< 500 μm) are used [27, 46]. The WAXRD-CFA, ATR-FTIR, and HRTEM utilised demineralised samples of -75 μm particle size, whereas demineralised and SmI_2 -treated samples of -75 μm particle size were used for solid state ^{13}C NMR analysis.

4.3.3 *Sample Characterisation*

4.3.3.1 *Conventional analyses*

The proximate and carbon, hydrogen, nitrogen (CHNS) elemental analyses of the coal samples were carried out at the laboratory of Advanced Coal Technology (ACT), Pretoria; using the standard methods given in Table 4.1 [47-51]. Fixed carbon and elemental oxygen contents were determined by difference.

4.3.3.2 *Petrographic analysis*

Petrographic analysis of the samples was conducted by Petrographics SA, Pretoria. Petrographic block preparation of the samples using epoxy resin was done according to ISO 7404-2:2009 [52]. The resulting sample blocks were ground, polished; and then examined under a Leica DM4500P microscope fitted with a 50x lens and a 10x internal reflected light oil immersion lens [2, 27, 46]; giving a total of 500x magnification. The mean vitrinite random reflectance of the samples was determined in accordance with ISO 7404-5:2009 standard [53]. The coal's rank classification based on the mean vitrinite random reflectance was done following the ISO 11760:2005 [54]. The group macerals were quantified by a 500 point-count technique following the ISO standard 7404-3:2009 [55]. A total maceral reflectance scan was also undertaken on each coal. 250 random reflectance readings were taken on all macerals over the polished surface of each petrographic block. The reactive inertinites (reactive semifusinite and reactive inertodetrinite) were distinguished from the inert inertinites and quantified according to the proposed method of Smith et al. [2, 56, 57] for South African coals.

4.3.3.3 *Chemical-structural properties*

The chemical-structural properties were investigated using various analytical techniques including: WAXRD-CFA, ATR-FTIR, solid state ^{13}C NMR, and HRTEM.

4.3.3.3.1 *Wide-angle X-ray diffraction- Carbon fraction analysis (WAXRD-CFA)*

WAXRD-CFA was conducted at the Laboratory of XRD Consulting, Pretoria. The samples were scanned on a PANalytical X'Pert Pro equipment with cobalt target at ambient

temperature. The X-ray intensities were measured in the range of $10^\circ \leq 2\theta \leq 110^\circ$ with a step size of $0.017^\circ 2\theta$ and a scan step time of 13.3s [58, 59]. The X-ray diffractograms were acquired automatically by the X'Pert Pro Highscore Plus™ software. The resulting diffractograms were further smoothened and background-subtracted to reduce noise, using in-built functions of the X'Pert Pro Highscore Plus™ software.

The average carbon crystallite lattice parameters: inter-layer spacing (d_{002}), crystallite height (L_c), crystallite diameter (L_a) and the average number of aromatic layers per carbon crystallite (N_{ave}) were determined using the empirical Braggs and Scherrer equations (Equations 4.2 – 4.5) [2, 3, 13, 17, 19, 27, 31, 58-60].

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (4.2)$$

$$L_c = \frac{K_c \lambda}{\beta_{002} \cdot \cos\theta_{002}} \quad (4.3)$$

$$L_a = \frac{K_a \lambda}{\beta_{10} \cdot \cos\theta_{10}} \quad (4.4)$$

$$N_{ave} = \frac{L_c}{d_{002}} + 1 \quad (4.5)$$

where: λ is the wavelength of the incident X-ray (in this case 1.78901 Å for cobalt K α radiation); $\theta_{002,10}$ is the peak position of (002) or (10) band ($^\circ$); $\beta_{002,10}$ is the full width at half maximum (FWHM) of the corresponding peak or band ($^\circ$); $K_{c,a}$ is a constant depending on X-ray refraction plane (0.89 for the (002) band and 1.84 for the (10) band).

If it is assumed that the area under the (002) band the γ band (A_{002} and A_γ) is equivalent to the number of aromatic and aliphatic carbons respectively, then the aromaticity (f_a) of the samples can be calculated using Equation 4.6 [2, 3, 19, 27, 28, 60].

$$f_a = \frac{A_{002}}{A_{002} + A_\gamma} \quad (4.6)$$

where: A_{002} and A_γ are the area under the (002) and the γ - band respectively.

The fraction of amorphous carbon (X_A) of the samples were determined from the (002) of the sample's diffractograms from the reduced X-ray intensity profile of the (002) band (I_{002}) [2, 13, 18, 19, 28, 29, 61]. By considering that the scattered X-ray intensity is a combination of intensities contributed by the crystalline and amorphous carbon structures [2, 13, 18, 61], the reduced intensity of the coal and other carbon materials (I_{002} or I') can be related to these two separate contributions. Furthermore, it has been shown that the intensity contributed by the fraction of amorphous carbon contained in the sample is constant over the whole scattering region and does not contribute to the peak intensity, but reflected only in the background [13, 18, 61]. The reduced intensity of the (002) band of the samples were determined using Equation 4.7 and the modified form (Equation 4.8) originally proposed by Franklin [18] and used regularly by other investigators [13, 19, 28, 29, 61].

$$I_{002} = \left(\frac{0.0606}{s^2} \right) \times \sum_n \left(p_n \times \frac{\sin^2(\pi N_{ave} d_{002} s)}{N_{ave} \sin^2(\pi d_{002} s)} \right) \quad (4.7)$$

$$I' = \frac{s^2}{0.0606} \times \frac{I - X_A}{1 - X_A} \quad (4.8)$$

where: I_{002} is the theoretical reduced intensity due to (002) reflection (atomic units); I' is the experimentally observed (002) profile of the samples incorporating the regressed value of X_A ; I is the observed reduced intensity; $s = 2\sin\theta/\lambda$ ($\text{\AA}^{-1}$); P_n is the fraction of aromatic carbons within the (002) band (since all the carbon within the (002) band are completely crystalline and aromatic, $\sum P_n = 1$).

The I_{002} is symmetrical about the maximum point (I_{max}), which is highly dependent on the proper choice of the N_{ave} . To determine the most symmetrical I_{002} profile, different values of N_{ave} (integers) was inserted into Equation 4.7 and the profile that is most symmetrical was equated to the experimental reduced intensity (Equation 4.8) and regressed linearly to obtain the fraction of amorphous carbon, X_A . The interlayer spacing can also be calculated from the I_{002} profile using the expression (Equation 4.9) [2, 13, 18, 29, 61, 62]:

$$d_{002} = \frac{1}{s_{max}} \quad (4.9)$$

Alternatively, X_A can be determined by Gaussian curve deconvolution of the (002) band into the amorphous carbon and the crystalline carbon peaks, and the fraction of amorphous carbon of the samples can be calculated using Equation 4.10 [3, 19, 27, 62, 63].

$$X_A = \frac{S_A}{S_A + S_C} \quad (4.10)$$

where: S_A is the calculated peak areas for the amorphous carbon fraction, and S_C is the calculated peak area of the crystalline carbon fraction from the Gaussian deconvoluted (002) band.

The index of disorder (IOD) of the samples was calculated from the aromaticity, f_a , and the fraction of amorphous carbon, X_A , using the relation [2, 3, 19, 27, 28, 62]:

$$DOI = X_A + (1 - X_A)(1 - f_a) \quad (4.11)$$

It should be noted that the WAXRD-CFA was repeated in triplicate for each of the samples and reported results are average results from the three independent analyses with the observed uncertainty at 95% confidence interval.

4.3.3.3.2 Attenuated total reflection- Fourier transform infra-red spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of the demineralised coal samples were acquired from a Bruker Alpha-P FTIR spectrometer in the absorbance mode, using the attenuated total reflection (ATR) platinum-diamond coupling. The samples were analysed at ambient temperature, from a collection of 32 scans per spectrum (interferograms), at a resolution of 4 cm^{-1} in the frequency range of $4000\text{--}500 \text{ cm}^{-1}$. Prior to analysis, the samples were dried in a vacuum oven at 60°C for 60 min to minimise the influence of adsorbed moisture on the surface of the samples. FTIR spectroscopy has the advantage of elucidating the functional groups present in coals as a function of the type of hydrogen bonding present [17, 46, 64, 65]. The qualitative analyses of the spectra and peak assignments followed the procedures described previously [20, 22, 23, 64–70]. It is worthy to note that there has been some success in obtaining semi-quantitative and quantitative data from FTIR spectra [23, 66, 70].

4.3.3.3 Solid state ^{13}C Carbon nuclear magnetic resonance spectroscopy (ss ^{13}C NMR)

Solid state ^{13}C NMR was performed at the Central Analytical Facility of Stellenbosch University, Stellenbosch, South Africa, using a combination of cross polarization magic angle spinning (CP-MAS) and dipolar dephasing magic angle spinning (DD-MAS) methods [8, 16, 27, 71]. The solid state ^{13}C NMR spectra were acquired from a Varian VN MRS 500 MHz two-channel spectrometer using 4 mm zirconia rotors and a 4 mm Chemagnetics™ T3 HX MAS probe. The cross-polarization (CP) experiments were conducted at ambient temperature with proton decoupling using a relaxation or recycle delay of 3 s. The power parameters were optimized for the Hartmann-Hahn match; with the radio frequency fields: $\gamma_{\text{H}}B_{1\text{C}} = \gamma_{\text{H}}B_{1\text{H}} \approx 56$ kHz. The contact time for cross-polarization was 2.0 ms. A total of 4000 scans per spectrum was collected for increased signal to noise resolution. Magic-angle-spinning (MAS) was performed at 12 kHz and Hydroxy methyl butyrate (HMB) was used as an external chemical shift standard where the methyl peak was referenced to 17.5 ppm. DD-MAS experiments (CP-MAS with interrupted ^1H decoupling) were carried out under similar conditions with the interrupted decoupling time constant ($t_{1X_{\text{idref}}}$) set to 40 μs , after evaluating different time constants [71].

Previous investigations have demonstrated the quantification challenges with ^{13}C NMR technique with respect to coals and other carbon-rich materials [8, 15-17, 26, 27, 44, 71, 72]. Generally, the CP-MAS experiment is dependent on the strength of the dipolar coupling between proton and carbons, and thus, the proton density and spatial proximity to the carbon nucleus is important [16]. Factors that decrease the strength of the dipolar coupling i.e. distance and or motion will reduce the CP efficiency and thus reduce the peak intensity in the spectrum. It is important to note that the CP efficiency is mainly influenced by two factors: the CP rate (T_{CH}) and the proton relaxation time in the rotating frame ($T_{1\rho}^{\text{H}}$) [71]. Supaluknari et al. [15] found that the proton relaxation time of the main carbon types present in coals are of similar range, while the CP rates decrease in the order: aliphatic- > aromatic- > carbonyl-carbons. Consequently, the aromatic and carbonyl carbons will be discriminated against the aliphatic carbons, leading to systematic errors in the calculated structural parameters [8, 15, 17, 26, 44]. In contrast to the CP-MAS, the single-pulse excitation MAS (SPE-MAS) experiment has been identified as a better quantitative method, because it provides the best approximation of the actual aromatic to aliphatic ratio [14, 15, 17, 25, 71]. However, the low natural abundance and long relaxation times of ^{13}C results in long measurement times (typically > 48 hours per coal

sample) in SPE MAS experiments [3, 8, 15, 17, 44, 71]; while CP-MAS spectra of coals can be typically acquired within 2 to 6 hours [71]. The CP-MAS in combination with DD-MAS is, therefore, widely used for coal characterisations [15, 16, 71]. The DD-MAS experiment is used to distinguish strongly proton-coupled carbons from weakly coupled or non-protonated carbons. The DD technique is based on the principle that in the absence of ^1H decoupling, that the ^{13}C magnetisation (corresponding to strongly ^1H coupled carbons) will de-phase much faster than those corresponding to weak coupled carbons [16]. As a result of this, a DD-MAS spectrum measured with long de-phasing delays (40 μs) is dominated by signals of non-protonated or weakly coupled carbons [15]. The DD-MAS method, therefore, allows the observation of weakly coupled carbons present in bridgehead aromatics, which gives a better approximation of the ss ^{13}C NMR parameters. In this paper, a combination of CP-MAS and DD-MAS experiments were used to determine the structural parameters of the coal samples [71]. Using the spectrum integral of these experiments, the fraction of bridgehead carbons, f_a^B , the mole fraction of bridgehead carbons, X_b , and the average number of aromatic carbons per cluster, C , were calculated [14, 25].

However, it has been shown that CP-MAS underestimates the aromaticity of coals by 10 - 15% [43, 44, 71], due mainly to the influence of inherent paramagnetic organic free radical and residual paramagnetic mineral matter after coal demineralisation; which can be reduced by treatment with SmI_2 [43, 44].

For data processing, each spectrum was phased and baseline-corrected before integration. Integration reset points were set according to Solum et al. [14, 25]. All spectra were processed in the same manner to minimise operator bias.

4.3.3.3.4 High resolution transmission electron microscopy (HRTEM)

The molecular structural features of coals have been studied by the HRTEM image analysis technique, using the acquired high resolution fringe images [3, 9-12, 17, 24, 27, 30]. The HRTEM images of the coal samples were acquired from a 200 kV Tecnai F20 FEGTEM and captured using a Gatan Inc. ORIUSTM CCD camera (Model 895). Image analyses were performed on the HRTEM micrographs to extract lattice fringes, using Adobe Photoshop CS5 in combination with an image processing tool kit (IPTK 5.0) plug-in (developed by Reindeer

Graphics, USA). HRTEM image analysis was achieved following the procedure proposed by Sharma et al. [12]. The detailed algorithm for the HRTEM aromatic fringe image analysis is provided in Appendix C (Figure C-2).

The aromatic fringe features (including the length and moment angle) of each of the fringes in the final image were extracted automatically, using the built-in functions of IPTK 5.0 plug-in on the Photoshop CS5 platform and exported to Microsoft Excel 2010 for further processing. The moment angle is the angle between an aromatic fringe and an arbitrary bedding plane, usually between 0 and 180°. The aromatic fringe lengths were quantified following the procedures used by Mathews et al. [10, 24, 27]. This procedure assumes that the aromatic fringes consist of polyaromatic structures of parallel catenation (i.e. the fringe is assumed to be as deep as it is wide). The assumed parallelograms' minimum (minL) and maximum (maxL) lengths for a series of aromatic fringes were measured ranging from perylene (2x2) to 19x19 aromatic rings; and using Equations 4.12 and 4.13 [10, 24], the minimum (C_{min}) and maximum (C_{max}) carbon atoms in the parallelogram-shape aromatic fringes was calculated. The average number of carbon atoms, C_{ave} , was determined by averaging the sum of C_{min} and C_{max} and the average molecular weight of each of the aromatic fringes was estimated from the C_{ave} , using Equation 4.14 [24].

$$C_{min} = 0.4312 \times (\min L)^{1.7132} \quad (4.12)$$

$$C_{max} = 0.7981 \times (\max L)^{1.7964} \quad (4.13)$$

$$MW = (12.106 \times C_{ave}) + ((0.1806 \times C_{ave}) + 8.98) \quad (4.14)$$

Mathews and co-workers [24] however noted that, although the assignment of the HRTEM fringe lengths to the number of carbon atoms is not 'absolute', it is a good approximation of the molecular feature of the assigned aromatic component. On this basis, some cut-offs were made for small molecules. Molecules with C_{ave} : < 3 Å were assigned to benzene; < 4.4 Å to naphthalene and < 5.9 Å to anthracene. Both the individual average molecular weight of the fringes and the overall average molecular weight of the samples' fringes were evaluated using this technique. Demineralised coal samples were used for this analysis.

4.4 Results and discussions

4.4.1 Conventional properties

Table 4.1 shows the proximate and ultimate analyses of the raw and demineralised (acid-washed) samples. These values are typical of South African coals [3, 17, 19, 27, 46, 57].

Table 4.1: Proximate, ultimate and total sulphur content analyses results of coal samples.

Sample ID / Properties	Analysis method	FOZ		DEN		OGS		TKD	
		Raw coal	Dem. ^a coal	Raw coal	Dem. coal	Raw coal	Dem. coal	Raw coal	Dem. coal
Proximate Analysis (wt.%, adb)									
Inherent moisture	ISO 11722: 2013	3.3	1.8	4.0	1.6	2.7	1.5	0.7	0.8
Ash yield	ISO 1171: 2010	22.0	1.3	25.9	1.9	24.5	1.0	16.8	0.4
Volatile matter yield	ISO 562: 2010	26.6	29.1	21.5	25.2	22.4	25.6	22	23.2
Fixed carbon	By difference	48.1	67.8	48.6	71.3	50.4	71.9	60.5	75.6
Demineralisation efficiency (%)	Calculated from Eq. 1	94.1		92.7		95.9		97.6	
Ultimate Analysis (wt.%, dafb)									
Carbon	ISO 17247:2013	78.5	79.4	78.7	79.5	81.3	81.1	86.9	86.2
Hydrogen	ISO 17247:2013	4.9	4.4	4.4	3.9	4.7	4.1	5.1	4.7
Nitrogen	ISO 17247:2013	2.0	2.1	2.2	2.3	2.0	2.0	2.1	2.1
Total sulphur content	ISO 19579:2006	1.4	1.2	1.7	1.4	1.3	1.0	1.0	0.9
Oxygen	By difference	13.2	13.0	13.0	12.9	10.6	11.8	4.8	6.1

^a-Demineralised coal sample

The effectiveness of demineralisation, E_d , of the samples is also presented in Table 4.1, and ranged from 92.7% for sample DEN to 97.6% for sample TKD. The raw coals were found to have fixed carbon contents in the range of 49-61 wt.%, adb and relatively high ash yields (22-26 wt.%, adb); with relatively low volatile matter yields (~ 22 wt.%, adb), except for the raw coal FOZ (26.6 wt.%, adb). The demineralised coal samples were found to exhibit low ash yields (< 2%) with corresponding increases in both the volatile matter and fixed carbon contents.

Table 4.1 shows that carbon contents ranged between 78.5 and 86.9 % (daf); while the elemental oxygen contents were comparatively lower for sample TKD than for the other samples. Both elemental nitrogen and total sulphur contents were low at approximately < 2% for both the raw and demineralised samples. These results compare well to the reported results of other investigators on other bituminous coals of South Africa [3, 17, 19, 27].

4.4.2 Petrographic properties

Petrographic analysis results (Table 4.2) show that coals DEN, FOZ and OGS were of bituminous medium rank C; while coal TKD was of bituminous medium rank B; with mean vitrinite random reflectance (Rr.%) and mean total maceral reflectance (Rsc.%) ranging from 0.65-1.2 and 1.05-1.5 respectively. The coal vitrinite and the maceral scan random reflectance histograms of the coal samples are given in Appendix A. Coal TKD was relatively vitrinite-rich; while the other three coal samples were inertinite-rich. All four coal samples were low in liptinite abundance.

The inert inertinites (TINS) accounts for over 70% of the total inertinites observed in all the four coal samples. However, the total reactive macerals abundance in all the four coal samples ranged from 50 vol. %, mmfb for coal DEN to 78.3 vol. %, mmfb for the vitrinite-rich coal TKD. The petrographic properties of these samples compare well with reported petrographic data on South African coals by other researchers [3, 17, 19, 27, 57].

4.4.3 Chemical-structural properties

4.4.3.1 Wide-angle X-ray diffraction- Carbon fraction analysis (WAXRD-CFA)

The background-subtracted wide angle X-ray diffractograms of the demineralised coal samples are presented in Figure 4.1 and exhibited features characteristic of coal: the (002), (10), (11) and γ -side bands [13, 17-19, 27, 31]. Minor peaks, occurring mainly in coals FOZ, DEN and OGS, were due to residual pyrite.

Table 4.2: Petrographic properties of coal samples.

Sample ID / Properties	FOZ	DEN	OGS	TDK
Reflectance properties (%)				
Mean vitrinite random reflectance (Rr.%)	0.63 (0.06) ^a	0.65 (0.08)	0.69 (0.08)	1.20 (0.18)
Mean total maceral reflectance (Rsc.%)	1.05 (0.54)	1.24 (0.51)	1.19 (0.51)	1.50 (0.46)
Rank (Bituminous)	Medium Rank C	Medium Rank C	Medium Rank C	Medium Rank B
Maceral analysis (% volume, mineral matter free basis (vol.%, mmfb))				
Vitrinite (VIT)	39.5	23.2	24.1	71.7
Pseudovitrinite (PV)	2.3	1.2	1.2	2.2
Total vitrinite (TV = VIT+PV)	41.9	24.4	25.3	73.9
Sporinite/resinite/cutinite (S/R/C)	5.8	3.7	6.0	1.1
Alginite (ALG)	-	-	-	-
Total liptinite (TL = S/R/C+ALG)	5.8	3.7	6.0	1.1
Reactive semifusinite (RSF)	7.0	13.4	13.3	2.2
Inert semifusinite (ISF)	18.6	22.0	20.5	10.9
Reactive inertodetrinite (RINT)	8.1	8.5	6.0	1.1
Inert inertodetrinite (IINT)	11.6	17.1	20.5	4.3
Fusinite/secretinite (F/SEC)	5.8	9.8	7.2	5.4
Micrinite (MIC)	1.2	1.2	1.2	1.1
Total inertinite (TI = RSF+ISF+F/SEC+MIC+RINT+IINT)	52.3	72.0	68.7	25
Total inerts (TINS = ISF + F/SEC + MIC IINT)	37.2	50.1	49.4	21.7
Total reactives (TR = TV+TL+RSF+RINT)	62.8	50.0	50.6	78.3

^a - Standard deviation of determined results in parenthesis

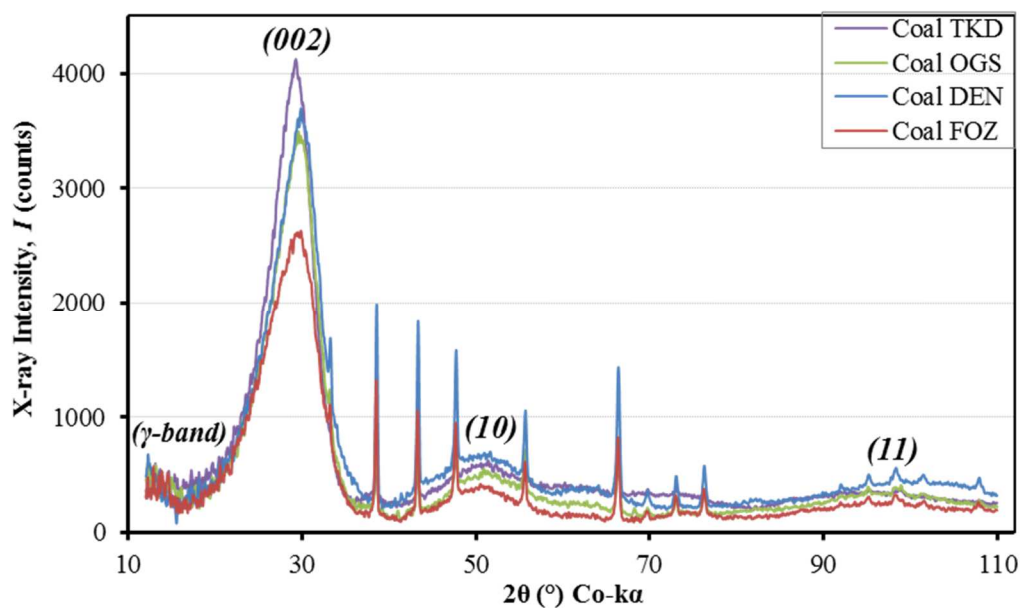


Figure 4.1: Background-subtracted wide angle X-ray (WAX) diffractograms of the demineralised coal samples.

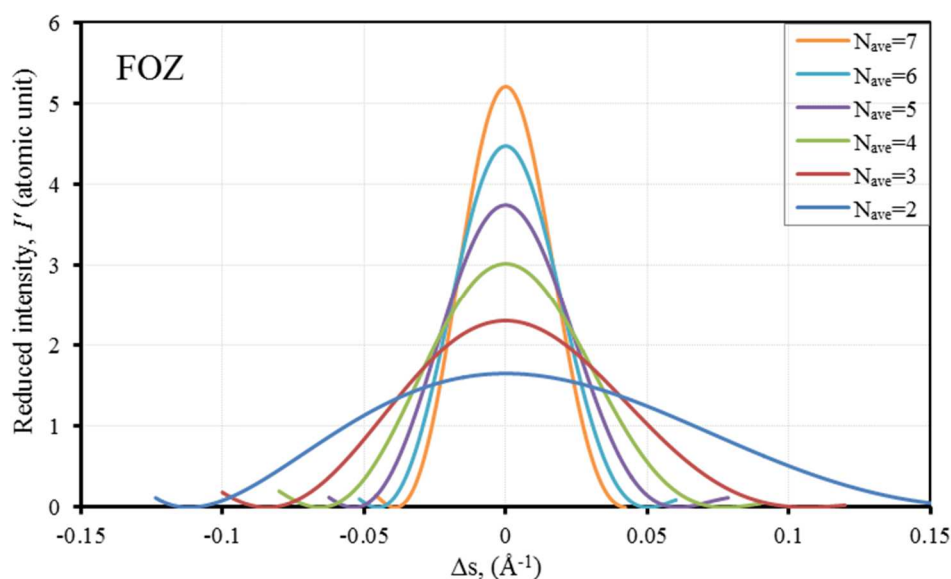


Figure 4.2: Theoretical (002) reduced intensity profiles of coal FOZ for 6 discrete values of N_{ave} .

From Figure 4.1, it can be seen that the intensity of the (002) peak of the samples increased (indicating a decreasing full width at half maximum (FWHM)), while the (002) peak angle shifted to the lower angle side with increasing vitrinite reflectance; consistent with

transformations due to increasing coalification in the bituminous coal range [2, 3, 19]. From Figure 4.1, the observed (002) peak positions ($^{\circ}2\theta$) used to determine d_{002} and L_c was: 29.679° for coal FOZ; 29.871° for coal DEN; 29.711° for coal OGS, and 29.216° for coal TKD. The identified (10) peak position used to evaluate L_a were: 50.535° , 51.234° , 51.103° , and 51.207° for coals FOZ, DEN, OGS, and TKD respectively.

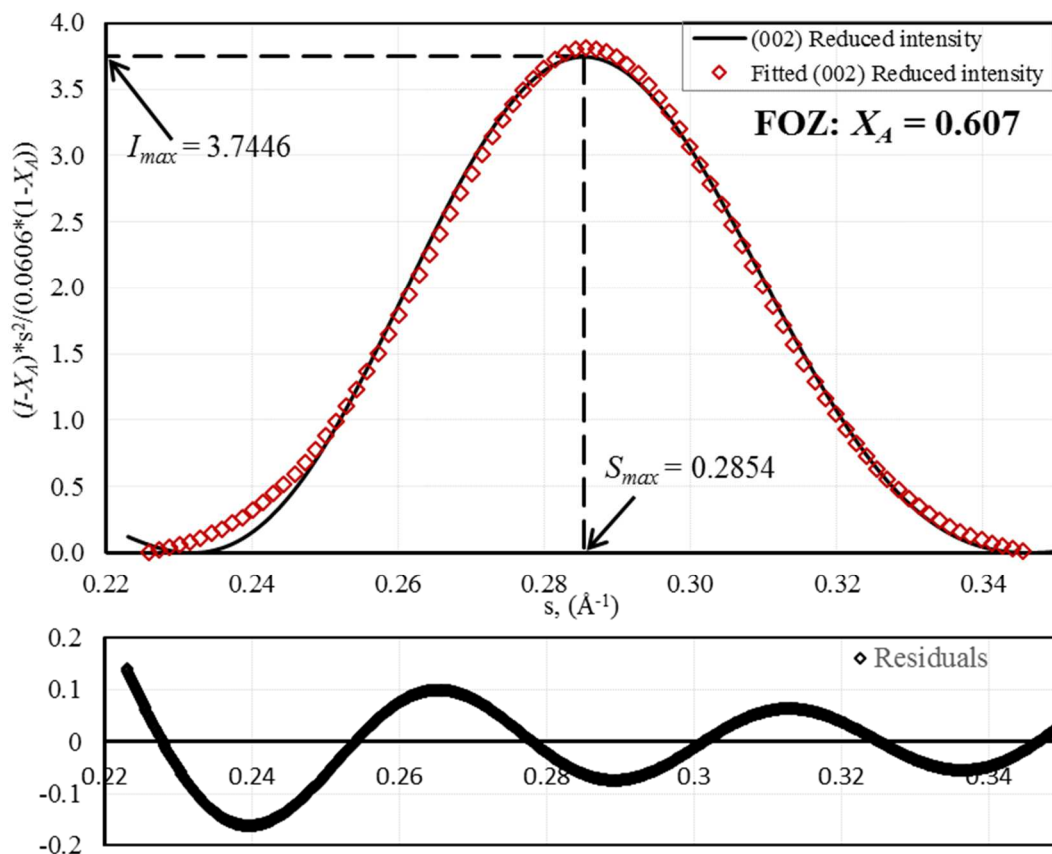


Figure 4.3: Determination of the fraction of amorphous carbon of coal FOZ from the (002) reduced intensity profile.

The (002) reduced X-ray intensity profiles used to determine the value of N_{ave} for which the (002) profile is most symmetric about $y = 0$ for coal FOZ is given in Figure 4.2. This was achieved by plotting I_{002} against $\Delta s = s - s_{max}$. The (002) reduced intensity profiles was found to be most symmetrical for $N_{ave} = 5$ for coals FOZ, DEN and OGS. However, the (002) reduced intensity profile was most symmetrical for $N_{ave} = 6$ for coal TKD; which is consistent with the determined N_{ave} data using the Scherrer equations. The regressed fitting of the (002) reduced

intensity profiles of coal FOZ used to determine the fraction of amorphous carbon is presented in Figure 4.3 with the resulting standard residuals plot indicating an excellent fit. The residual sum of squares was 5.338 ($R^2 = 0.997$) for coal FOZ; 4.580 ($R^2 = 0.997$) for coal DEN; 3.637 ($R^2 = 0.998$) for coal OGS and 5.3875 ($R^2 = 0.997$) for coal TKD. The Gaussian deconvoluted (002) band used to determine the fraction of amorphous carbon using Equation 10 is given in Figure 4.4.

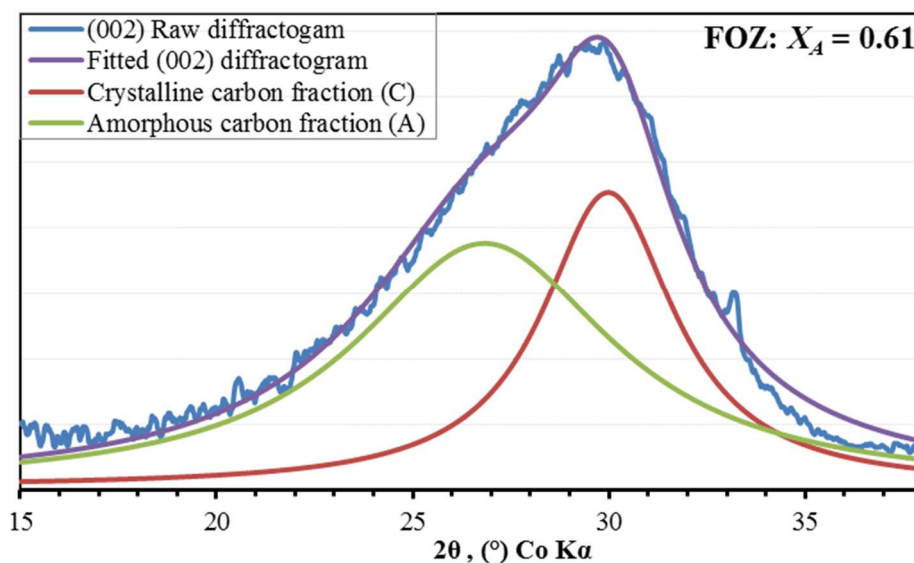


Figure 4.4: Determination of X_A by Gaussian curve deconvolution of the (002) for coal FOZ.

A summary of the of the structural properties and the lattice parameters of the samples determined from WAXRD-CFA are presented in Table 4.3, and the reported values agree very well with data on coals [2, 13, 17, 19, 27, 31]. It is note-worthy that the d_{002} and X_A determined from the empirical equations and the (002) reduced X-ray intensity profile (values in parenthesis) are quite similar within the limits of experimental uncertainty, with discrepancies in reported average values $< \pm 2\%$. The relationships between the WAXRD-CFA results and the vitrinite reflectance of the coal samples are shown in Figure 4.5.

Table 4.3: WAXRD-CFA lattice parameters and chemical structural properties of the samples.

Sample ID	FOZ	DEN	OGS	TKD
WAXRD-CFA determined structural properties of the samples				
Aromaticity, f_a (-)	0.73 ± 0.005	0.81 ± 0.006	0.83 ± 0.008	0.86 ± 0.004
Fraction of amorphous carbon, X_A (-)	0.614 ± 0.005 (0.607 ± 0.010)*	0.543 ± 0.006 (0.534 ± 0.013)	0.514 ± 0.005 (0.509 ± 0.017)	0.503 ± 0.004 (0.496 ± 0.012)
Fraction of crystalline carbon, X_C (-)	0.39 ± 0.005	0.46 ± 0.007	0.49 ± 0.004	0.50 ± 0.007
Index of disorder, IOD (-)	0.72 ± 0.006	0.62 ± 0.005	0.59 ± 0.006	0.57 ± 0.004
WAXRD-CFA determined lattice parameters of the samples				
Inter-layer spacing, d_{002} (Å)	3.493 ± 0.003 (3.504 ± 0.008)**	3.471 ± 0.004 (3.465 ± 0.007)	3.489 ± 0.002 (3.494 ± 0.009)	3.547 ± 0.003 (3.551 ± 0.006)
Crystallite height, L_c (Å)	13.74 ± 0.2	15.87 ± 0.2	15.94 ± 0.1	17.44 ± 0.2
Average number of aromatic layers, N_{ave} (-)	4.934 ± 0.03	5.572 ± 0.04	5.570 ± 0.04	5.917 ± 0.04
Crystallite diameter, L_a (Å)	17.59 ± 0.3	16.91 ± 0.2	17.40 ± 0.3	17.62 ± 0.2

* X_A determined from the (002) reduced intensity profile of the samples.

** d_{002} determined from the (002) reduced intensity profile of the samples using Equation 4.9.

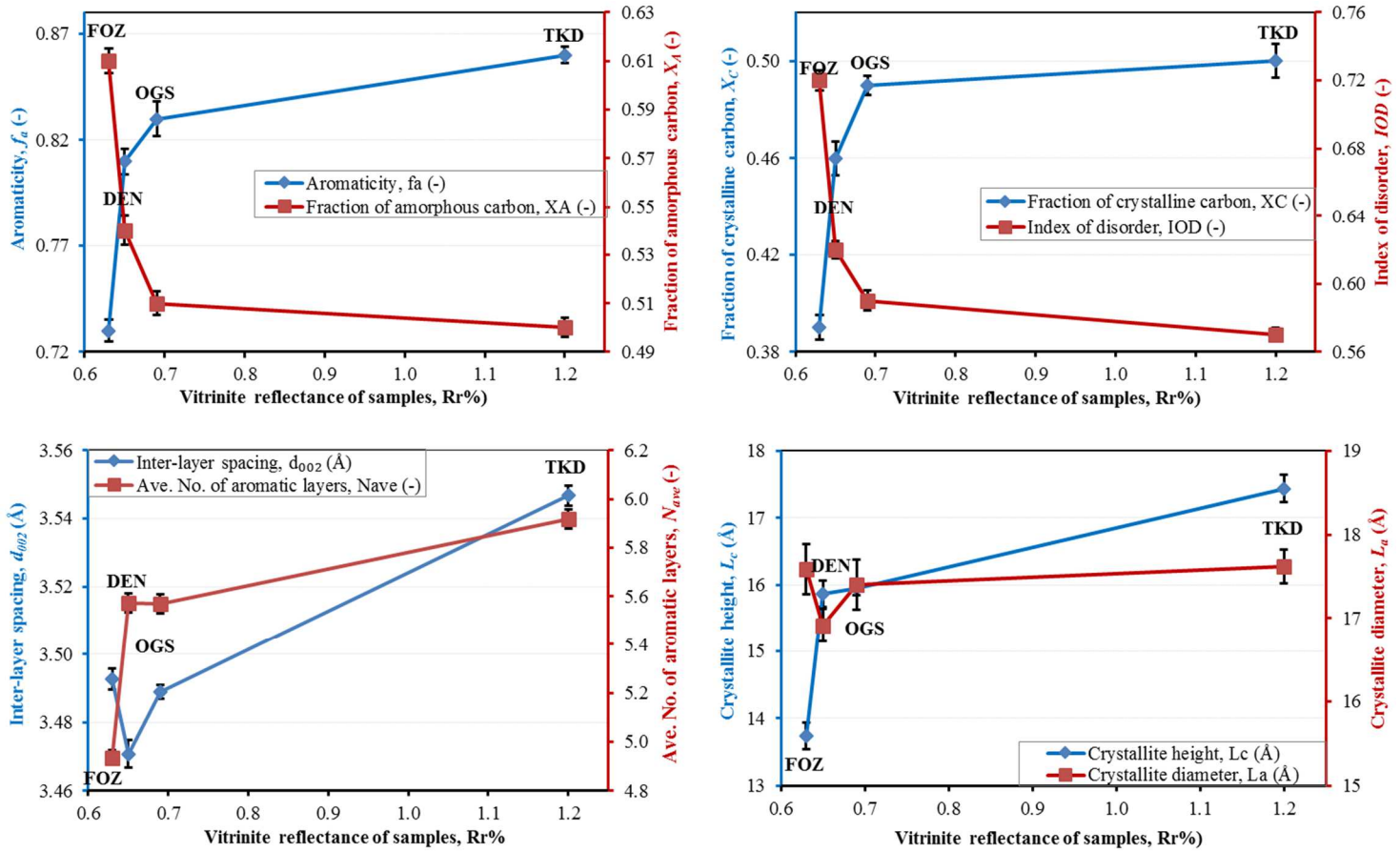


Figure 4.5: Relationships between the WAXRD-CFA determined properties and the vitrinite reflectance (Rr.%) of the coal samples.

The aromaticity and the fraction of crystalline carbon of the samples determined from WAXRD-CFA decreased from coal TKD to coal FOZ, similar to the trend exhibited by the aromaticity from solid state ^{13}C NMR analysis (Table 4.5 and Figure 4.8). The fraction of amorphous carbon and the index of disorder (IOD) exhibited the opposite trend, increasing from coal TKD to coal FOZ. From Figure 4.5 and Table 4.3, the lattice parameters (d_{002} , L_c , and N_{ave}) of the samples were found to relatively increase with increasing vitrinite reflectance, from coal FOZ (Rr.% = 0.63) to coal TKD (Rr.% = 1.2); suggesting crystallite growth with increasing vitrinite reflectance for this range of bituminous coals. However, the lattice parameter, L_a , did not show a systematic trend, in agreement with the previous findings of Lu and co-workers [13]. These parameters followed the transformation trends expected for coalification in the bituminous coal range [2, 13, 19, 27, 31], despite the small range of the mean random vitrinite reflectance of the investigated samples. The carbon crystallites present in lower rank coals in this sequence are structurally less well-ordered than the higher rank coal

TKD, which agrees with trends observed in the HRTEM study. The bigger carbon crystallites in coal TKD (in the vertical direction) compared with those of the other three lower rank coals may also explain its lower skeletal density observed in our earlier work [73], although its higher vitrinite content may be a major contributor.

4.4.3.2 *Attenuated total reflection-Fourier Transform Infra-Red Spectroscopy (ATR-FTIR)*

The ATR-FTIR spectra of the demineralised coal samples are presented in Figure 4.6, and exhibited well-resolved peaks and bands and flat baselines. The three lower iso-rank coals (coals DEN, FOZ and OGS; Rr.% 0.63-0.69) possessed similar spectral features and functional groups compared with the spectral properties and functional groups of the higher rank coal TKD (Rr.% 1.2).

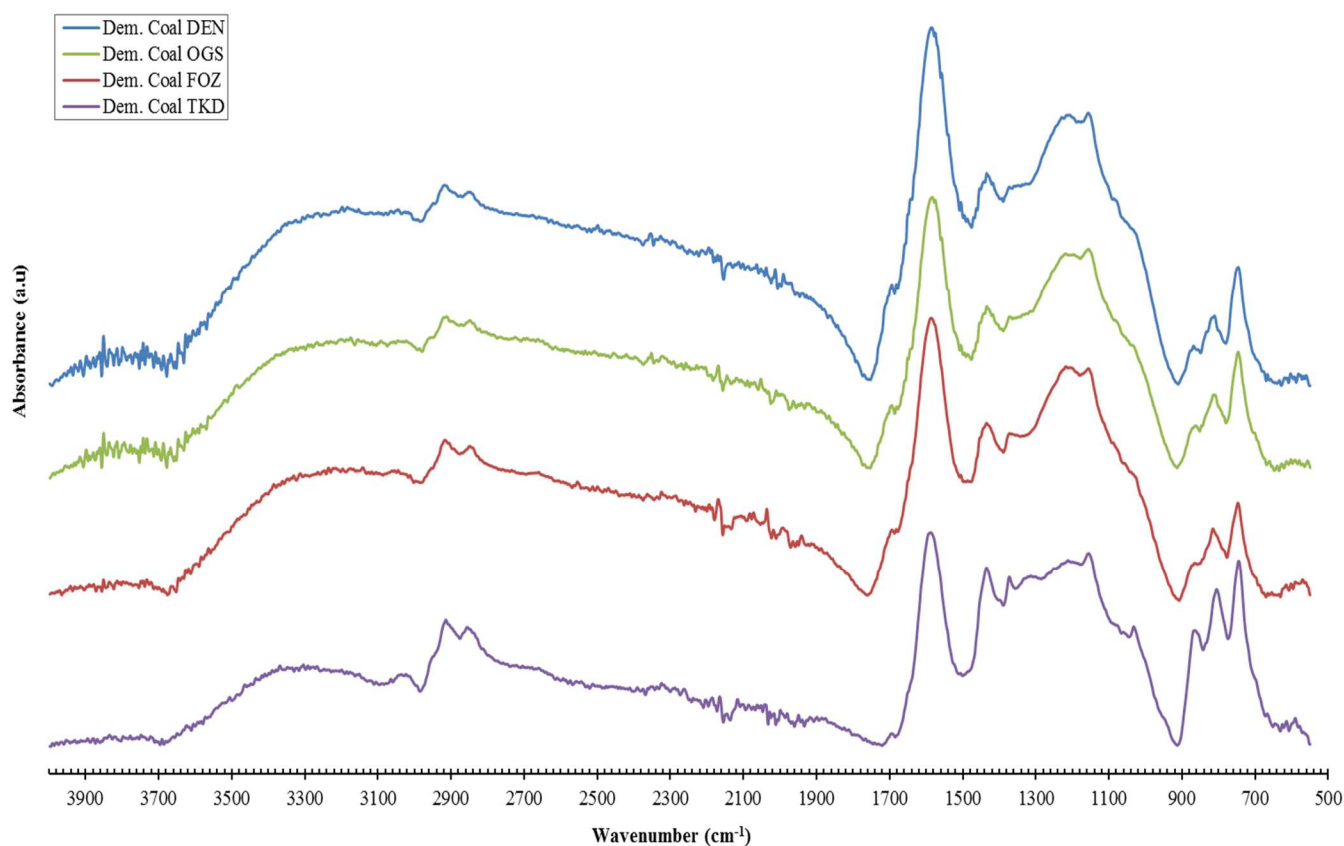


Figure 4.6: ATR-FTIR spectra of coal demineralised coal samples.

Table 4.4: Peak assignment from FTIR spectra and characteristic absorbance intensity with respect to rank and maceral abundance.

Wavenumber (cm ⁻¹)	Band/peak Assignment	Characteristic IR absorbance intensity [#]			
		Low rank	high rank	Inertinite-rich	Vitrinite-rich
3600-3100	– OH stretching vibration	s, b	w, b	s, b	w, b
3100-3000	Aromatic C – H stretching vibration	w	s	w-m	s
3000-2800	Aromatic C– H stretching vibration	w-m	m-s	w	s
2960	Asymmetric aliphatic CH ₃ stretching vibration	w-m	m-s	w	s
2920	Symmetric aliphatic CH ₃ stretching vibration	w-m	m-s	w	s
2850	Symmetric aliphatic CH ₂ stretching vibration	w-m	m-s	w	s
1700	Aliphatic C = O and – COOH stretching vibrations	m-s	m-w	s	w
1680-1500	Aromatic C = C stretching modes	s	m-w	v	v
1650	Aromatic C = O stretching vibration	s	m-w	v	v
1600	Aromatic C = C stretching vibrations of aromatic rings	s	w	v	v
1460	Aromatic C = C stretching vibration	w	s	m-w	m-s
1435	Aliphatic CH ₂ and CH ₃ bending vibration	v	v	m-w	m-s
1373	CH ₃ groups in aliphatic chains	v	v	m-w	m-s
1312	Aliphatic CH in-plane bending vibration	w	m	w	m
1280-1000	Aliphatic skeletal C – C; C – O stretching; and – OH bending vibrations	s	m-w	s	m-w
900-700	Out-of-plane aromatic C – H bending vibrations	w	s	m-w	m-s
866	Aromatic nucleus CH bending vibration (one adjacent H deformation)	w	s	m-w	m-s
805	Aromatic nucleus CH bending vibration (two adjacent H deformation)	w	s	m-w	m-s
745	Aromatic nucleus CH bending vibration (three to four adjacent H deformations in long CH ₂ chains)	w	s	m-w	m-s
720-680	Long aromatic alkanes ((CH ₂) _n ; n > 4) side rings	w	s	m-w	m-s

[#]- s- strong; b- broad; w- weak; m- medium; v- variable

The broad region, 3700-3100 cm^{-1} , was observed in all the four samples and was assigned to –OH stretching vibrations. Absorbance in this region has been attributed to intermolecular H bonds, free OH groups and associated OH groups at the terminal of the aromatic clusters of coal [17, 46]. The three lower iso-rank coals showed stronger IR absorbance in this region than the higher rank coal TKD. This observation compared well with the inherent moisture contents of the samples determined from proximate analysis (Table 4.1). A peak observed in the region 3100-3000 cm^{-1} was assigned to the aromatic C–H stretching vibration, and was higher for coal TKD, and significantly weak or absent in the other three coals. Spectra peaks observed in the region 3000-2800 cm^{-1} was assigned to C–H stretching mode due to aliphatic side chains. This region consists of two distinct peaks at 2850 cm^{-1} and 2920 cm^{-1} assigned to aliphatic symmetric CH_2 and CH_3 , and asymmetric CH_2 aliphatic stretching vibrations respectively; while the shoulder peak at 2960 cm^{-1} was assigned to asymmetric aliphatic CH_3 stretching vibration. The vitrinite-rich and higher rank coal TKD exhibited stronger absorbance in this region compared with the three lower iso-rank coals. This is in good agreement with the reported findings of other investigators [17, 23, 65, 70]. The observed peak at 1700 cm^{-1} was assigned to the aliphatic C=O and –COOH stretching vibrations due to the presence of acids, ketones and aldehydes [23, 64, 65].

Figure 4.6 shows that the vitrinite-rich and higher rank coal TKD has lower absorbance at 1700 cm^{-1} than the three other samples rich in inertinites and lower in rank. The spectral region, 1680-1500 cm^{-1} , was assigned to aromatic stretching modes. The peak at ~ 1600 cm^{-1} was assigned to the C=C aromatic stretching vibrations of aromatic rings or aromatic nucleus [17, 22, 23, 64, 67]. A shoulder observed on the left-hand side of the C=C stretching vibration of the aromatic nucleus at 1650 cm^{-1} was assigned to C=O aromatic stretching vibrations. The presence of these peaks (1700 cm^{-1} and 1650 cm^{-1}) suggests carbonyl groups are present. [17, 23, 65, 66]. It can be seen from Figure 4.6 that the three inertinite-rich coals exhibited higher absorbance in both the aliphatic C=O and –COOH stretching vibrations; and aromatic C=C and C=O stretching modes than for the vitrinite-rich coal TKD; which is in agreement with published results [17, 23]. An aliphatic bending vibration due to CH_2 and CH_3 was observed at ~ 1435 cm^{-1} of the spectra in all the four samples, with a stronger absorbance exhibited by the vitrinite-rich coal TKD. At around 1460 cm^{-1} , a shoulder was observed on the left-hand side of the peak at 1435 cm^{-1} on the spectra of the coal samples which was attributed to the aromatic C=C stretching vibration [17, 64]. The intensity of this shoulder was found to be stronger for the vitrinite-rich and higher rank coal TKD and very weak or almost absent for the three

inertinite-rich lower iso-rank coals. A low absorbance peak was observed at 1373 cm^{-1} that was assigned to CH_3 groups in aliphatic chains; it was found to be stronger and sharper in the vitrinite-rich coal TKD compared to the other samples. Visual inspection shows that coal FOZ exhibited stronger absorbance at this peak than the other two iso-rank inertinite-rich coals, which may be due to its higher volatile matter compared to the other two lower iso-rank inertinite-rich coals (Table 4.1). At 1312 cm^{-1} , a small peak due to aliphatic CH in-plane bending vibration [64], was found on the spectrum of coal TKD which was very diffuse or entirely absent in the spectra of the other three coal samples. In the wavenumber region, 1280 to 1000 cm^{-1} , multiple peaks assigned to saturated aliphatic skeletal C–C vibration; C–O stretching vibration of ether groups; and O–H bending vibrations in phenolic, phenoxy and hydroxybenzene structures were observed in the spectra of all the four coals [17, 23, 64–66, 70]. The three lower iso-rank coals were found to exhibit higher absorbance in this region compared with the higher rank coal TKD. Out-of-plane aromatic C–H bending vibrations indicating the presence of substituted aromatic species in aromatic rings; and *trans*- and *cis*- CH_2 in long saturated aromatic –CH–CH chains were observed in the 900 to 700 cm^{-1} region of the spectra of the entire coal sample [17, 23, 46, 64, 65]. The peaks at 866 cm^{-1} , 805 cm^{-1} , and 745 cm^{-1} were assigned to aromatic nucleus CH bending vibration involving one adjacent H deformation, two adjacent H deformation and three to four adjacent H deformations in long CH_2 chains respectively, in the aromatic cluster of the coals. The ATR-FTIR spectra of the samples (Figure 4.6) showed that the higher rank coal TKD had higher absorbance in the 900 cm^{-1} to 700 cm^{-1} aromatic region, than for the three other coals. Shoulder peaks present in the region 720 – 680 cm^{-1} on the right hand side of the 745 cm^{-1} peak were attributed to long aromatic alkanes $((\text{CH}_2)_n, n > 4)$ side rings [23, 46, 64], and stronger absorbance was observed in this region for coal TKD when compared with the other three coal samples. The absorbance intensity patterns of the three lower iso-rank coals were similar in the region 1500 – 680 cm^{-1} , but were entirely different to that of coal TKD. The differences in absorbance at these peaks may indicate that the vitrinite-rich coal TKD and the other three inertinite-rich coals have different substitution patterns in their aliphatic and aromatic ring structures [17] and aromatic chain substitutions [65]. A summary of the peak assignment from the FTIR spectra and the characteristic absorbance intensity with respect to rank and maceral abundance compiled from the results from this work and the reported findings of Speight [65], Van Niekerk et al. [17], and Malumbazo et al. [46] is given in Table 4.4.

4.4.3.3 Solid state ^{13}C Carbon nuclear magnetic resonance spectroscopy (ss ^{13}C NMR)

Figure 4.7 shows the ^{13}C CP-MAS with interrupted ^1H decoupling (DD-MAS) NMR spectra of the four demineralised and SmI_2 -treated bituminous coal samples. All four coals were found to exhibit two distinct peaks: an aromatic region occurring from 100 to 200 ppm and an aliphatic peak (0 – 60 ppm).

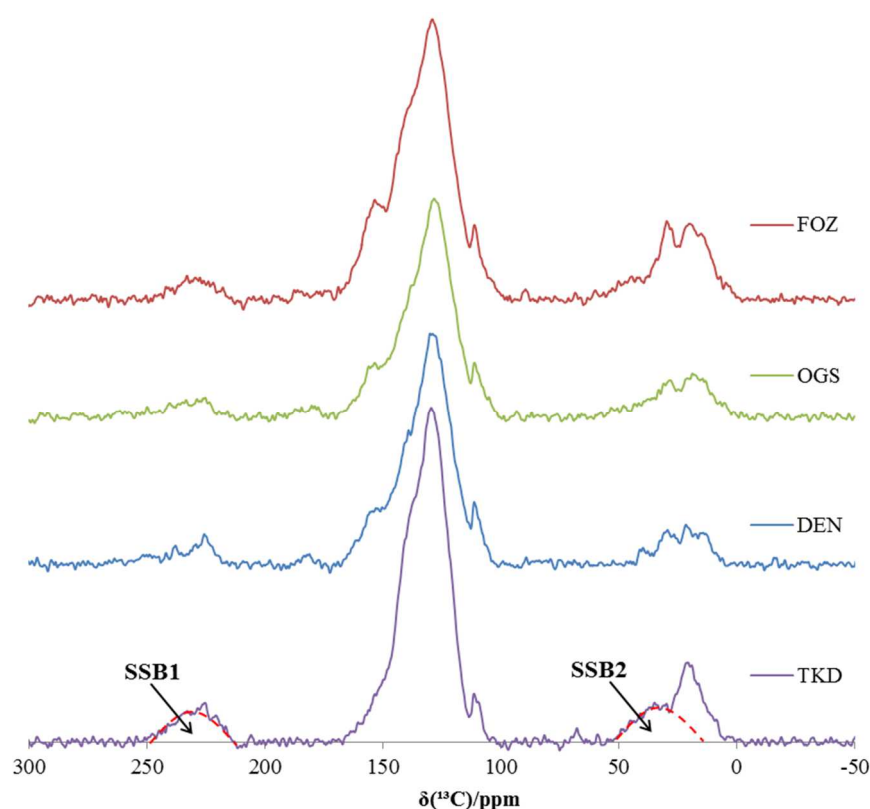


Figure 4.7: ^{13}C CP-MAS with interrupted ^1H decoupling (DD-MAS) NMR spectra of demineralised and SmI_2 -treated coal samples.

The signal (around 225 ppm) is a spinning sideband (SSB1) arising from the chemical shift anisotropy (CSA) associated with aromatic carbons [71]. Since SSB's arise in distances of the spinning frequency apart from the isotropic line (the aromatic signal about 120 ppm), a second spinning sideband (SSB2) will overlap with the aliphatic signal in the region, 0 to 60 ppm. The signal contribution of SSB2 is considered in the calculation of the ^{13}C NMR determined structural parameters, by subtracting the SSB2 integral from the aliphatic region and adding it to the total aromatic integral. SSB2 is assumed to be of similar intensity as SSB1 (Note that

SSB1 and SSB2 annotated in Figure 4.7 are not drawn to scale). The coal samples' structural parameters were determined from the integral values of ^{13}C NMR spectra, while the lattice parameters were calculated; according to the methods proposed by Solum and co-workers [14, 25]. These results are summarised in Table 4.5.

Table 4.5: Solid state ^{13}C NMR structural and derived lattice parameters of the coal samples.

Sample ID	FOZ	DEN	OGS	TKD
Solid state ^{13}C NMR structural parameters				
Aromatic carbons, f_a	0.74	0.79	0.79	0.87
Aliphatic carbons, f_{al}	0.26	0.21	0.21	0.13
Aliphatic carbons bonded to oxygen, f_{al}^O	0.008	0.018	0.002	0.00
Carbonyl/ carboxyl and amide carbons, f_a^{CO}	0.023	0.020	0.006	< 0.001
Phenolics fraction, f_a^P	0.08	0.08	0.07	0.04
Alkylated aromatic carbons, f_a^S	0.17	0.18	0.17	0.20
Non-protonated aromatic carbons, f_a^N	0.59	0.63	0.64	0.70
Protonated aromatic carbons, f_a^H	0.09	0.11	0.11	0.10
Aromatic bridgehead carbons, f_a^B	0.34	0.37	0.39	0.45
Aliphatic CH and CH_2 , f_{al}^H	0.26	0.21	0.21	0.13
Solid state ^{13}C NMR derived lattice parameters				
Average number of intact bridges, P_0	0.33	0.63	0.60	0.90
Average number of bridges and loop per cluster (cross-links), $B.L$	2.97	5.47	5.23	8.42
Average number of side chains per cluster, $S.C$	6.10	3.19	3.48	0.96
Mole fraction of aromatic bridgehead carbons, X_b	0.50	0.50	0.53	0.57
Average number of aromatic carbons per cluster, C	24.67	24.83	26.65	30.84
Average number of clusters per 100 carbon atoms	2.78	3.00	2.81	2.60
Ave. number of attachments (bridges, loops, side chains) per cluster, $\sigma + 1$	9.07	8.65	8.71	9.39
Fraction of aromatic ring carbons with a directly attached proton, M_G	0.13	0.15	0.15	0.13
Average molecular weight of side chain or half of bridge mass, M_δ	27.01	23.41	23.38	17.30
Average molecular weight per cluster, MW	544.4	504.1	527.2	536.4

The aromaticity, f_a , ranges from 74% for coal FOZ (0.63 Rr.%) to 86% for coal TKD (1.2 Rr.%), in agreement with published results on South African coals [3, 17, 19, 27]. These values showed a satisfactory comparison with the aromaticity of the samples determined from WAXRD-CFA (Table 4.3), which ranged from 0.73 to 0.81; and exhibited the same trend with the vitrinite reflectance. A graphical comparison of the aromaticity data of the samples from these two techniques (WAXRD-CFA and ss ^{13}C NMR) is included in Appendix C.

The fraction of phenolic aromatic carbons, f_a^P , was observed to be low (4%) in coal TKD; and higher and fairly similar values of around 7-8% for the other three coals. The fraction of aliphatic carbons bonded to oxygen, f_{al}^O , was found to be significantly low (0.2-1.8%) in the three lower iso-rank coals, and completely absent in the higher rank coal TKD. The carbonyl, carboxyl and amide carbons fraction, f_a^{CO} , was also found to be very low in coal TKD (< 0.1%), but comparatively higher (0.6-2.3%) in the other three lower iso-rank coals. It was observed that coal FOZ, with the lowest vitrinite reflectance amongst the four samples, contained greatest amount of the oxygen functionalities (f_{al}^O , f_a^{CO} , f_a^P), while the higher rank coal TKD possessed the least amount of oxygen functional groups. These results followed the trend of the qualitative ATR-FTIR analysis results (Table 4.4 and Figure 4.6), where coal TKD showed lower absorbance in the regions, bands or peaks assigned to different oxygen functionalities (–OH, C–O, C=O, –COOH). These results also agreed with the lower moisture content from proximate analysis and the lower elemental oxygen content from ultimate analysis of coal TKD relative to the other three lower iso-rank coal samples (Table 4.1), and highlight the rank dependency of the chemical-structural features of the examined coals. Similar results have been reported for a suite of South African bituminous coals with vitrinite reflectance ranging from 0.61-1.23 Rr.% [3].

The three lower iso-rank coals did not exhibit significant differences with regard to their fraction of alkylated aromatic carbons, f_a^S contents (17-18%), but coal TKD contained more alkylated aromatic carbons (20%). This was consistent with the greater absorbance observed for the ATR-FTIR of coal TKD in the out-of-plane aromatic C–H bending vibrations region ($900\text{--}700\text{ cm}^{-1}$) and the long aromatic alkanes region ($720\text{--}680\text{ cm}^{-1}$), and corroborates the higher aromaticity value of coal TKD from both WAXRD-CFA and ^{13}C NMR. The fraction of non-protonated carbons in the aromatic region, f_a^N , was found to increase with increasing

vitritine reflectance of the coals. Thus, f_a^N was observed to be lower in coal FOZ (59%) with 0.63 Rr.%, and maximum in coal TKD (70%) with Rr.% of 1.2. The fraction of aromatic bridgehead carbons, f_a^B , was found to be higher in coal TKD (45%) than in the other samples (34-39%) and was lowest in coal FOZ (34%). However, the fraction of protonated aromatic carbons remains fairly constant in all the four coals (9-11%). The fraction of aliphatic CH and CH₂, f_{al}^H , was also found to be higher in coal FOZ (26%) and least for coal TKD (13%). These results may explain the higher volatile matter yield in coal FOZ (Table 4.1), compared to the other three samples. Furthermore, Coal FOZ also exhibited a higher content of aliphatic carbons, which are more easily affected by heat [2, 19, 27], as measured by both the WAXRD-CFA and solid state ¹³C NMR spectroscopy analysis; and confirms the higher aromaticity from both WAXRD-CFA and ¹³C NMR and the lower index of disorder, *IOD*, of coal TKD from WAXRD-CFA. It is worthy to note that the aromaticity of the samples determined from both ¹³C NMR and WAXRD-CFA are quite similar (Tables 4.3 and 4.5).

A structural comparison of the four coals with respect to the lattice parameters determined by ¹³C NMR show that the higher rank coal TKD exhibited higher contents of most likely intact bridges, *P₀* (90%); average number of cross-links per cluster, *B.L* (8.4); mole fraction of aromatic bridgehead carbon or aromatic skeleton, *X_b* (57%); and average number of carbons per cluster, *C* (31), than the other coal samples; the lowest rank coal FOZ showed the lowest values for these parameters. Remarkably, coal FOZ contained more side-chains per cluster, *S.C* (6.1) than for the other coals, with coal TKD having the least number of side-chains per cluster (0.96). These results are in agreement with the greater aromaticity and smaller fraction of amorphous carbons of the higher rank coal TKD (1.2 Rr.%), compared to the other samples and indicates that coal TKD has larger aromatic chains and cross-links than the three other samples. The average molecular weight of the samples calculated from ¹³C NMR analysis ranged from 504 to 544 amu for the four coal samples. The relationship of some of the structural properties of the coal samples determined from ¹³C NMR with the vitritine reflectance of the samples is presented graphically in Figure 4.8. The trends exhibited by the ¹³C NMR results are consistent with the structural features of the samples determined from WAXRD-CFA and the qualitative ATR-FTIR techniques; in that they confirm that the structure of coal TKD is different to that of the other three coals, which is consistent with its higher rank (or possibly, greater vitritine abundance).

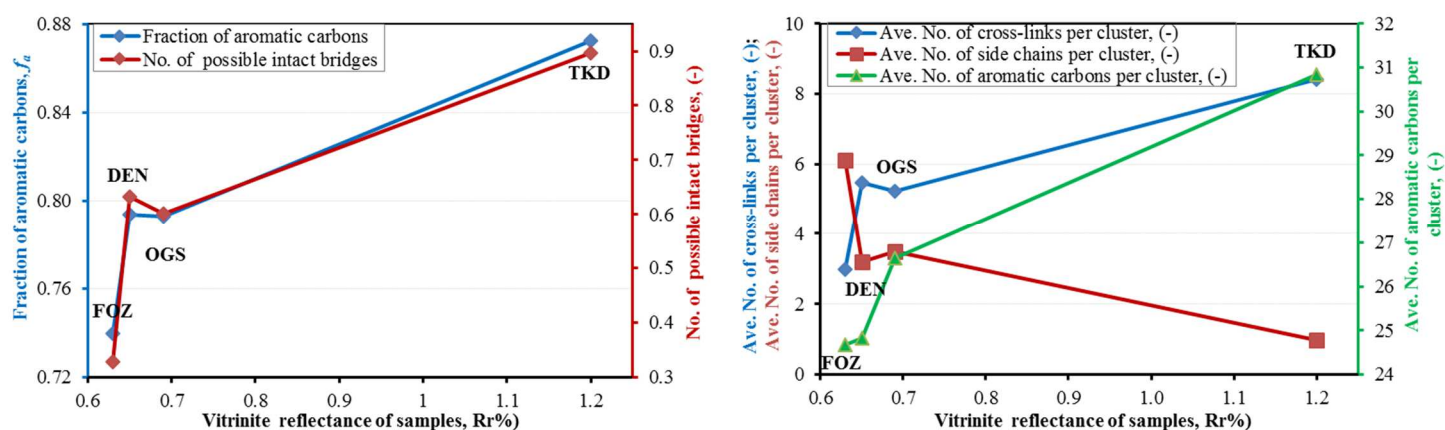


Figure 4.8: Correlation of some solid state ^{13}C NMR determined properties with the vitrinite reflectance (Rr.%) of the coal samples.

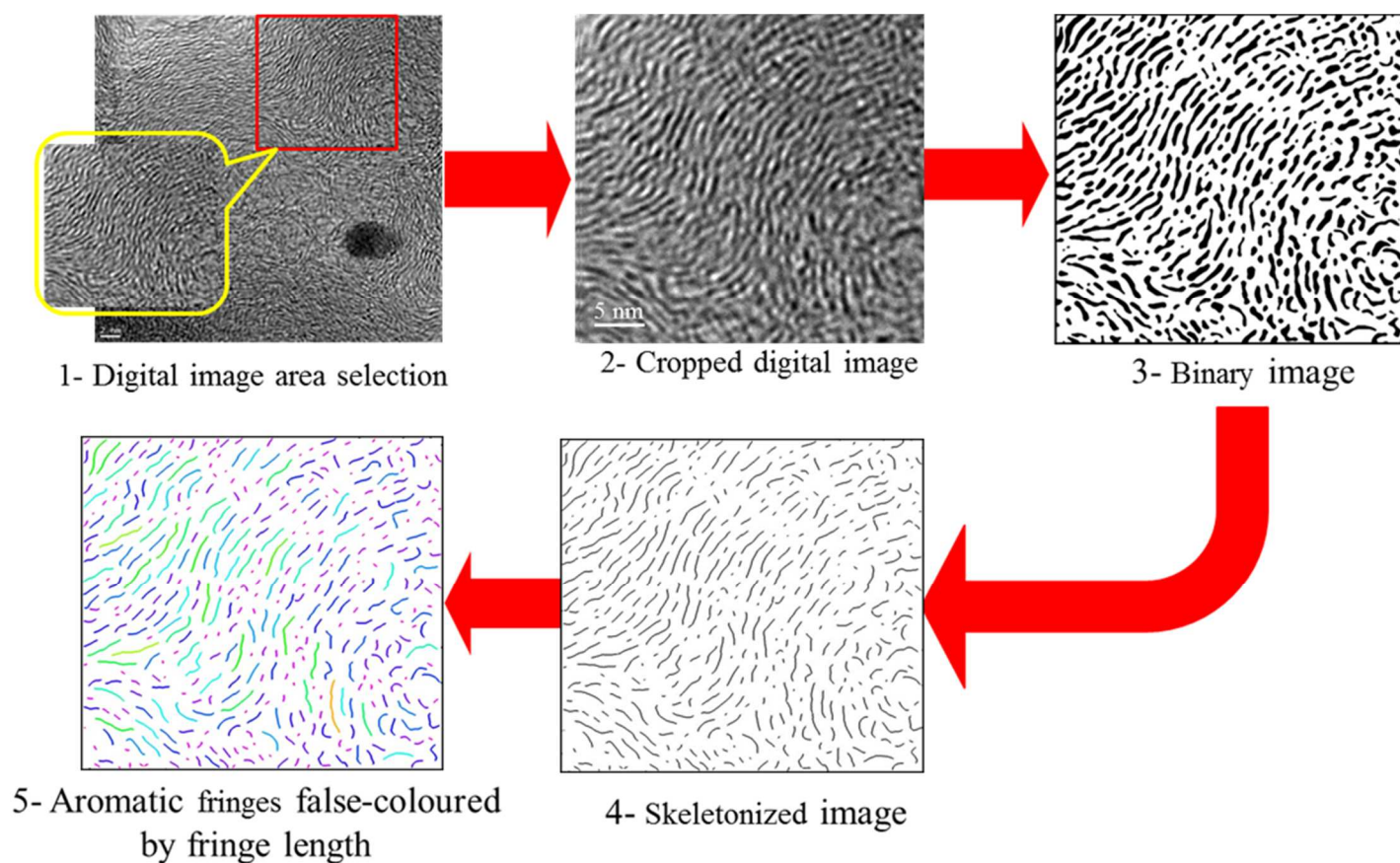


Figure 4.9: HRTEM aromatic fringe image analysis sequence of demineralised coal TKD.

However, structural properties are also impacted by maceral diversity [11, 27, 74]. In the set of coal samples used in this investigation, the largest differences are between coal FOZ and coal TKD. The presence of reactive inertinite (reactive semifusinite and reactive inertodetrinite) is thus, expected to have a lower impact than inert inertinite where greater ordering and larger aromatic structures are envisaged [11, 74].

4.4.3.4 *High resolution transmission electron microscopy (HRTEM)*

Figure 4.9 shows the different stages of image processing as applied to the HRTEM digital image of coal TKD. The number of the identified features (aromatic fringes) in the skeletonised images of the samples was: 675 for coal DEN; 765 for coal FOZ; 754 for coal OGS and 447 features for coal TKD.

Table 4.6 presents a summary of the grouping of the aromatic fringes by fringe lengths and by average molecular weight ranges; as well as their frequency of occurrence in the aromatic fringes population and individual contribution to the average molecular weight of the aromatic fringe of the samples (Also see Appendix C, Figures C-3 and C-4). The average molecular weights, *MW*, of the sample's aromatic fringes are also given in Table 4.6.

Results from the HRTEM image analysis show that the identified fringes ranged from benzene (< 3 Å) to 19x19 aromatic rings (fringe length: 95-99.9 Å) corresponding to molecular weight distributions ranging from 75 to 1925 amu.

Coal TKD possessed a higher percentage of longer fringes corresponding to higher molecular mass aromatic components [10, 17, 24, 27] relative to the other studied samples. Coal FOZ was found to contain a higher distribution of smaller aromatic fringes representing lower molecular mass components. The average molecular weight of the HRTEM aromatic fringes ranged from 506.9 amu for coal FOZ to 659.5 amu for coal DEN, which compared well with the solid state ¹³C NMR determined results (Tables 4.5 and 4.6). A graphical comparison of the average molecular weight of the coal samples from these two techniques (HRTEM and solid state ¹³C NMR) is included in Appendix C.

Table 4.6: Structural assignments, frequency and average molecular weight contributions based on HRTEM fringes image analysis.

Sample ID		FOZ		DEN		OGS		TKD	
Grouping by fringe length range (Å)	Grouping by MW range (amu)	% Freq.	MW contribution	% Freq.	MW contribution	% Freq.	MW contribution	% Freq.	MW contribution
Benzene (< 3 Å)	50-99	3.8	0.9	1	0.3	1.1	0.3	0.7	0.7
Naphthalene (< 4.4 Å)	100-149	3.4	4.2	1.6	2	2.3	2.8	1.6	5
Anthracene (< 5.9 Å)	150-199	5.5	9.6	2.4	4.1	3.1	5.3	2.2	8.2
5.9 - 9.9 (2x2)	200-249	13.2	29.6	8	18	12.3	27.7	10.1	23.8
10.0 - 14.9 (3x3)	300-349	14.4	46.7	10.5	34.1	13.1	42.6	10.3	38.2
15.0 - 19.9 (4x4)	400-449	14.6	62.1	11.1	47.2	13	55.2	9.8	53.9
20.0 - 24.9 (5x5)	500-549	10.5	54.8	10.8	56.7	14.9	77.9	9.4	51.8
25.0 - 29.9 (6x6)	600-649	8.8	54.7	9.9	62	12.5	77.9	7.6	50
30.0 - 34.9 (7x7)	700-749	7.5	54	10.2	74.1	9.2	66.3	6.7	51.1
35.0 - 39.9 (8x8)	800-849	5.8	47.4	7.7	63.5	6.2	51.4	7.2	54.3
40.0 - 44.9 (9x9)	900-949	3.9	36.3	7.4	68.5	3.8	35.6	6.3	50
45.0 - 49.9 (10x10)	1000-1049	2.5	25.4	6.2	63.7	3.8	39.4	6.3	45.8
50.0 - 54.9 (11x11)	1100-1149	2.4	26.5	4.3	48.3	1.1	11.9	5.4	37
55.0 - 59.9 (12x12)	1200-1249	1.3	16	3.6	43.5	1.5	17.9	4.3	25.9
60.0 - 64.9 (13x13)	1300-1349	0.9	12.1	2.5	33.4	0.9	12.3	3.1	24.9
65.0 - 69.9 (14x14)	1400-1449	0.7	9.3	1.6	23.2	0.5	7.6	2.5	20.1
70.0 - 74.9 (15x15)	1500-1549	0.5	8	0.4	6.8	0.3	4	2	17.9
75.0 - 79.9 (16x16)	1600-1649	0.1	2.1	0.3	4.8	0.3	4.3	1.8	11.5
80.0 - 84.9 (17x17)	1700-1749	0.1	2.3	0.1	2.6	0.1	2.3	1.1	8.1
85.0 - 89.9 (18x18)	1800-1849	0.1	2.4	0.1	2.7	0.1	2.4	0.9	8.6
90.0 - 94.9 (19x19)	1900-1949	0.1	2.5	0	0	0	0	0.4	4.5
95.0 - 99.9 (20x20)	2000-2049	0	0	0	0	0	0	0	0
Average molecular weight of aromatic fringes (amu)		506.9		659.5		545.1		591.3	

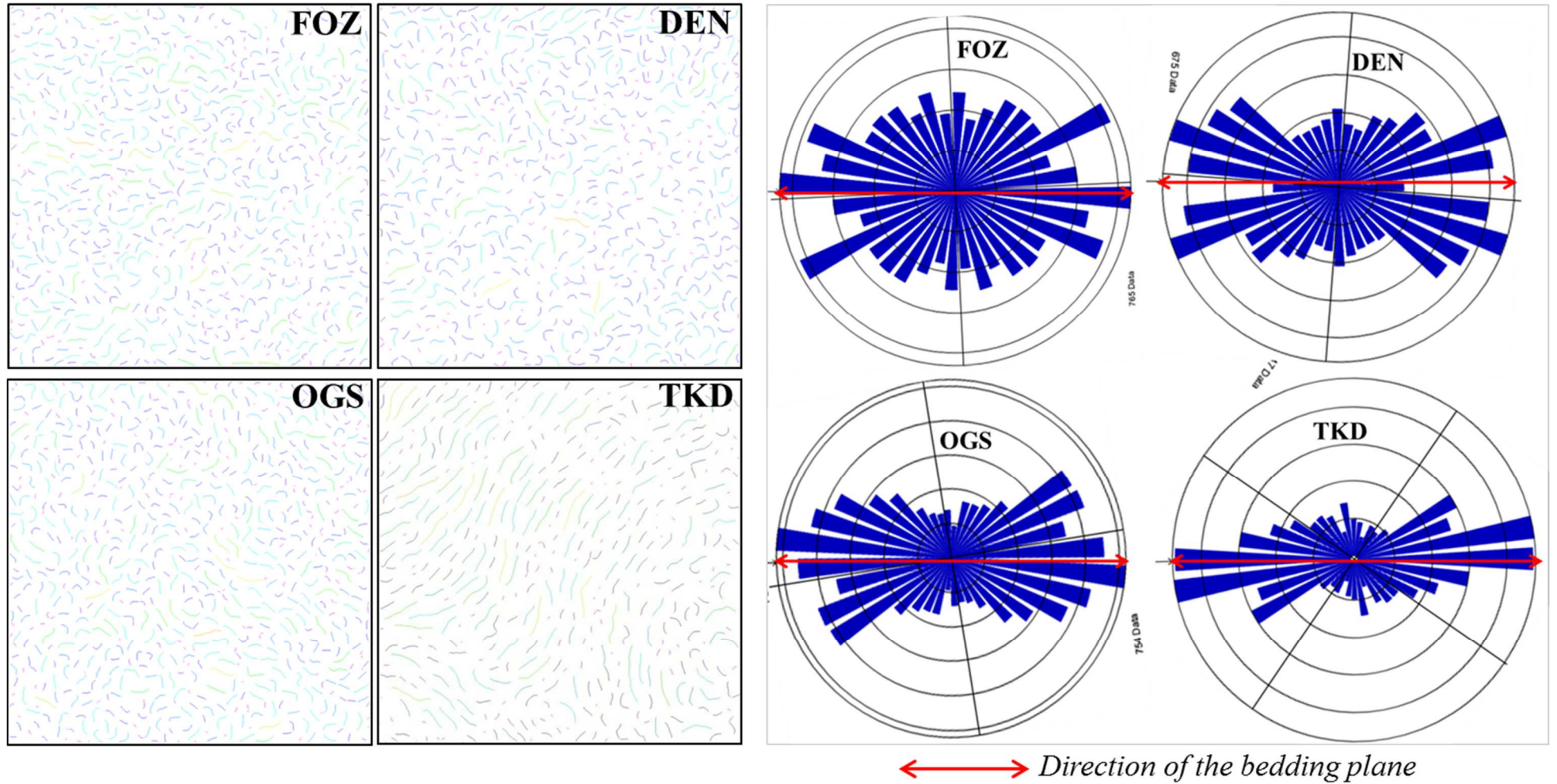


Figure 4.10: Rose diagrams showing the orientation of the of the HRTEM fringes relative to the bedding plane of the coal samples.

Assuming that the dominant moment angle of the HRTEM fringes is aligned parallel to the bedding plane [9]; it was possible to construct rose diagrams to visualise the orientations of the aromatic fringes with respect to the bedding plane. This was achieved by utilising the orientations of the fringes extracted from the moment angles of the skeletonised image using the IPTK 5.0 plug-in on the Adobe Photoshop CS5 application platform. The entire aromatic fringe population of each sample was used for this exercise and plotted using GEOrient Version 9.5.0 software [75]. The resulting rose diagrams of the coal samples are shown in Figure 4.10; they are comparable to reported results by Mathews and Sharma [9]. The small arrowed red lines through the rose diagrams indicate the calculated bedding plane. Visual inspection and interpretation of the rose diagrams reveals that the orientation of the fringes normal to the bedding plane increases in the order: coal TKD < coal OGS < coal DEN < coal FOZ. This correlates well with the trends observed from the solid state ^{13}C NMR, WAXRD-CFA and qualitative ATR-FTIR analysis results, and further substantiates the increasing structural orderliness of the coals with increasing vitrinite reflectance (rank).

4.5 Conclusions

Various analytical techniques were successfully applied in the characterisation and elucidation of the chemical structural properties of four South Africa bituminous coals.

- ✓ Aromaticity of the coals increases with increasing vitrinite reflectance of the samples from both solid state ^{13}C NMR and WAXRD-CFA data. Qualitative ATR-FTIR show that coal TKD (with greatest vitrinite reflectance of the samples investigated) contained greater amounts of polyaromatic moieties and longer chains of saturated aromatic hydrocarbons than the other samples, and these increase with increasing Rr.%.
- ✓ HRTEM image analysis revealed that the aromatic fringe length of the coals increases with increasing vitrinite reflectance of the samples. Thus, coal TKD (with higher Rr.%) consists of longer chains of polyaromatic hydrocarbon compared with the other three lower iso-rank coals. The average number of aromatic carbons per cluster determined from solid state ^{13}C NMR analysis was higher for coal TKD which is consistent with WAXRD-CFA, ATR-FTIR and HRTEM analyses results.

- ✓ The lattice parameters determined from WAXRD-CFA show that the three lower rank coals investigated are structurally less well-ordered than the higher rank coal TKD, even though it exhibited a higher d_{002} , L_c values.
- ✓ Crystallite height, L_c , relatively increased with increasing coalification; while crystallite diameter, L_a , remains fairly constant across the coal ranks.
- ✓ The rose diagrams constructed from the moment angle of the aromatic fringes from the HRTEM image analysis shows that the aromatic fringes become more strongly aligned as rank increases.
- ✓ There is a good agreement between average molecular weight of the aromatic fringes determined from HRTEM and solid state ^{13}C NMR data. The aromaticity of the samples as measured by WAXRD-CFA was very similar to the solid state ^{13}C NMR determined values. Both the fraction of amorphous carbon and the index of disorder were found to correlate well with the aromaticity of the samples, and decreases with increasing Rr.%.
- ✓ It has been demonstrated that, for the four South African bituminous coals studied in this investigation, that vitrinite reflectance impacted more on the chemical-structural properties of the samples than maceral compositions.

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Chapter 5

5.0 High pressure CO₂, CH₄, and N₂ sorption experiments: Results and discussion

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Highlights

- The coals can store up to 4.1 – 8.7 wt.% CO₂, 1.0 – 1.8 wt.% CH₄, and 1.0 – 2.2 wt.% N₂.
 - The DR-HH model provided better fits to the sorption isotherm data than the M-DR model.
 - Physisorption is the dominant sorption mechanism, while storage is by structural trapping.
 - Rr.%, microlithotype abundance, and micropore properties of the coals impact the sorption properties.
 - Polarisability and the van der Waal's attractive constants of the gases also influence the sorption properties.
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5.1 Abstract

In this paper we report the CO₂, CH₄ and N₂ sorption isotherms of four South African bituminous coals at pressures up to 16 MPa at 55 °C. The sorption capacities of the samples with respect to the adsorbate gases decreased in the order: CO₂ > CH₄ ≈ N₂ by weight, and CO₂ > CH₄ > N₂ by volume. A new model, based on a hybrid Dubinin-Radushkevich and Henry law approach (DR-HH), provided substantially better fits to the sorption isotherm data than the previously used modified DR (M-DR) model. Obtained uncertainty metrics show that the DR-HH model generally returned lower error sum of squares (ESS) and root mean square (RMS) residuals, and higher quality of fit (QOF) compared to the M-DR model. The net heat of sorption, βE_s , of the samples for the three adsorbate gases were generally low (8.5 - 12.8 kJ/mol), indicating that physisorption was the dominating sorption mechanism. The sorption capacities of the samples were found to be rank-dependent as they decreased with increasing vitrinite reflectance and elemental carbon content. The micropore properties of the samples as measured by both CO₂ low pressure gas adsorption (LPGA) and small angle X-ray scattering (SAXS), significantly impacted the sorption properties of the sample more than both the mesopore and macropore properties determined from N₂ LPGA, SAXS, and mercury intrusion porosimetry. The sorption capacities of the samples were found to increase with increasing intermediate maceral abundance, suggesting that lithotype bandings enhances either the fluid transport processes or the micropore properties of the coal matrix. Mineralogical analysis of

the samples showed that, of the minerals present, only pyrite and calcite showed a trend with sorption capacity, which may be related to rank differences of the coals. In addition, it has been demonstrated that critical properties of the adsorbate gases influenced their sorption properties.

Keywords: *GHG emissions, sorption capacity, Dubinin-Radushkevich-Henry law hybrid, coal properties, micropore properties, critical properties of gases.*

5.2 Introduction

Increasing anthropogenic greenhouse gas (GHG) emissions emanating from the utilisation of fossil fuels for energy production and other industrial processes (cement production, metallurgical uses, etc.), has been largely blamed for the global climate change [1, 2]. Data from the Earth System Research Laboratory (ESRL) at Mauna Loa, Hawaii show that global CO₂ emission into the atmosphere has increased from 278 parts per million (ppm) during the pre-industrial era (approximately 280 ppm) to over 400 ppm as at February, 2016 [3]. This has effectively contributed to different climate change scenarios [1, 2, 4, 5], resulting in global warming with a predicted increase of 1.8 - 3.9 °C by 2100 [2, 6].

South Africa operates a highly energy-intensive economy, with considerable dependency on fossil fuels to meet its energy needs. This, together with a relatively small population, means that South Africa is a significant contributor with respect to per capita emissions of CO₂ on the global scale [7]. Considering electricity production alone, 92% of electricity produced in South Africa is from coal combustion, complemented by nuclear energy [8]. South Africa emits about 440 Mt CO₂ per annum, and is responsible for over 40% of CO₂ emitted in the African continent. South Africa accounts for about 1% of global emission and is ranked 11th highest CO₂ emitter in the world [7-9].

Carbon capture and sequestration or storage (CCS) has been demonstrated as a viable and strategic option for climate change mitigation. Furthermore, geological storage of carbon dioxide in deep “unmineable” or unprofitable coal seams has been shown as one of the feasible geological sequestration strategies for captured CO₂, with the synergy for enhanced coalbed methane production [10]. Viljoen and co-workers [8] reported that up to 1.30 Gton of CO₂ can be stored in identified unmineable coal seams of South Africa, with an estimated gas content

of about 0.14 - 0.28 trillion m³ (4.9 - 9.9 Tft³). Moreover, a good source-sink match exists between the emission point sources and the unmineable coal seams [8].

However, a fundamental knowledge of the sorption properties of these coals to various adsorbate gases, especially CO₂ and CH₄ is necessary in determining the storage capacity of unmineable coal seams. Although, sorption data abound for northern hemispheres' coals, information on South African coals at supercritical conditions is still limited. Several investigators [11-16] have studied simultaneously the CO₂, CH₄, and N₂ sorption properties of northern hemispheres' bituminous coals of various ranks.

Sakurovs and co-workers [11] studied the CO₂, CH₄, and N₂ sorption properties of Australian bituminous coals under supercritical conditions and further investigated the relationship between the critical properties of different adsorbate gases on their supercritical sorption behaviour on the coals [12]. Their reported findings show that the maximum sorption capacities of the coals under supercritical conditions correlated well with the critical properties of the gases.

Cui et al. [13] have demonstrated experimentally and by numerical modelling (using a slit-shaped pore and bidisperse model) that selective transport of CO₂, CH₄, and N₂ through the coal matrix is highly dependent on the micro- and meso-pore structures of the coals. They also found that the apparent diffusivity of the adsorbate gases through the pore structures (especially the micropores), which is a function of the adsorption kinetics, is highly dependent on the kinetic diameter of the gases [13]. Morse et al. [14] examined the sorption behaviour of 16 coal samples from the Tanquary injection site in Illinois, USA under sub- and super critical conditions. They reported that the microlithotype compositions and abundances of the samples in combination with their mineral matter content impacts the micro- and meso-pore properties of the coals, which in turn, significantly influences the sorption capacities of the samples.

Pini et al. [15] investigated the CO₂, CH₄, and N₂ sorption capacities of bituminous coals from Europe and found that the maximum sorption capacities of the dry coals fall within the range: 5 - 14 wt.% for CO₂, and 1 - 3 wt.% for both CH₄ and N₂. They also reported that the sorption capacities of the coal samples for the three studied gases decreased with increasing vitrinite reflectance.

Reported maximum sorption capacities of dry coals of various ranks up to anthracite by weight vary in the range: 20.7 - 1514 kg/t, db for CO₂ [11-15, 17-20], 7.4 - 29.0 kg/t, db for CH₄ [11-15, 20-23], and 3.4 - 35.9 kg/t, db for N₂ [11-15]. These translates to sorption capacities of 2.1

to 15.1 wt.% of dry coal for CO₂, 0.7 - 2.9 wt.% of dry coal for CH₄, and 0.3 - 3.6 wt.% of dry coal for N₂. Thus, the sorption capacities of coals by mass of gas per unit mass of dry coal decrease in magnitude in the order: CO₂ > CH₄ $\approx$ N₂. However, expressed as volume of gas (at standard temperature and pressure (STP)) per unit volume of coal, the sorption capacities of coals decrease in the order: CO₂ > CH₄ > N₂ [12, 15]. The determined net heat of sorption, βE_s , of coals of different ranks vary in the range: 8.2 - 13.5 kJ/mol for CO₂ [11, 12, 17, 19, 21], 8.8 - 11.8 kJ/mol for CH₄ [12, 21, 23], and 8.6 - 10.4 kJ/mol for N₂ [12]; and seem to decrease in the order: CO₂ > CH₄ > N₂.

In this paper, we report the CO₂, CH₄ and N₂ sorption properties of four bituminous coals from underground coal seams of South Africa at supercritical conditions, up to 16.4 MPa at 55 °C. Different isotherm models were studied and coal and gaseous adsorbate properties impacting the sorption properties of these coals were examined.

5.3 Experimental

5.3.1 Origin and preparation of the coal samples

Four run-of-mine South African bituminous coal samples were used in this study. These samples were collected from underground coal seams within the Highveld, Witbank, and Tshipise-Pafuri coalfields [24, 25]. The coal samples were code-named as coals: DEN, FOZ, OGS and TKD. Respective depths of mining of these samples were: OGS, 90 m; FOZ, 120 m; DEN, 200 m; and TKD, 250 m. The coal samples were received as -50 mm particles. Representative 1 mm average particle size of the samples, used for both petrographic analysis and the sorption experiments, were obtained following the procedure detailed elsewhere [25].

5.3.2 Sample characterisation

5.3.2.1 Proximate, ultimate, and free swelling index analyses

The chemical properties of the sample of the coal samples were examined by proximate, ultimate (CHNS) and total sulphur content analyses which were conducted at the Bureau Veritas laboratory, Pretoria, following standard procedures given in Table 5.1. Both the fixed carbon content from proximate analysis and the elemental oxygen content from ultimate

analysis of the samples were calculated by difference. The free swelling index (FSI) was also determined.

5.3.2.2 *Petrographic properties*

The petrographic properties of the coals were studied using standard petrographic analysis methods at the laboratory of Petrographics SA, Pretoria. Sample blocks set in epoxy resin were prepared according to SANS ISO 7404-2:2009 [26]; ground, polished, and then studied under a Leica DM4500P microscope coupled with a 50x magnification lens and a 10x magnification internal reflected light oil immersion lens [24, 25, 27]. This gives a total magnification of 500x. The mean vitrinite random reflectance (Rr.%) of the coals was determined following SANS ISO 7404-5:2009 [28]. The rank classification of the coal samples based Rr.% was conducted according to the SANS ISO 11760:2005 method [29]. The macerals were quantified by a 500 point-count technique following the SANS ISO 7404-3:2009 procedure [30]. Coal microlithotype, carbominerite and minerite analyses (to determine the organic/inorganic associations) were carried out in accordance with the SANS ISO 7404-4:1998 [31].

5.3.2.3 *Physical-structural properties*

The physical structural properties of the samples encompassing the surface area, porosity, average pore diameters were determined using different techniques including: CO₂ and N₂ low pressure gas adsorption (LPGA), mercury intrusion porosimetry (MIP) and small angle X-ray scattering (SAXS). Details of the analytical procedures were reported by Okolo et al. [24].

5.3.2.4 *Mineralogy of the samples*

The mineralogy of the coal samples was investigated using wide angle X-ray diffraction (WAXRD) crystalline minerals analysis. About 30 g of 1 mm average particle size of each coal sample was initially ground to fine powder (< 75 µm), and further oxidised at low temperature (about 110 °C) using a radio frequency oxygen-plasma asher, following the procedures described elsewhere [32-35]. The resulting low temperature ashes (LTA's) were used for mineralogical characterisation. The WAXRD LTA analysis was performed on a Philips PW

1729 goniometer using Cu K α radiation at 40kV and 35 mA. Step scans were undertaken from 2 to 90° 2 θ , with a step interval of 0.04° 2 θ and 5 seconds count time per step. Approximately one gram of the sample's LTAs was pressed into an aluminium sample holder. Mineral identification was performed using Bruker Eva search/match software. A quantitative XRD analysis software package, SIROQUANT™, was used to determine the relative concentrations of the identified mineral phases.

5.3.3 Sorption experiments

The high pressure sorption experiments were conducted on a high pressure gravimetric sorption system (HPGSS) at CSIRO Energy, North Ryde, Australia. Figure 5.1 shows the schematic of the HPGSS. The sorption equipment and the analysis procedure has been described in detail elsewhere [17, 36, 37].

For sorption measurements, the 0.8-1 mm size fractions of the coals were prepared and used. These samples were dried and degassed for 2 weeks under vacuum at 60 °C in a vacuum drying oven. When shorter degassing times were used, significantly smaller measured sorption amounts were obtained and the sample mass showed a further reduction when degassed after the experiment. The samples were then weighed, loaded into the stainless steel sample cells and transferred to the HPGSS system. The coal samples weighing between 220.48 g and 229.04 g, now in the sample cells, were degassed at a low pressure of < 0.5 mbar at 55 °C for 24 hrs to ensure adequate removal of any moisture from the pores of the coal samples that may have been adsorbed during the transfer.

For the adsorption experiments, step-wise pressure increments from about 0.1 MPa up to 16 MPa were used. All the experiments were conducted at 55 °C, and both the ambient temperature and the temperature inside the HPGSS were monitored by thermocouples. All four samples were analysed simultaneously as the HPGSS can hold up to four high pressure stainless steel sample cells at a time. Each sample was exposed to the adsorbate gas in this sequence: CO₂, N₂, and lastly CH₄. The sample cells were evacuated after each experiment (the vacuum level in the cells was $\leq$ 0.5 mbar). Sakurovs and co-workers [11, 12, 37] had shown that sequential exposure of coals to these adsorbate gases, under conditions and procedures similar to this study, has negligible influence on the subsequent sorption capacity of the coals.

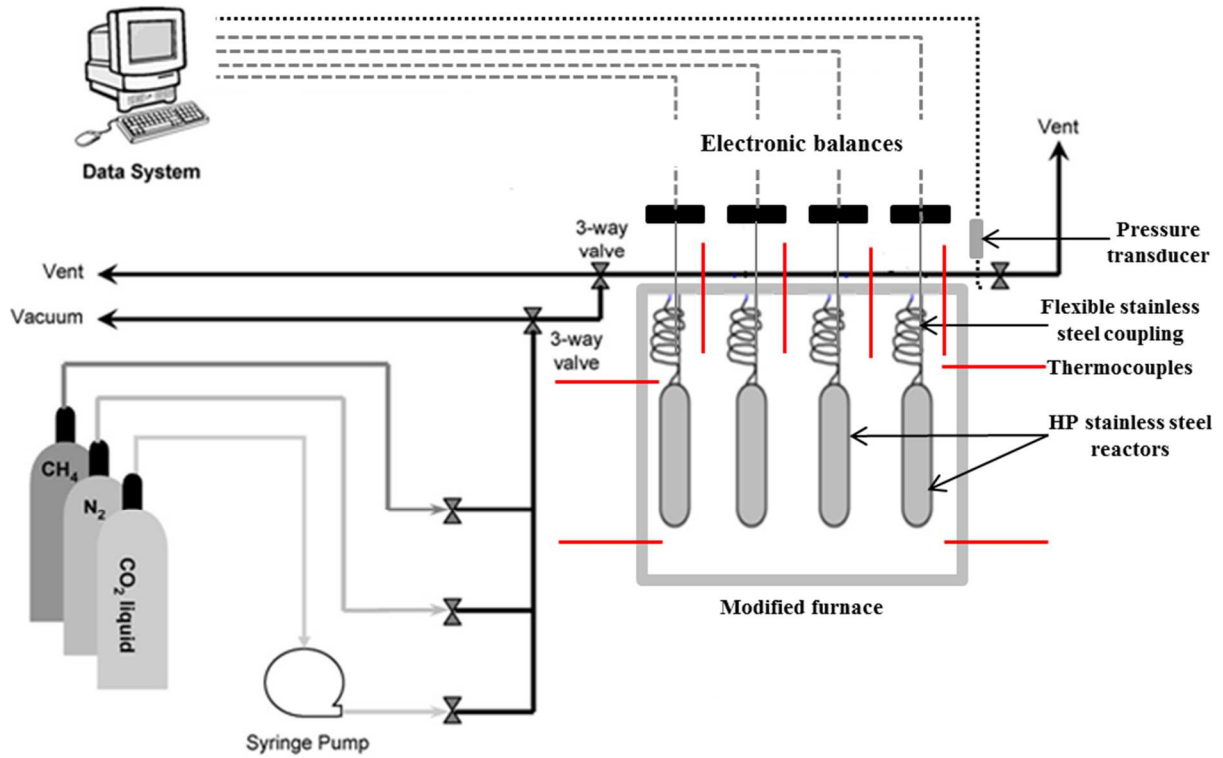


Figure 5.1: Schematic diagram of the high pressure gravimetric sorption system (HPGSS) (Adapted from Day et al. [17]; *Not drawn to scale*).

The resulting data (time, instantaneous mass (mass gain), pressure, and temperature) were acquired via a data logging hardware and software connected to the facility. At each pressure step, the sample was allowed to equilibrate for about 24 hrs; and data were logged from the HPGSS every 2 hours. The long equilibration time also stabilises the thermal equilibration of the adsorbate gases due to compression [11, 12, 17, 19, 37, 38]. Each set of experiments takes about 16 days to complete. The adsorptive gas densities, ρ_g , at the different pressure steps were measured using a reference cell. The excess (Gibbs') sorption, Q_{exc} of the samples were determined from the gravimetric data using Equation 5.1 [11]; while the sorption isotherms were plotted using the excess sorption data.

$$Q_{exc} = M_{mea} - (V_{cell} - V_{sample})\rho_g \quad (5.1)$$

The maximum sorption capacities of the samples with respect to the examined adsorbates at 55 °C up to 16 MPa pressure were evaluated using the modified Dubinin-Radushkevich (M-DR) isotherm model (Equation 5.4) and the Dubinin-Radushkevich/Henry law hybrid (DR-HH) isotherm model (Equation 5.5) for gravimetric systems.

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{P_s}{P} \right)^2 \right] \quad (5.2)$$

$$D = \left[\frac{RT}{\beta E_s} \right]^2 \quad (5.3)$$

The affinity constant, D , is related to the heat of sorption of the coals for the adsorbate gases as defined by Equation 5.3 [10, 17, 20, 39, 40] and the affinity of the gases for the adsorbent pore surfaces [17, 19, 39, 40]. The term βE_s is the net heat of sorption [17, 23], which is a function of the affinity coefficient, β , and the characteristic heat of sorption, E_s , of the coals [17, 19, 20, 39].

In the classical DR equation, the term $(1 - \rho_g / \rho_a)$ corrects for the volume occupied by the condensed phase on the surface of the sample, which displaces the gas phase of the adsorbate. This term can as well be applied to all "absolute" sorption isotherm functions to convert them to "excess" sorption isotherm functions. The classic DR equation is only valid when the instantaneous experimental pressure is less than the saturation pressure of the adsorbate gas, i.e. $P < P_s$. Thus, the DR cannot be used to model gas sorption at or above supercritical conditions where the saturation pressure of the adsorbate gas, P_s , is undefined. In fact, some investigators [11, 41, 42] have criticised the applicability of this important equation over a wide range of pressures and temperatures where $P \gg P_s$, including at and above supercritical conditions of most gases. To assuage this discrepancy in the use of the DR model at supercritical conditions, Sakurovs et al. [11] proposed a modification to the classical DR equation by replacing the P_s term by the adsorbed phase density, ρ_a , and the pressure term by gas density, following the critical observations of other investigators regarding the P_s term in the original DR equation [41, 42]. This modified DR (M-DR) isotherm equation is given in

Equation 5.4 and can be applied over wider pressure and temperature ranges, including supercritical conditions.

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{\rho_a}{\rho_g} \right)^2 \right] \quad (5.4)$$

To further account for observations [11, 19, 43-48] such as imbibition (Henry's law dissolution) especially for coal-CO₂ interactions at high pressures, differences in accessibility between helium and the other gaseous adsorbates to coal pore network, and errors and uncertainties in measured helium density and cell volume; a proportionality term was added to the M-DR equation to improve their applicability at supercritical conditions, especially for coals. The hybrid equation hereinafter referred to as Dubinin-Radushkevich/Henry law hybrid (DR-HH) takes the form (Equation 5.5):

$$Q_{exc} = Q_0 \left(1 - \frac{\rho_g}{\rho_a}\right) \exp \left[- \left(D \ln \frac{\rho_a}{\rho_g} \right)^2 \right] + k \rho_g \quad (5.5)$$

The DR-HH isotherm equation has been applied in the study of sorption properties of different adsorbate gases in coal at both sub- and super-critical conditions using volumetric [19] and gravimetric systems [11, 17].

The resulting excess sorption data were also fitted by the M-DR and the DR-HH equations to ascertain the adsorption mechanism underlying the adsorption process [49]. The affinity constants, D ; the maximum sorption capacities of the samples, Q_0 and V_0 ; and the DR-HH proportionality constants, k ; are unknowns that can be evaluated by model fitting via minimum convergence. This was achieved using the Visual Basic for Applications (VBA) macros, scripted and executed on Microsoft™ Excel 2013. The net heat of sorption of the three adsorbate gases for the coals was evaluated from the determined affinity constants, D , using Equation 5.3 [17, 19].

5.4 Results and discussions

5.4.1 Proximate, ultimate, and FSI analyses results

Table 5.1 shows the proximate and CHNS elemental analyses results of the examined coals, and the standard methods used for their determination. The ash yields for the coals ranged from 16.9 wt.%, db to 27.0 wt.%, db; with coal TKD having a considerably lower ash yield than the other coals. Of all the four coal samples, only coal TKD was found to exhibit appreciable propensity to swell on heating with a free swelling index (FSI) of 8.5. These results are comparable and within the range of published proximate and elemental CHNS analyses data on South African bituminous coals [9, 50-53].

Table 5.1: Proximate, ultimate and FSI analyses data of samples.

Sample ID/ Properties	Standard method	FOZ	DEN	OGS	TKD
Proximate analysis (dry basis, (wt. %, db))					
Ash yield	SANS ISO 1171: 2010	22.8	27.0	25.2	16.9
Volatile Matter yield	SANS ISO 562: 2010	27.5	22.4	23.0	22.2
Fixed carbon	by difference	49.7	50.6	51.8	60.9
Elemental CHNS analysis (dry ash free basis, (wt. %, dafb))					
Carbon	SANS ISO 17247: 2013	78.5	78.7	81.3	86.9
Hydrogen	SANS ISO 17247: 2013	4.9	4.4	4.7	5.1
Nitrogen	SANS ISO 17247: 2013	2.0	2.2	2.0	2.1
Total sulphur	SANS ISO 19579: 2006	1.4	1.7	1.3	1.0
Oxygen	by difference	13.2	13.0	10.6	4.8
Free swelling index (FSI)	SANS ISO 501: 2012	0	0	0.5	8.5

5.4.2 Petrographic properties

Detailed petrographic data of the samples reported on mineral matter basis (vol.%, mmb) are presented in Table 5.2. Based on the mean random vitrinite reflectance, Rr,%, of the coal samples, coal TKD (1.2 Rr.%) was classified as bituminous medium rank B; while the other three samples with Rr.% ranging from 0.63 to 0.69 were classified as bituminous medium rank C. The coal random vitrinite reflectance histograms of the samples are given in Appendix A. Coals DEN and OGS were found to be richer in inertinite than the other samples, while coal TKD was found to be richer in vitrinite. Liptinite abundance was low at ≤ 5 vol.%, mmb, in all the coals.

Coal microlithotype analysis results (Table 5.2) revealed that vitrite was the dominant mono-maceral in coal TKD (45 vol.%, mmb); while inertite was the main mono-maceral in coals FOZ, DEN, and OGS (19 – 33 vol.%, mmb). The bi-maceral vitrinertite (vitrinite + inertinite > 95 vol.%) was also in high abundance in coal TKD (22 vol.%, mmb) compared with the other three samples (10 – 13 vol.%, mmb). The amounts of the other intermediate macerals: clarite, durite, and trimacerite were significantly low in coal TKD, < 1 vol.%, mmb, with respect to the other three samples, which can be attributed to the considerably low volume of liptinite in coal TKD. Pure liptinite, liptite, was not identified in any of the four samples. Liptinite was only identified in the intermediate macerals (clarite, durite, and trimacerite) in all four samples examined. The presence of higher volumes of vitrinite components (vitrite and vitrinertite) in coal TKD agree well with its higher total vitrinite volume (68 vol.%, mmb) compared with the other three samples (20 – 36 vol.%, mmb). It is worthy of note that the total intermediate macerals (maceral-maceral associations) abundance was highest for coal FOZ at 40 vol.%, mmb and lowest for coal TKD (23 vol.%, mmb). It was observed from the carbominerite analysis result that carbargilite and carbosilicite were the more abundant maceral-mineral associations occurring in the coal samples; which was corroborated by the higher volumes of clay and quartz mineral groups from minerite analysis data. These show that clay and quartz minerals are the most prevalent minerals in the examined samples, similar to the published findings of other investigators on South African coals [35, 51, 53, 54]. The petrographic data of these coal samples also compared well to the reported petrographic properties of South African bituminous coals [35, 51-53].

Table 5.2: Petrographic properties of samples.

Sample ID / Properties			FOZ	DEN	OGS	TDK
Reflectance properties						
Mean vitrinite random reflectance (Rr.%)			0.63	0.65	0.69	1.2
Rank (Bituminous)			Medium Rank C	Medium Rank C	Medium Rank C	Medium Rank B
Maceral analysis data (vol.%, mmb)						
Total vitrinite			36	20	21	68
Total liptinite			5	3	5	1
Total inertinite			45	59	57	23
Visible minerals			14	18	17	8
Total (vol.%, mmb)			100	100	100	100
Microlithotype analysis data (vol.%, mmb)						
"Pure" Mono-macerals	Vitrinite		17	5	8	45
	Liptinite		0	0	0	0
	Inertinite		19	37	33	12
Intermediates	Bi-macerals	Clarite	2	1	1	<< 1
		Durite	6	6	7	<< 1
		Vitrinertite	10	13	13	22
	Tri-macerals	Trimacerite	22	11	12	1
Total intermediates (vol.%, mmb)			40	31	33	23
Carbominerite- Organic /inorganic associations	Maceral / mineral associations	Carbargilite and Carbosilicite	10	9	15	12
		Carbopyrite	1	3	1	<< 1
		Carbankerite	3	4	1	2
	Total Carbominerite (vol.%, mmb)		14	16	17	14
	Mineral-rich particles	Clay and quartz group	6	9	8	4
		Pyrite	2	1	<< 1	<< 1
		Carbonate group	2	1	1	2
	Total Minerite (vol.%, mmb)		10	11	9	6
Total microlithotype volume (vol.%, mmb)			100	100	100	100

5.4.3 Physical-structural properties

Table 5.3 summarises the physical-structural properties of the samples, including the surface area and porosity properties determined using different analytical techniques (adapted from Okolo et al. [24]). From the CO₂ LPGA results, it was observed that coals FOZ and DEN exhibited similar values for the micropore surface area, characteristic adsorption energy, micropore volume, and microporosity, and these were higher than the values obtained for the other two coals. Conversely, Coals FOZ and DEN were found to possess lower average micropore diameter than the other two coals did. Coal FOZ had lower micropore surface area and microporosity and relatively higher average micropore diameter than the other samples. These observed trends can be attributed to the coalification or maturity of the coal samples [24, 55, 56].

The results of the N₂ LPGA analysis, which probes the mesopore ($17 \text{ \AA} \leq d_p \leq 500 \text{ \AA}$) properties, show that the mesopore surface area of the samples ranged from 2.6 - 5.7 m²/g, and decreases with increasing vitrinite reflectance (rank) of the samples. However, the medium rank B coal TKD was found to have a relatively higher total pore volume ($2.03 \times 10^{-2} \text{ cm}^3/\text{g}$), average pore diameter (261 Å), and mesoporosity (2.63%) compared to the three medium rank C coals. Data from MIP measurements (corrected for coal compressibility [24, 57]) and the N₂ LPGA results exhibited similar trends, although the values for MIP were generally greater, except for the average pore diameter. This similarity in trends may be related to both techniques probing the entire mesopore properties of the samples, but to different extents. In addition, MIP also examines the macropore features of the sample, specifically, the pore throat diameters, which may have contributed to its higher values [24].

Results from the SAXS analysis (Table 5.3) reveal that the surface areas of the coal samples determined by this method were greater than the sum of the specific surface areas from the other three techniques (CO₂- and N₂- LPGA, and MIP) combined, and decrease with increasing vitrinite reflectance (rank) of the samples. This can be attributed to SAXS probing pores that are inaccessible by the other three techniques [24, 55, 58]. While the microporosity of the samples determined by SAXS decreased with increasing maturity of the coals, no systematic trend was found for the mesoporosity. The macroporosities of all of the studied samples as determined by SAXS were similar [24].

Table 5.3: Porosity and surface area properties of the samples (Adapted from Okolo et al. [24]).

Properties	Analysis method	FOZ	DEN	OGS	TKD
CO₂ LPGA data					
Micropore surface area (m ² /g)	DR	127.9	129.3	117.8	107.3
Characteristic adsorption energy (kJ/mol)	DR	23.1	22.8	22.3	19.4
Micropore volume x10 ⁻² (cm ³ /g)	DR	5.1	5.2	4.7	4.3
Average micropore diameter (Å)	H-K	3.87	3.85	3.89	4.1
Microporosity (3 Å ≤ d _p ≤ 5 Å) (%)	CO ₂ Ads data	5.36	5.27	4.58	2.91
N₂ LPGA data					
Surface area (m ² /g)	BET	3.6	5.7	2.9	2.6
Total pore volume x10 ⁻² (cm ³ /g)	BJH	1.99	1.89	1.46	2.03
Average pore diameter (Å)	BJH	187	125	196	261
Mesoporosity (17 ≤ d _p ≤ 500 Å) (%)	N ₂ Ads data	2.23	1.60	1.32	2.63
MIP Measurements (corrected for coal compressibility [24])					
Total pore area (m ² /g)	MIP	13.9	14.1	12.5	10.9
Total intrusion pore volume x10 ⁻² (cm ³ /g)	MIP	4.4	3.9	5.2	5.7
Average pore diameter (Å)	MIP	127	111	168	208
Porosity (30 ≤ d _p ≤ 600000 Å) (%)	MIP	6.2	6.1	7.1	7.6
Helium Pycnometer measurements					
Skeletal (Apparent) density (kg/m ³)	HP	1595	1668	1623	1495
SAXS analysis data					
Specific surface area (m ² /g)	SAXS	162.6	171.7	158.2	147.4
Microporosity (%)	SAXS	10.3	10.1	9.5	8.7
Mesoporosity (%)	SAXS	8.6	7.7	8.6	6.6
Macroporosity (%)	SAXS	11.0	9.9	10.5	11.1
Total Porosity (%)	SAXS	29.9	27.7	28.6	26.4

5.4.4 Mineralogy of the samples

Table 5.4 lists the relative abundances of the mineral phases identified from the quantitative WAXRD crystalline mineral analysis results of the low temperature oxygen-plasma ashes (LTA) of the samples and are reported on ash basis. Kaolinite and quartz were the most

abundant mineral phases in all four samples with both accounting for 67.7 wt.% to 78.9 wt.%, LTA basis, similar to other reported data on coals [20, 35, 51]. This corroborates the findings from the petrographic analysis where greater volumes of carbargilite and carbosilicite were obtained for the maceral-mineral associations and clay and quartz mineral group were found to be the more ubiquitous mineral-rich particles. Dolomite, calcite, pyrite, and illite were present in smaller amounts in the samples; coal DEN had the highest abundance of dolomite (9.5 wt.%) and pyrite (5.4 wt.%). Greater amounts of illite and mixed-layer illite-smectite, both of the clay minerals group, were present in coal TKD. Rutile, anatase, apatite, crandallite, and goyazite were present in some of the samples; while albite, microcline, and siderite were identified only in coal TKD.

Table 5.4: Relative concentrations of the mineral phases identified in the LTA of the coal samples (wt.%, LTA basis).

Mineral	Chemical formula	FOZ	DEN	OGS	TKD
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	55.7	40.0	58.0	44.3
Quartz	SiO ₂	18.1	31.6	20.9	23.4
Dolomite	CaMg(CO ₃) ₂	6.0	9.5	1.3	2.8
Calcite	CaCO ₃	3.8	3.2	2.0	0.9
Rutile	TiO ₂	0.7	0.8	0.4	0.0
Anatase	TiO ₂	0.6	0.8	0.5	0.0
Pyrite	FeS ₂	3.7	5.4	2.8	1.3
Illite	(K,H ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂	5.0	2.5	6.8	13.3
Smectite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·n(H ₂ O)	-	0.3	-	-
Illite-smectite	-	-	-	-	5.9
Albite	NaAlSi ₃ O ₈	-	-	-	1.9
Microcline	KAlSi ₃ O ₈	-	-	-	1.3
Siderite	FeCO ₃	-	-	-	3.3
Apatite	Ca ₅ (PO ₄) ₃ F	-	-	1.8	-
Crandalite	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	-	-	1.4	0.1
Goyazite	SrAl ₃ (PO ₄)(PO ₃ OH)(OH) ₆	-	-	0.6	0.3
Bassanite	CaSO ₄ ·0.5H ₂ O	6.5	5.9	3.5	1.1

Bassanite, most likely an artefact formed during the low temperature oxygen-plasma ashing from organically associated (non-mineral) calcium and sulphur within the organic matrix of coal [32-35, 54, 59], was observed in all the samples. However, basanite abundance was greater

in the three lower iso-ranked (medium rank C) coal samples. It is well known that the amount of organically associated mineral species and elements decrease as the coal rank (maturity) increases [32, 33, 60]. Thus, the amount of bassanite obtained decreased as the coal rank increases in the order: FOZ > DEN > OGS > TKD. These results are within the range of published data on the mineralogy of South African bituminous coals [35, 54, 60].

5.5 Sorption capacity of the samples

The raw data from the HPGSS for CO₂ adsorption at 55 °C for the four coal samples are presented in Figure 5.2, showing the mass gain of the samples, pressure steps (increments), and the temperature readings from the thermocouples: 4 inside, and 4 outside the furnace. Similar raw data were also acquired for N₂ and CH₄.

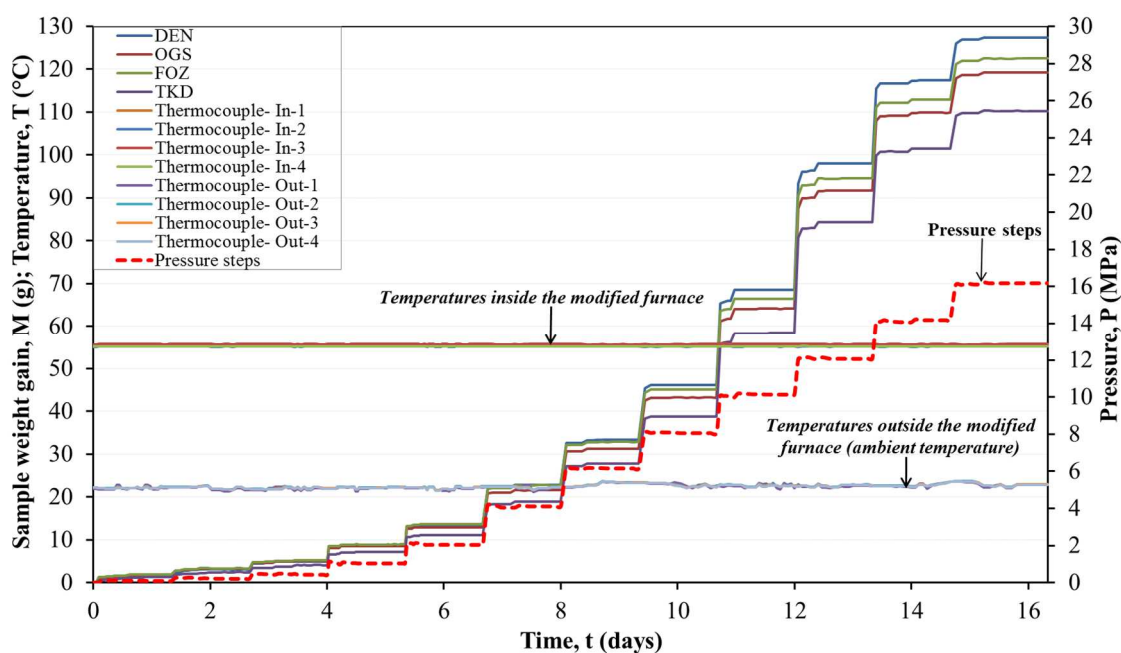


Figure 5.2: Raw data from the HPGSS for CO₂ adsorption at 55 °C for the coal samples.

It can be seen from Figure 5.2 that the mass gain data were well resolved, and fluctuations and noise were adequately minimised. Temperatures inside the modified furnace varied between 55.1 and 55.9 °C with an average of 55.4 ± 0.23 °C. The room (ambient) temperature i.e., outside the furnace, varied from 21.2 to 23.7 °C with an average of 22.4 ± 0.45 °C. The CO₂, CH₄, and N₂ excess sorption isotherms of the four coal samples reported in kg/tonne (kg/t) of

coal, resulting from the raw data of Figure 5.2, using Equation 5.1 are shown in Figure 5.3 in 3D rendering. The properties of the three gases are given in Table 5.5.

Table 5.5: Properties of the three gases used in this study.

Properties / gases	CO ₂	CH ₄	N ₂	Reference
Molecular mass, m (g/mol)	44	16	28	-
Critical temperature, T_c (K)	304.2	190.5	126.2	[12, 61]
Critical pressure, P_c (MPa)	7.4	4.6	3.4	[12, 61]
Critical density, ρ_c (kg/m ³)	467.6	162.7	313.3	[62]
Adsorbed phase density, ρ_a (kg/m ³)	1028	372	726	[12, 61]
van der Waals attractive constant, a (kJ ² /mol ² Pa)	0.365	0.230	0.137	calculated
Molar polarisability, α_m (cm ³ /mol)	7.34	6.54	4.39	[40, 63, 64]
Compressibility factor at maximum pressure at 55 °C, Z (-)	0.3839	0.8941	1.0482	calculated
Kinetic diameter, σ_k (Å)	3.30	3.80	3.64	[12, 61, 65]
Collision diameter, σ_{col} (Å)	4.00	3.82	3.68	[65]
Effective molecule diameter, $\sigma_{eff} = \sqrt{\sigma_k \cdot \sigma_{col}}$ (Å)	3.63	3.81	3.66	[65]

It can be seen from Figure 5.3 that the mass of excess sorption for the coals was highest for CO₂, but considerably lower and relatively similar for CH₄ and N₂. The excess sorption of CO₂ increased with increasing pressure and adsorbed phase density until near its critical pressure (7.4 MPa), and then decreased with increasing pressure and adsorbed phase density. This was not observed for either of the other gases: CH₄ and N₂, due to the fact the experimental temperature were much farther away from their critical temperatures. The increased sorption of CO₂ compared to that of CH₄ and N₂ is attributed to the critical properties of the gases [12, 61], relative to the experimental conditions. Figure 5.4 shows the relationship between the critical properties of the adsorbate gases and both the maximum sorption capacities on percent volume of gas (at STP) per volume of the coal samples and the net heat of sorption of the coals. It was observed that the maximum sorption capacities and the net heats of sorption of the coals exhibited similar trends with respect to both the critical temperature and the critical pressure of the gases. In both cases (Figure 5.4 (a - d)), the maximum sorption capacities of the coals (on

vol.% of coal) and their net heats of sorption were found to increase with increasing critical temperatures and critical pressures of the gases, following a 2nd order polynomial fit. It can also be seen from Table 5.5 that at maximum experimental pressure (16 MPa at 55 °C), CO₂ has lower compressibility factor value than the other two adsorbates (CH₄ and N₂), indicating relatively higher compressibility at the experimental conditions.

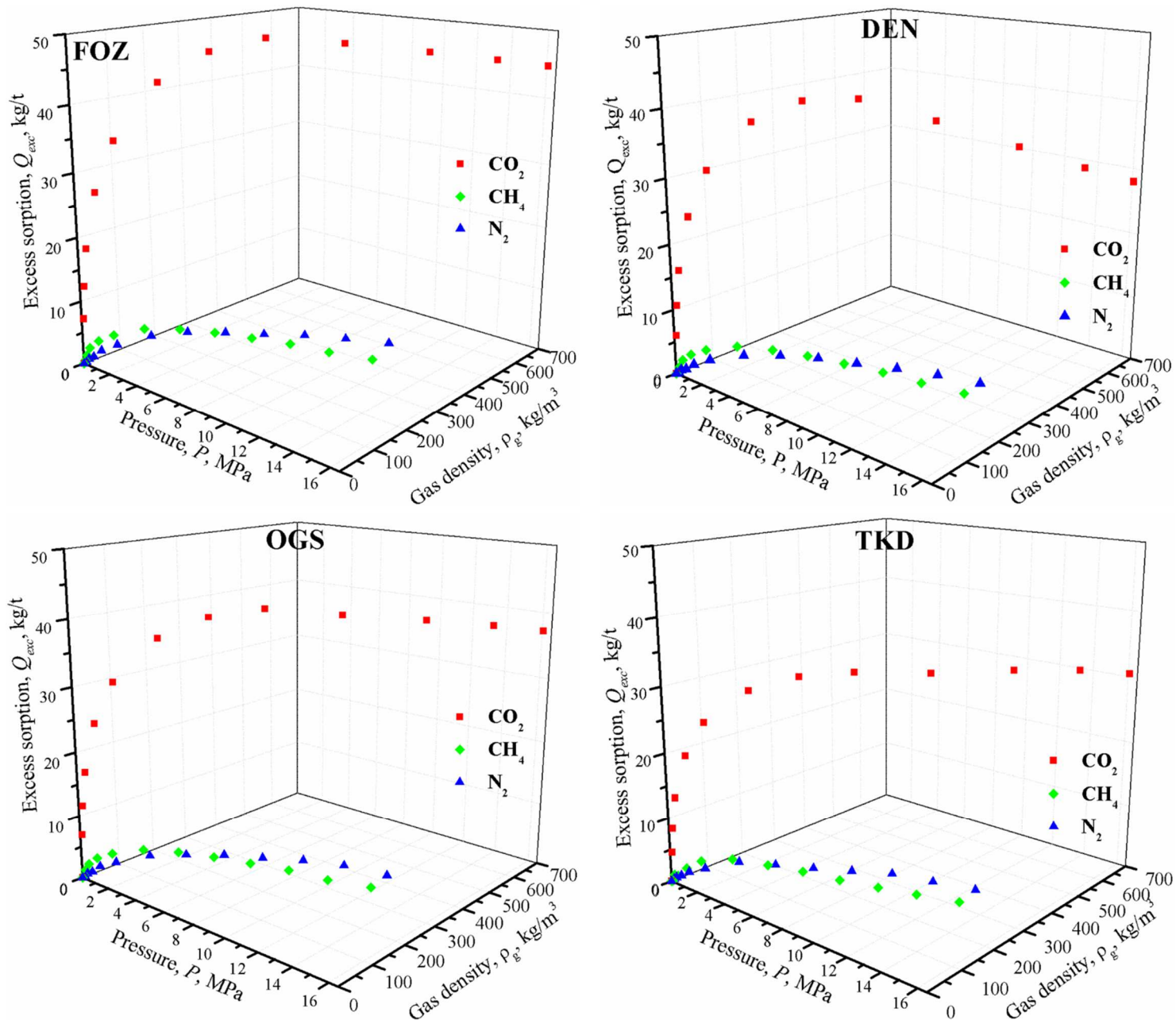


Figure 5.3: CO₂, CH₄ and N₂ excess sorption isotherms of the coals at 55 °C.

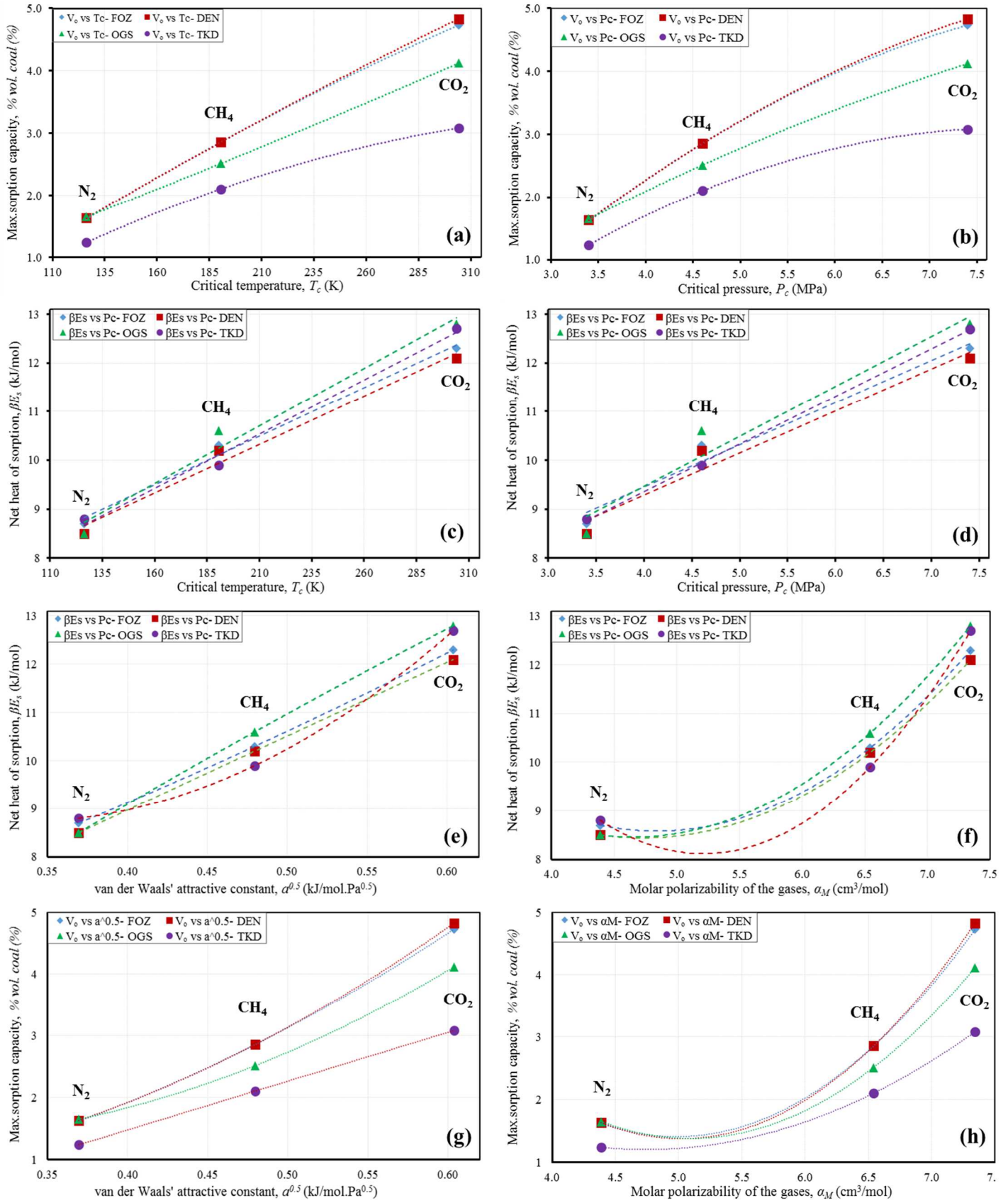


Figure 5.4: Relationship between the critical properties of the gases, and the maximum sorption capacities (in vol.% of coal) and the net heat of sorption of the coals.

This may imply that the adsorbates are adsorbed onto the coals in the highly compressible (densified) gaseous phase and not actually in the condensed liquid phase. Similar finding has been reported by Sakurovs et al. [12, 61]. In addition, other critical properties of the adsorbate such as van der Waals' attractive constants and the polarizabilities of the gases, were found to impact on both the sorption capacities of the samples as well as the sorption energies (Figures 5.4 (e – h)). It has been demonstrated that the easier a gas is to polarise, the stronger the interaction with the adsorbent surface, as well as neighbouring adsorbate molecules [12, 40, 61, 63, 64]. The polarisability of a gas is related to the square root of the van der Waals attractive constant (the 'a' term of the van der Waal equation) (Equation 5.6). These properties of the gases are given in Table 5.5. While the van der Waal's attractive constants were evaluated from Equation 5.6, the molar polarisabilities of the gases were determined from data [63, 64] and conversion factor [40] reported by other authors.

$$a = 0.421875 \frac{(RT_c)^2}{P_c} \quad (5.6)$$

Figures 5.4 (e - h) show that both the maximum sorption capacities of the samples and the net heat of sorption increase with increasing $\sqrt{a}$, and α_M . Hence, CO₂ with higher van der Waals' attractive constant and higher molar polarizability exhibited both higher sorption capacities and net heat of sorption for all four coals than the other two gases. This shows that both adsorbent-adsorbate and adsorbate-adsorbate interactions was higher for CO₂ and supports the pore filling adsorption mechanism [24, 66]. It may as well be argued that the relationship between both the sorption capacities and the net heat of sorption of the samples, and the critical pressures of the gases, may be coincidental as the critical pressure of a gas is a function of the critical temperature and polarizability of the gas. Correlation of the maximum sorption capacities of the coals with the kinetic-, collision-, and effective molecule- diameter does not yield a systematic trend. Although these parameters influence the kinetics of the sorption process, they do not influence the amount of adsorbate sorbed by the coals [12].

Two gravimetric sorption models—the M-DR and DR-HH models—were also tested for their ability to fit the experimental excess sorption isotherms of the samples as shown in 3D in Figure 5.5. The sorption properties of the samples: the maximum sorption capacity (by weight and by

volume), Q_0 and V_0 ; affinity constant, D ; net heat of sorption, βE_s , and the uncertainty parameters—the error sum of squares, ESS; root mean square residuals, RMS; and the quality of fits, QOF [24] were determined from the models. The proportionality constant, k , was evaluated from the DR-HH model. These results are summarised in Table 5.6.

From Figure 5.5, showing the M-DR and DR-HH isotherm model fittings to the experimentally determined excess sorption data (excess sorption isotherms), it is clear that the DR-HH model generally exhibited better fittings to experimental data than the M-DR model for all four coal samples and the three studied adsorbate gases. While CH₄ and N₂ showed similar fitting trends, CO₂ gas sorption isotherms displayed a different trend. This is especially more noticeable for the CO₂ sorption results. Evaluated uncertainty metrics reported in Table 5.6 show that, lower ESS and RMS residuals, and higher QOF values were obtained for the DR-HH model—compared with the M-DR model—determined maximum sorption capacities of the coals. However, coal DEN N₂ sorption isotherm QOF was an outlier.

From Table 5.6, it can be seen that the M-DR isotherm model generally over-estimated the maximum sorption capacities of the samples for all three gases. Based on the DR-HH isotherm model, the maximum sorption capacities of the samples by weight ranged from 40.7 – 60.6 kg/t_{coal} for CO₂, 10.1 – 13.3 kg/t_{coal} for CH₄, and 10.4 – 13.2 kg/t_{coal} for N₂; and decreases with increasing Rr.%. The sorption capacities of the samples by volume, reported on Table 5.6, exhibited similar trend as the sorption capacities by weight. With respect to the adsorbate gases, the sorption capacities of the samples decreased in magnitude in the order: CO₂ > CH₄ ≈ N₂ by weight (db), and CO₂ > CH₄ > N₂ on volume basis (db) similar to other reported findings [12, 15]. The CO₂:CH₄:N₂ sorption capacity ratios (by weight and by volume) of the samples presented in Table 5.6 were found not to be uniform but relatively varied across the coal samples. These variations can be attributed to the differences in coal properties especially the micropore structural and surface properties, and the affinity of the gases to the heterogeneously energetic surfaces of the micropores [13], which can be explained by the Polanyi potential theory [41, 67], upon which the DR isotherm model was based [41, 68]. These determined sorption capacity ratios were comparatively different to the ratios of 4:2:1 reported by Chaback et al. [16], but agreed well with ratios from the published data of other investigators [11, 12, 14, 15].

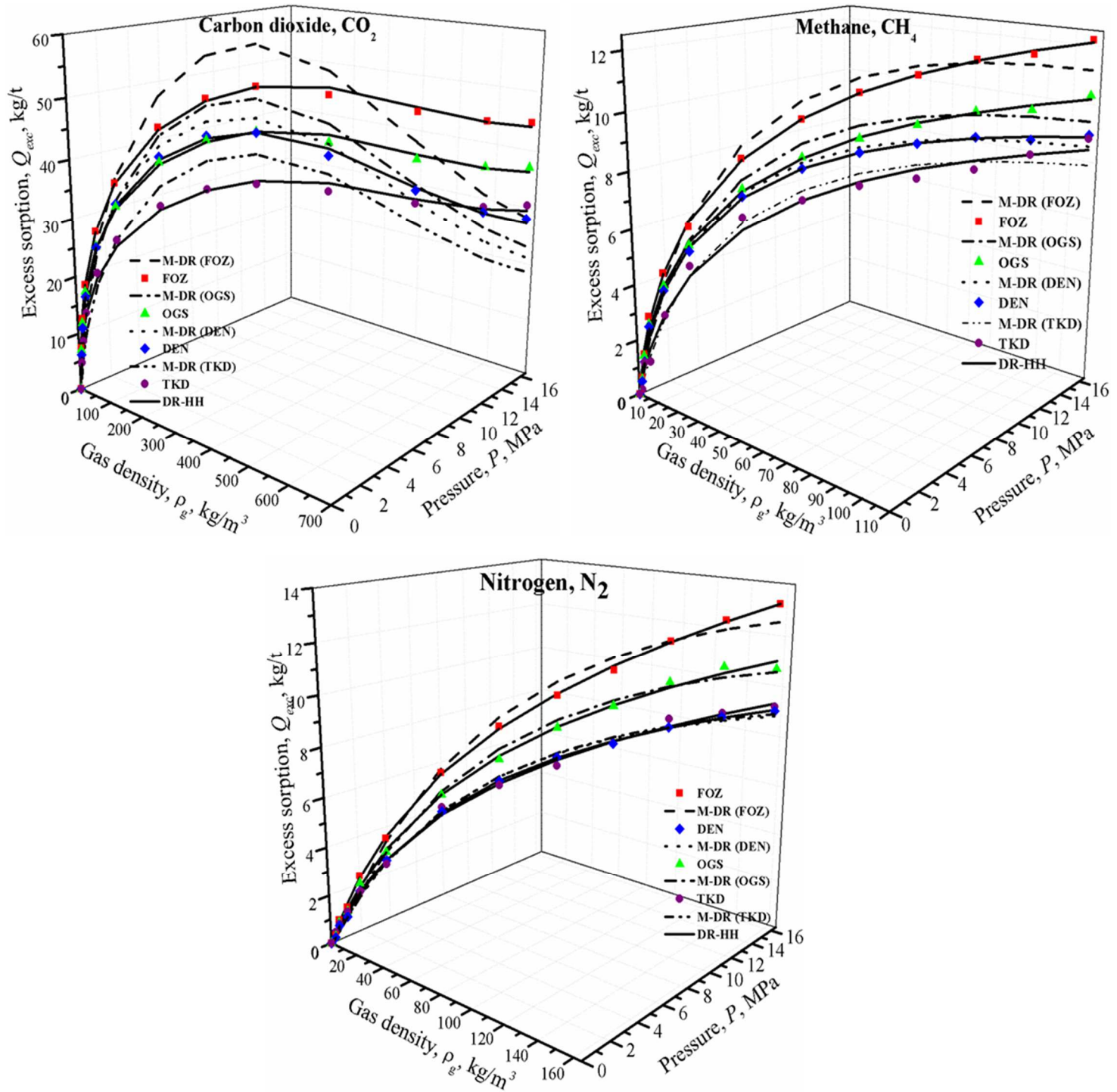


Figure 5.5: M-DR and DR-HH fitting of the CO₂, CH₄ and N₂ excess sorption isotherms of the coals at 55 °C.

Table 5.6: CO₂, CH₄, and N₂ sorption properties of the coal samples on dry basis.

Properties / Sample ID	Carbon dioxide (CO ₂)							
	FOZ		DEN		OGS		TKD	
Method used	M-DR	DR-HH	M-DR	DR-HH	M-DR	DR-HH	M-DR	DR-HH
Maximum sorption capacity by weight, Q_0 (kg/t _{coal} , db)	86.9	60.6	65.4	56.3	71.6	51.4	57.7	40.7
Maximum sorption capacity, % weight of coal (% Q_0 , db)	8.7	6.1	6.5	5.6	7.2	5.1	5.8	4.1
Maximum sorption capacity by volume, V_0 at STP (m ³ /t _{coal} , db)	44.2	30.9	33.3	28.7	36.5	26.2	29.4	20.7
Maximum sorption capacity, % volume of coal (% V_{0coal} , db)	6.8	4.7	5.6	4.8	5.7	4.1	4.4	3.1
Affinity constant, D (-)	0.076	0.049	0.060	0.051	0.068	0.045	0.070	0.046
Net heat of sorption, βE_s (kJ/mol)	9.9	12.3	11.1	12.1	10.5	12.8	10.3	12.7
Proportionality constant, k (ml/g)	-	0.035	-	0.013	-	0.029	-	0.024
ESS (-)	454.3	4.6	100.2	4.2	454.3	4.6	454.3	4.6
RMS residuals (-)	7.13	0.54	2.78	0.57	5.91	0.60	5.01	0.86
QOF (%)	81.4	97.4	91.4	97.3	81.4	97.4	81.4	97.4
Methane (CH ₄)								
Maximum sorption capacity by weight, Q_0 (kg/t _{coal} , db)	18.1	13.3	13.6	12.1	15.1	11.4	12.9	10.1
Maximum sorption capacity, % weight of coal (% Q_0 , db)	1.8	1.3	1.4	1.2	1.5	1.1	1.3	1.0
Maximum sorption capacity by volume, V_0 at STP (m ³ /t _{coal} , db)	25.3	18.6	19.0	16.9	21.1	16.0	18.1	14.1
Maximum sorption capacity, % volume of coal (% V_{0coal} , db)	3.9	2.9	3.2	2.9	3.3	2.5	2.7	2.1
Affinity constant, D (-)	0.090	0.070	0.079	0.071	0.084	0.067	0.092	0.077
Net heat of sorption, βE_s (kJ/mol)	9.1	10.3	9.7	10.2	9.4	10.6	9.0	9.9
Proportionality constant, k (ml/g)	-	0.034	-	0.011	-	0.027	-	0.020
ESS (-)	1.97	0.18	1.97	0.18	1.97	0.18	2.87	0.19
RMS residuals (-)	0.47	0.12	0.20	0.12	0.39	0.12	0.39	0.29
QOF (%)	92.6	94.4	92.6	94.4	92.6	94.4	90.8	94.9

Table 5.6 (contd): CO₂, CH₄, and N₂ sorption properties of the coal samples on dry basis.

Properties / Sample ID	Nitrogen (N ₂)							
	FOZ		DEN		OGS		TKD	
Method used	M-DR	DR-HH	M-DR	DR-HH	M-DR	DR-HH	M-DR	DR-HH
Nitrogen (N ₂)								
Maximum sorption capacity by weight, Q_0 (kg/t _{coal} , db)	21.7	13.2	14.8	12.1	18.1	13.1	15.0	10.4
Maximum sorption capacity, % weight of coal (% Q_0 , db)	2.2	1.3	1.5	1.2	1.8	1.3	1.5	1.0
Maximum sorption capacity by volume, V_0 at STP (m ³ /t _{coal} , db)	17.4	10.6	11.8	9.7	14.5	10.5	12.0	8.3
Maximum sorption capacity, % volume of coal (% V_{0coal} , db)	2.7	1.6	2.0	1.6	2.3	1.7	1.8	1.2
Affinity constant, D (-)	0.130	0.099	0.116	0.104	0.124	0.104	0.118	0.096
Net heat of sorption, βE_s (kJ/mol)	7.6	8.7	8.0	8.5	7.8	8.5	7.9	8.8
Proportionality constant, k (ml/g)	-	0.032	-	0.010	-	0.019	-	0.018
ESS (-)	1.88	0.11	0.26	0.06	0.87	0.28	0.94	0.31
RMS residuals (-)	0.38	0.09	0.14	0.07	0.26	0.15	0.27	0.15
QOF (%)	87.1	94.9	95.1	94.5	90.1	94.4	87.6	95.3
Maximum sorption capacity ratios by weight: CO ₂ :CH ₄ :N ₂ (-)	-	4.6:1:1	-	4.7:1:1	-	3.9:0.9:1	-	3.9:1:1
Maximum sorption capacity ratios by volume: CO ₂ :CH ₄ :N ₂ (-)	-	2.9:1.8:1	-	3:1.7:1	-	2.5:1.5:1	-	2.5:1.7:1

The affinity constants determined for the four coals with respect to the three gases generally increased in the order: CO₂ < CH₄ < N₂ as shown in Figure 5.6. This means that CO₂ is more strongly attracted to the pore surfaces of the coals than CH₄ and N₂; while N₂ exhibited the least affinity. These are similar to the findings of other investigators on coals [11, 12, 61, 69], activated carbons [38, 70], and even metal-organic frameworks (MOFs) [71]. It can thus be inferred that pore-filling mechanism and or densification of gaseous adsorptives in the micropores of the coals is the more predominant adsorption mechanism. This follows the fact that pore-filling is more favoured by smaller kinetic and effective molecular gas diameter [24, 66], exhibited in this case by CO₂, compared with CH₄ and N₂. This leads to faster diffusion rate through the pores and greater gas molecule to gas molecule interaction (van der Waals forces). Although adsorbent pore surface to gas molecule interactions (layers formations) are the primary mechanism at the start of the sorption process; pore-filling and adsorbate densification becomes more significant after the complete layer coverage of the pores till the pores are finally filled by the adsorbate.

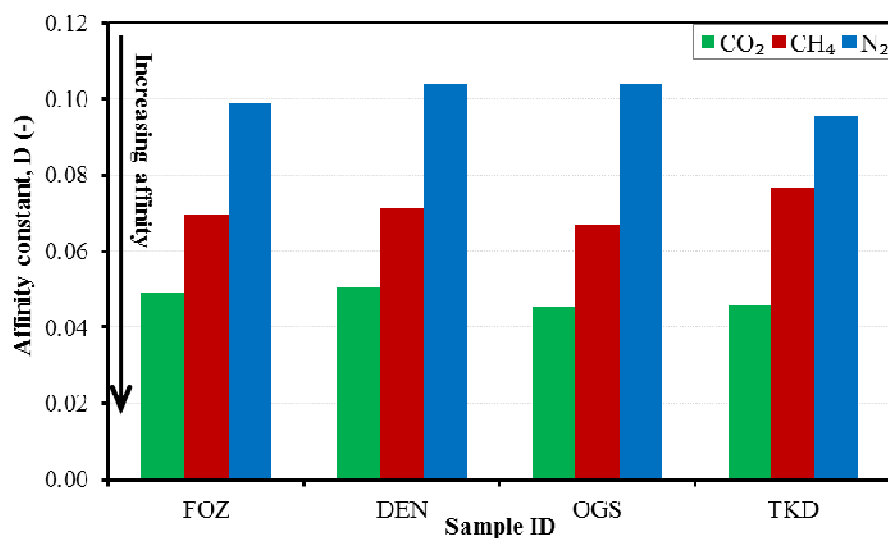


Figure 5.6: Affinity constant, D , of samples for the three gaseous adsorbates from DR-HH model.

The net heats of sorption, βE_s , determined from the DR-HH model were generally found to be ≤ 12.8 kJ/mol for all three adsorbates, indicating that physisorption is the prevailing sorption process occurring during the experiments [12, 17, 36, 61]. The net heat of sorption was found to decrease in magnitude for the different adsorbates in the order: CO₂ > CH₄ > N₂. This may be explained by the higher polarizability of CO₂ relative to the other two gases. The heat of sorption is related to the polarisability of the adsorbing gas molecule – the easier it is to polarise,

the greater the induced electrostatic attraction between coal pore surfaces and the gas, resulting in higher heat of sorption. It should also be noted that the van der Waals' attractive constant was also higher for CO₂, indicating more interactions with both the adsorbent surface and the neighbouring molecules, culmination to higher sorption energy.

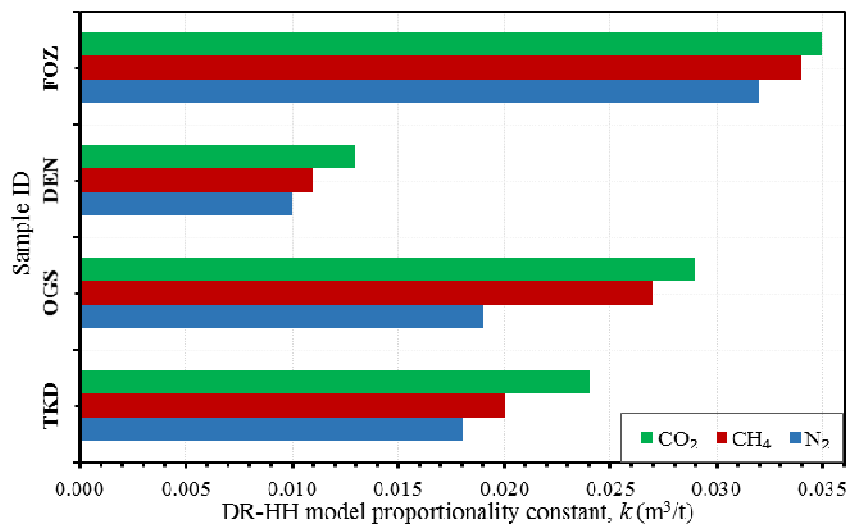


Figure 5.7: Proportionality constants, k , determined from the DR-HH model.

The proportionality constants, k , determined from the DR-HH isotherm model presented in Figure 5.7 were found to be very low (0.010 - 0.035) and distinct for each coal. This shows that the extent of coal volume penetrated by the adsorbate gases are not very different to that penetrated by helium [12, 61], from which it may be deduced that imbibition and swelling may only have small effects on the sorption properties of the samples in this study. The proportionality constants also tend to slightly decrease in magnitude in the order: CO₂ > CH₄ > N₂, indicating that CO₂ penetrates a greater volume of coal than both CH₄ and N₂. The positive k values indicates that the gases can penetrate more coal than expected from the helium density (or that the free space volume may be in error by [k * volume of coal], which in this case would be about 1 - 3 ml). The k values can also be indicative of the differences in accessibility of the coal pore voids between the adsorbate gases. For example, $k_{\text{CO}_2} - k_{\text{CH}_4}$ gives the extra accessibility of CO₂ compared to CH₄ in each coal in ml/g. From coal TKD k values, the extra CO₂ accessibility of coal TKD volume compared to CH₄ can be estimated to be 0.4 ml/g. However, these differences are small and may not be significant, with regards to the maximum sorption capacities of the samples. Nevertheless, these differences do provide a lower limit to the difference in accessibility of the different gases, and do support the well-

known fact the accessibility as well as affinity of coal pores for these adsorbate gases decreases in the order: of the CO₂ > CH₄ > N₂. The proportionality constant was also found to relatively vary linearly with sorption capacities of the coals as shown in Figure 5.7, although coal DEN was an outlier.

5.6 Influence of coal properties on the sorption capacity of the samples

5.6.1 Influence of coal rank and petrography

Figures 5.8 (a-d) show the relationships between the high pressure sorption capacities of the coals at 55 °C and their coal rank and petrographic properties. Figure 5.8 (a) shows that the CO₂, CH₄, and N₂ maximum sorption capacities of the coals decreases with increasing vitrinite reflectance of the coal samples. This is further corroborated by Figure 5.8 (c), where the sorption capacities of all four coals were found to decrease with increasing elemental carbon content- another indicator of coal rank, with correlation coefficients (R^2) > 0.88 for CH₄ and N₂, and > 0.97 for CO₂. Hence, the three medium rank C bituminous coals, generally exhibited higher sorption capacities for all three adsorbates compared with the medium rank B coal TKD. This can be attributed to their superior micropore properties: higher micropore volume, microporosity, micropore surface area, etc., of the lower iso-ranked coals [20] compared with those of coal TKD. Similar findings have been reported by other investigators [9, 17, 72]. However at higher vitrinite reflectance ($R_r.\%$ > 1.3), this trend may considerably change, especially for CO₂ and CH₄. Day et al. [17] and Zhang et al. [72] have reported a U-shaped trend; where the CO₂ and CH₄ maximum sorption capacities of coals of various ranks decreased with increasing $R_r.\%$ until a point of inflection at around 1.3 $R_r.\%$, after which sorption capacities increased.

In Figure 5.8 (b), the relationship between the CO₂/CH₄ and CO₂/N₂ maximum sorption capacities ratios and the vitrinite reflectance (rank) of the coal samples is presented. While the CO₂/CH₄ maximum sorption capacities ratios were found to be between 4.0 and 4.7; the CO₂/N₂ maximum sorption capacities ratios ranged from 3.9 to 4.6, for all four coals. Generally, these sorption capacity ratios were observed to decrease with increasing $R_r.\%$ [61], and correlates well with the affinity constants of the coals. These ratios give insight into the selectivity of these adsorbates in a binary or mixed gases system.

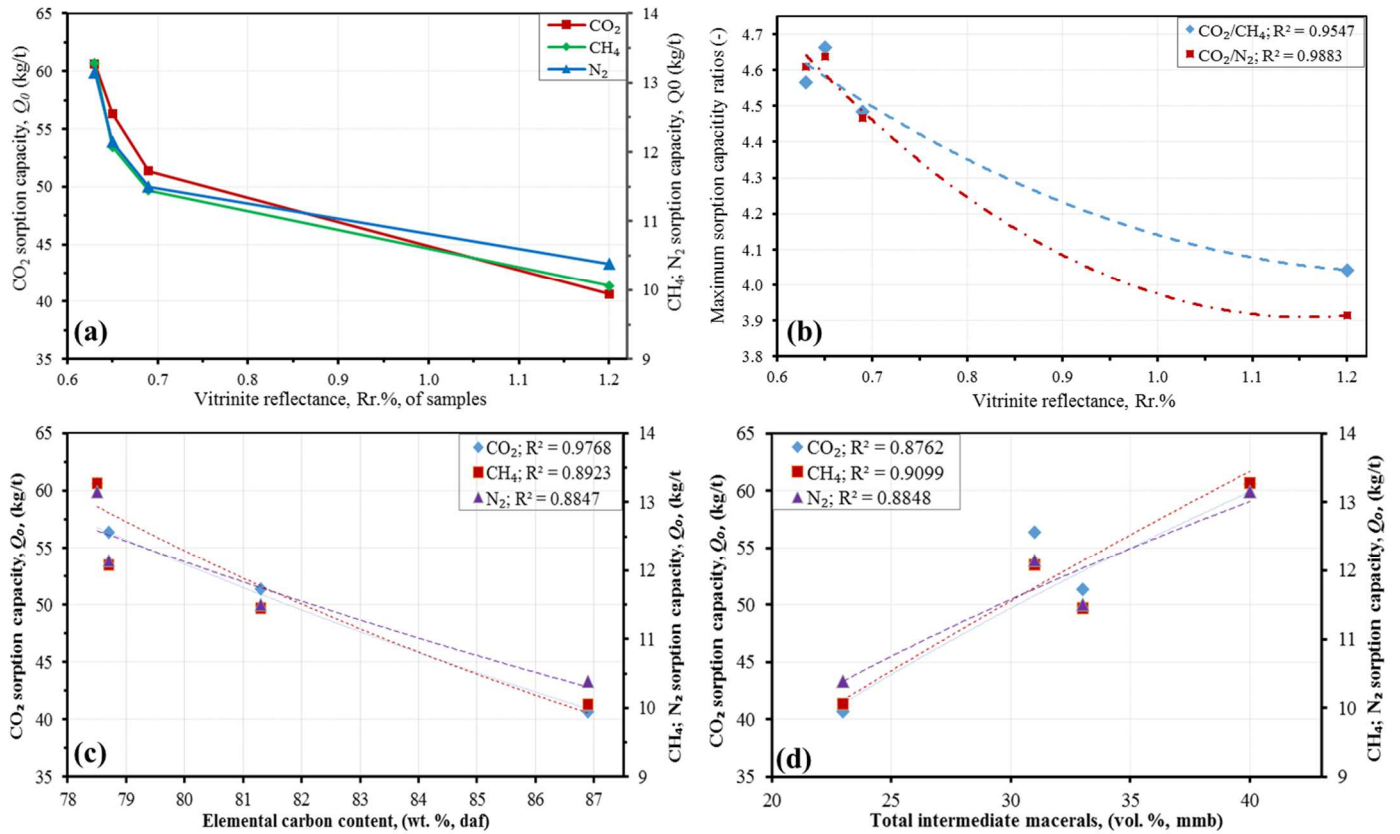


Figure 5.8: Influence of coal rank and petrography on the CO₂, CH₄, and N₂ sorption capacities of the coal samples: (a) Sorption capacities vs Rr.%; (b) Sorption capacity ratios vs Rr.%; (c) Sorption capacities vs elemental C; (d) Sorption capacities vs total intermediate macerals.

Most of the petrographic properties of the coal samples, especially maceral abundance and compositions, yielded a wide scatter without any systematic trend [9, 17, 20]. In fact, Weishauptová, et al. [20] described the influence of maceral compositions of some European bituminous coals from the Upper Silesian basin on the CO₂ and CH₄ maximum sorption capacities of the samples as ambiguous. However, a good correlation was observed between the CO₂, CH₄, and N₂ sorption capacities and the total intermediate macerals shown in Figure 5.8 (d), with $R^2 > 0.87$. It is well known that coal microlithotype which is a reflection of the variety of combination(s) of maceral groups is not evenly distributed in coal; but tend to occur in band or layers, which gives coal its layered luster. Banding in coal develops or rather becomes more apparent with the increased compaction during rank advance from lignite to bituminous coal [73]. Thus, microlithotypes becomes less observable with increasing rank as the more reactive macerals (vitrinites and liptinites) lose their volatile components with concomitant increase in elemental carbon content, and thus appear more comparable to

inertinites under the petrographic microscope, in terms of shade and gray [74]. However, it is still possible to distinguish between vitrinites and inertinites in anthracites, and thus possible to distinguish the different microlithotypes in anthracites, although significantly less in volume compared to microlithotypes in bituminous coals [73]. Cleats in coal matrices and often, fractures occur along these bands; and are the conduits and principal pathways for the migration of fluids in coal seams [73, 75-77], which may aid in the accessibility of remote pores [24, 77], and enhance the pore volume of the geological storage media [77]. Hence, coal FOZ with the highest abundance of intermediate macerals: bi- and tri-macerals (40 vol.%, mmb) amongst the four studied coals, exhibited the highest maximum sorption capacities for the three adsorbates used in this study. Coal TKD with the lowest volume of bi- and tri-macerals (23 vol.%, mmb) was found to return the lowest sorption capacities for the three adsorbates. Furthermore, the abundance of these intermediate macerals decreases with increasing rank [51, 73].

5.6.2 Influence of coal pore and porosity properties

It is well known that the physical-structural properties of coal including: surface area, porosity, pore size distribution, and pore structure, significantly impact coal utilisation processes such as the use of deep seated and economically unprofitable coal seams as a geological carbon sink as a global climate change mitigation option [10, 17, 24, 25]. The relationship between the micropore, mesopore, and macropore properties of the coal samples on the CO₂, CH₄, and N₂ sorption capacities is presented in Figure 5.9. It can be seen from Figure 5.9 (a-d) that the CO₂, CH₄, and N₂ sorption capacities of the samples increase with increasing DR micropore surface area, microporosity from both CO₂ LPGA and SAXS data, and DR micropore volume; and decreasing average micropore diameter. This shows that the micropore properties of coals largely determine the high pressure sorption properties of the coals [9]. The correlation of the samples' sorption capacities for these adsorbates with the micropore properties also yielded appreciable systematic trends (Figure 5.9 (a-e)) with $R^2 > 0.8$; which was more significant for CO₂ sorption, with $R^2 > 0.9$ in most instances. This may be attributed to the greater affinity exhibited by coal pore surfaces to CO₂ compared with coal pore surfaces affinity to CH₄ and N₂ [11, 38, 40, 49, 52, 61, 69, 71].

In contrast, no systematic trends of either the mesopore properties (Figure 5.9 (f-j)) and macropore properties (Figure 5.9 (l-o)) with their sorption capacities for the three studied adsorbates was found, even for mesoporosity and macroporosity from SAXS analysis.

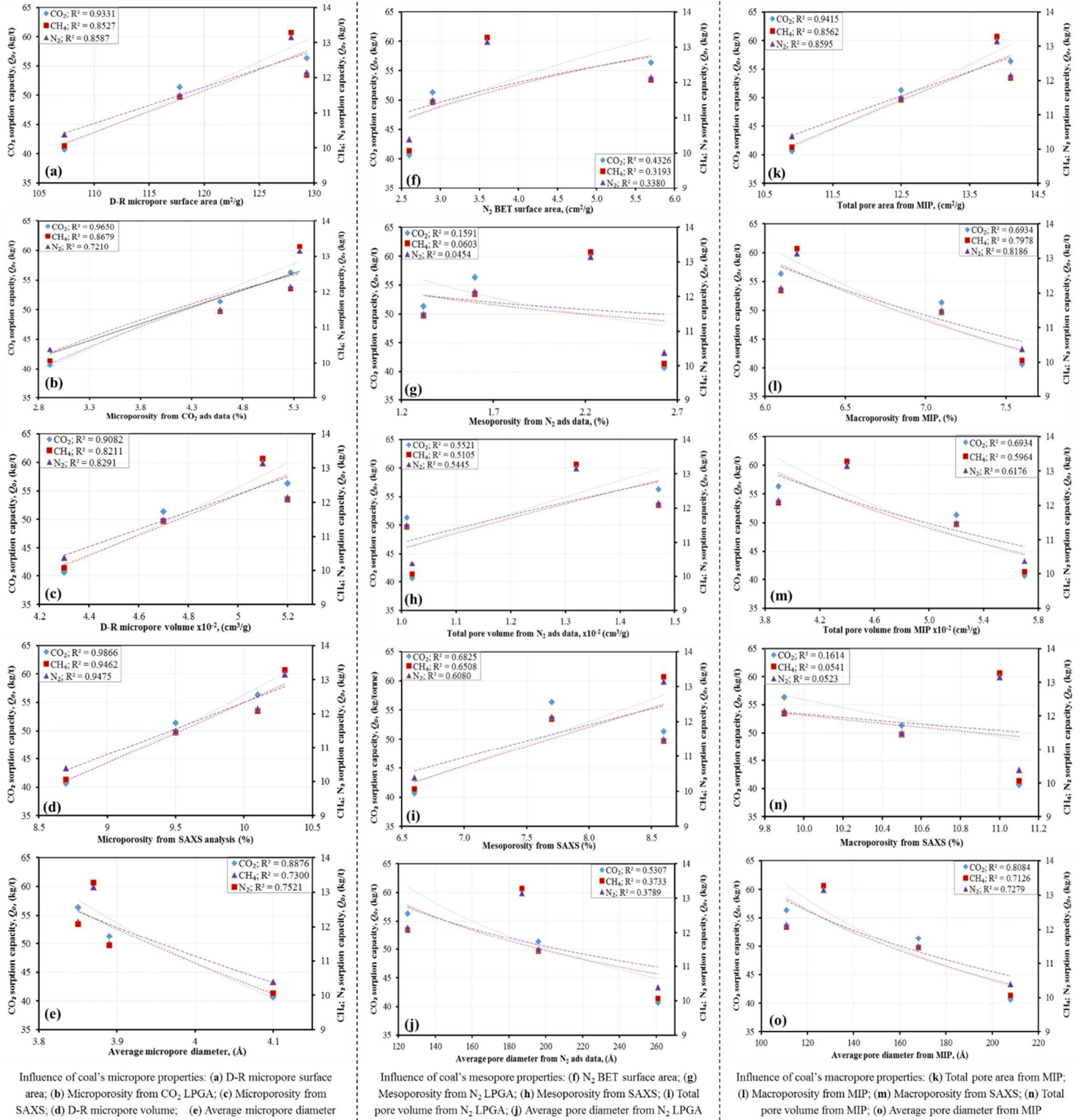


Figure 5.9: Influence of the micropore, mesopore, and macropore properties of the coal samples on the CO₂, CH₄, and N₂ sorption capacities.

These suggest that detailed characterisation of the micropore properties of coal seams can give useful insights into their gas storage capabilities, if it is intended to be used as a geological sink for CO₂. However, knowledge of the meso- and macro-pore properties is still important as they form channels for fluid transport in coal seams, and thus, may influence the kinetics of sorption [14].

5.6.3 Influence of mineral matter in coal

The influence of ash yields, low temperature ash (LTA) contents and some mineral phases of the coal samples on the CO₂, CH₄, and N₂ sorption capacities of the samples is given in Figure 5.10. Both the ash yields from proximate analysis and the LTA contents tend to give weak opposite trends with irregular scatter pattern and lower correlation coefficients.

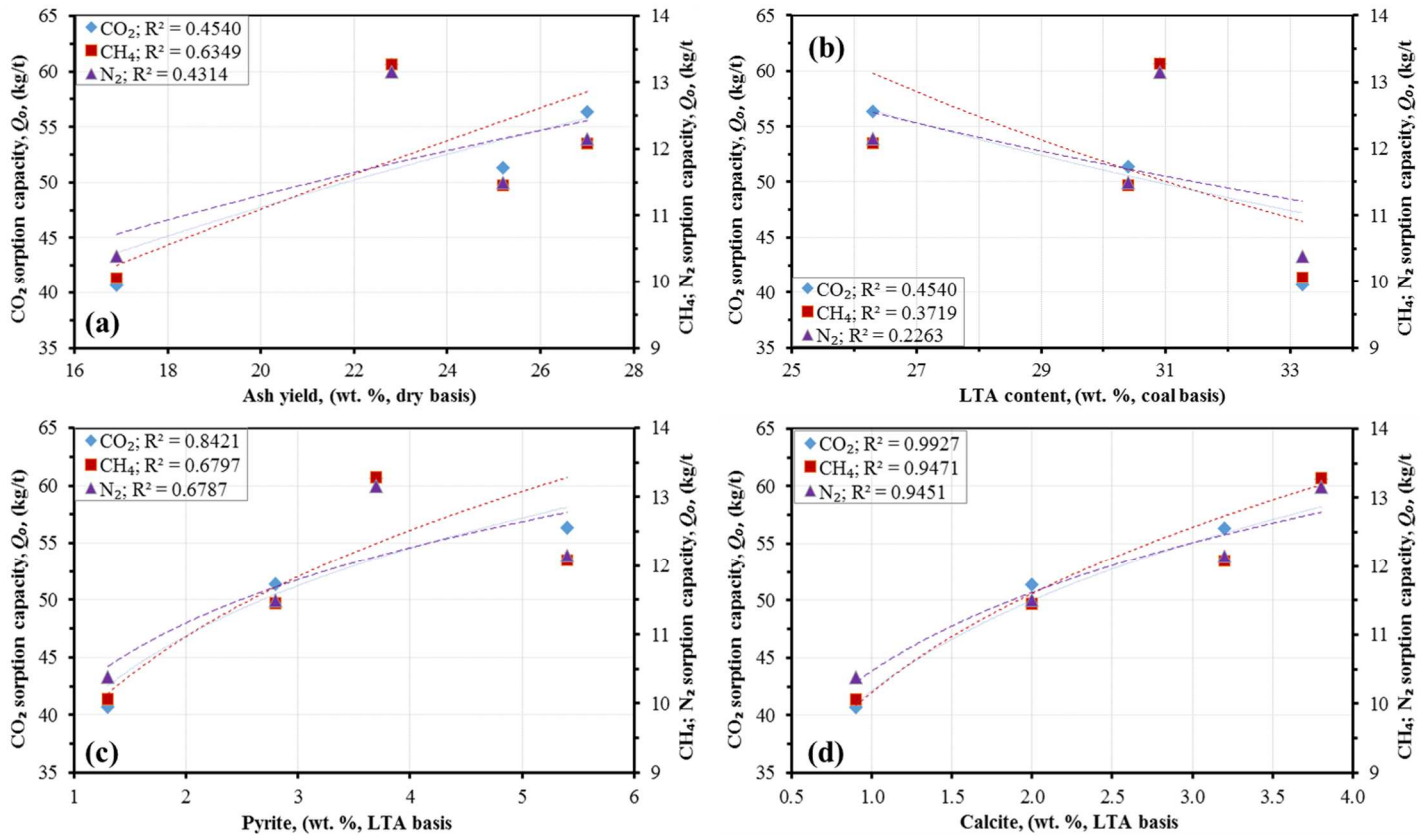


Figure 5.10: Influence of mineral matter contents of the coal samples on the CO₂, CH₄, and N₂ sorption capacities.

These may suggest that the overall (total) mineral matter contents (ash yields) of the samples, although very important geological storage site consideration in CCS value chain, with respect to porosity, permeability, and containment; have not exhibited appreciable control on the sorption capacities of the samples, under the current experimental conditions. It is worthy of note that the sorption experiments were conducted on dry (moisture-free) samples. In contrast, appreciable mineral matter-gas reactions (especially for reactive CO₂) will be expected in the presence of moisture (aqueous phase), under coal seam conditions, which may further be enhanced by CO₂ dissolution by coal seam water [17]. With respect to the mineral phases from the LTA process, only pyrite and calcite gave a reasonable trend where, the sorption capacities increased with increasing pyrite and calcite contents, which may as well be related to the rank differences of the coals. However, this observation was more significant for CO₂ sorption data with higher R², which may probably be attributed to the relatively higher reactivity of CO₂ compared with the other two adsorbates. Although mineralisation is an important aspect of CO₂ geological storage, this usually occurs in aqueous medium or in the presence of moisture, over geological time [20, 78-80], which was lacking under the current experimental conditions.

5.7 Conclusions

The high pressure CO₂, CH₄, and N₂ sorption properties of four South African bituminous coals were studied using HPGSS at 55 °C, up to 16 MPa.

- Generally, the maximum sorption capacity of the coals with respect to the examined adsorbates decreased in the order: CO₂ > CH₄ ≈ N₂ by weight, and CO₂ > CH₄ > N₂ on volume basis.
- The DR-HH model was found to describe the sorption processes better than the modified Dubinin-Radushkevich (M-DR) model.
- The net heats of sorption of the samples were generally in the range: CO₂: 12.1 – 12.8 kJ/mol; CH₄: 9.9 – 10.6 kJ/mol; N₂: 8.5 – 8.8 kJ/mol (consistent with previous findings) indicating that physisorption was the dominant sorption process. The heat of sorption was also found to relatively increase with increasing sorption capacity and tends to be

closely related to the adsorptive gases' critical properties such as van der Waals' attractive constants and polarisability.

- The proportionality constants, k , determined from the DR-HH model were generally low, indicating that the accessible volume of coal penetrated by the adsorbate gases is not very different to that penetrated by helium, from that it can be concluded that processes such as swelling and imbibition were minimal during the sorption process. The proportionality constant tends to decrease with increasing vitrinite reflectance. k was also found to be fairly peculiar to each coal sample and decrease from CO₂ to N₂, suggesting that CO₂ penetrates more volume of the coals than both CH₄ and N₂.
- For all three adsorbates, the maximum sorption capacities of the four investigated samples decreased with increasing vitrinite reflectance (rank) and elemental carbon content. The microlithotype (intermediate macerals) abundance of the samples was also found to impact on the sorption capacity of the samples.
- The micropore properties of the coal samples were found to significantly influence the sorption processes of the adsorbate more than the mesopore and macropore properties; this supports the observation that the micropores are the primary fluid storage locations in coals.
- Critical properties of the adsorptive gases such as critical temperature, van der Waals' attractive constant and molar polarisability influenced the sorption properties of the samples.
- Under the experimental conditions used in this study, both the ash yields and mineral matter contents of the samples gave wide and irregular scatter, when correlated with the sorption capacities of the samples. Only pyrite and calcite were found to exhibit a systematic trend to the sorption capacities of the samples.

Nomenclature

<u>Symbol</u>	<u>Definition</u>
%Q ₀	Maximum sorption capacity, % weight of coal (db)
%V ₀	Maximum sorption capacity, % volume of coal (db)
<i>a</i>	van der Waals attractive constant (kJ ² /mol ² Pa)
<i>D</i>	Affinity constant (-)
<i>dp</i>	Pore diameter (Å)
<i>E_s</i>	Characteristic heat of sorption (kJ/mol)
ESS	Error sum of squares (-)
FSI	Free swelling index (-)
<i>k</i>	Proportionality constant (ml/g)
kg/t	Kilogram per tonne
<i>m</i>	Molecular mass (g/mol)
<i>M_{mea}</i>	Measured mass of adsorbate at a given pressure (kg)
<i>P</i>	Instantaneous experimental pressure (MPa)
<i>P_c</i>	Critical pressure (MPa)
<i>P_s</i>	Saturation vapour pressure at 55 °C (MPa)
<i>Q₀</i>	Maximum sorption capacity by weight (kg/t _{coal})
<i>Q_{exc}</i>	Excess (Gibbs') sorption (kg)
QOF	Quality of fit (%)
<i>R</i>	Universal gas constant (J/mol.K)
RMS	Root mean square (-)
Rr.%	Vitrinite reflectance (%)
<i>T</i>	Absolute temperature (K)
<i>T_c</i>	Critical temperature (K)
<i>V₀</i>	Maximum sorption capacity by volume (m ³ /t _{coal})
<i>V_{cell}</i>	Volume of sample cell (m ³)
vol.%	Volume percent (%)
<i>V_{sample}</i>	Volume of sample (m ³)
wt.%	Weight percent (%)
<i>Z</i>	Compressibility factor (-)

Greek symbols

<u>Symbol</u>	<u>Definition</u>
α_M	Molar polarisability (cm ³ /mol)
β	Affinity coefficient (-)
βE_s	Net heat of sorption (kJ/mol)
ρ_a	Adsorbed phase density (kg/m ³)
ρ_g	Adsorbate gas density (kg/m ³).
σ_{col}	Collision diameter (Å)
σ_{eff}	Effective molecule diameter (Å)
σ_k	Kinetic diameter (Å)

Abbreviations

<u>Acronym</u>	<u>Definition</u>
BET	Brunauer-Emmet-Teller method
BJH	Barrett-Joyner-Halenda method
CCS	Carbon capture and sequestration (or storage)
CO ₂ Ads data	CO ₂ adsorption data
dafb	Dry ash free basis
db	Dry basis
DR	Dubinin-Radushkevich isotherm model
DR-HH	Dubinin-Radushkevich/Henry law hybrid isotherm model
H-K	Horvath-Kawazoe method
HP	Helium pycnometry
HP	High pressure
HPGSS	High pressure gravimetric sorption system
ISO	International Organization for Standardisation
LPGA	Low pressure gas adsorption
LTA	Low temperature ash
M-DR	Modified Dubinin-Radushkevich isotherm model
MIP	Mercury intrusion porosimetry
mmb	Mineral matter basis

N ₂ Ads data	N ₂ adsorption data
SANS	South African National Standards
SAXS	Small angle X-ray scattering
WAXRD-CFA	Wide angle X-ray diffraction – carbon fraction analysis

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Chapter 6

6.0 Conclusion

6.1 Introduction

The CO₂, CH₄, and N₂ sorption properties of South African bituminous coals relevant for CO₂ sequestration in unmineable coal seams, as candidate geological storage site have been investigated. Four coal samples from underground coal seams of the Highveld, Witbank and Tshipise-Pafuri coalfields were used in the study. The coal samples were rigorously characterised using both conventional and advanced analytical techniques. CO₂, CH₄, and N₂ sorption experiments were conducted on the dry coal samples at 55 °C, up to 16 MPa pressure. CO₂, CH₄, and N₂ sorption isotherms were constructed from the resulting data and the sorption properties of the samples including the maximum sorption capacities with respect to the studied

adsorptive gases were determined. A hybrid isotherm model was developed and fitted to the experimental data. Sorption properties of the coal samples were also correlated with both the coal and adsorptive gases' properties to determine factors impacting the gas storage process.

6.2 Concluding summary

The main findings from this thesis are:

1. Standard and advanced analytical techniques were successfully applied in the detailed characterisation of the chemical, petrographic, physical- and chemical- structural properties and the mineralogy of four bituminous South African coals. Three of the coals (FOZ, DEN, and OGS) were bituminous medium rank C (0.63 – 0.69 Rr.%), while coal TKD was bituminous medium rank B (1.20 Rr.%). The effective PSD analysable by gas adsorption (CO_2 and N_2) and MIP with regard to this study are: $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ for CO_2 LPGA; $17 \text{ \AA} \leq d_p \leq 500 \text{ \AA}$ for N_2 LPGA; and $30 \text{ \AA} \leq d_p \leq 600,000 \text{ \AA}$ for MIP. These show that the ranges of pores sizes analysed significantly depend on the equipment and technique used. SAXS analysis was found to return higher values of surface area and porosity than any of the three other methods used in this study, as SAXS technique probes a wider pore size distribution (PSD) range in coal and covers PSD in the range: $5 \text{ \AA} \leq d_p \leq 17 \text{ \AA}$, not captured by the other three standard methods. Coal compressibility effect due to mercury intrusion at high pressures accounted for 20-25% of the recorded surface area, porosity and pore volume of coals from MIP measurements.
2. Aromaticity of the coals increases with increasing vitrinite reflectance of the samples from both solid state ^{13}C NMR and WAXRD-CFA data. Qualitative ATR-FTIR show that the higher ranked coal TKD contained greater amounts of polyaromatic moieties and longer chains of saturated aromatic hydrocarbons than the other samples, and these increase with increasing vitrinite reflectance. Both the fraction of amorphous carbon and the index of disorder were found to correlate well with the aromaticity of the samples, and decreases with increasing Rr.%. HRTEM image analysis revealed that the aromatic fringe length of the coals increases with increasing vitrinite reflectance of the samples, and greater preferential alignment of fringes was observed for the higher ranked coal TKD. The average number of aromatic carbons per cluster determined from

solid state ^{13}C NMR analysis was also higher for coal TKD, compared with the three other iso-ranked coals, which is consistent with results obtained from WAXRD-CFA, ATR-FTIR and HRTEM analyses.

3. Data from both WAXRD-CFA and HRTEM image analysis show that the three lower rank coals are structurally less well-ordered than the higher rank coal TKD, while crystallite height, L_c , relatively increased with increasing coalification; while crystallite diameter, L_a , remains fairly constant across the coal ranks. Constructed rose diagrams from HRTEM data reveals that the aromatic fringes of the coals tend to be more strongly aligned with increasing maturity of the samples.
4. There is a good agreement between results WAXRD-CFA, solid state ^{13}C NMR, and HRTEM. It has been demonstrated for the coals samples examined in this study, that vitrinite reflectance impacted more on the physical- and chemical-structural properties of the samples than maceral compositions.
5. Kaolinite and quartz were the most abundant minerals in all four coals examined in this study using low temperature oxygen-plasma ashes (LTA) WAXRD analysis. These results corroborated the carbominerite and minerite data from the microlithotype analysis of the coals.
6. High pressure CO_2 , CH_4 , and N_2 sorption experiments were conducted at operational conditions (55 °C and up to 16 MPa) simulating in-situ conditions in coals seams using a gravimetric sorption facility. Results from the sorption experiments show that the maximum sorption capacity of the coals ranged from 40.7 – 86.9 kg/t_{coal}, db by weight (20.7 – 44.2 m³/t_{coal}, db by volume) for CO_2 , 10.1 – 18.1 kg/t_{coal}, db by weight (14.20.7 – 44.2 m³/t_{coal}, db by volume) for CH_4 , and 10.4 – 21.7 kg/t_{coal}, db by weight (8.3 – 17.4 m³/t_{coal}, db by volume) for N_2 . These show that the coal samples can store up to 4.1 – 8.7% of CO_2 , 1.0 – 1.8% of CH_4 , and 1.0 – 2.2 % of N_2 relative to its weight at the experimental conditions. With respect to the investigated adsorptive gases, the maximum sorption capacities of the samples generally decreased in the order: $\text{CO}_2 > \text{CH}_4 \approx \text{N}_2$ by weight, and $\text{CO}_2 > \text{CH}_4 \approx \text{N}_2$ on volume basis. The $\text{CO}_2:\text{CH}_4:\text{N}_2$ maximum sorption capacity ratios ranged from 4.6:1:1 to 3.9:1:1 on weight basis, and between 2.9:1.8:1 and 2.5:1.7:1 by volume.

7. The DR-HH model was found to describe the sorption processes better than the modified Dubinin-Radushkevich (M-DR) model. The net heat of sorption of the samples were generally in the range: CO₂: 12.1 - 12.8 kJ/mol; CH₄: 9.9 - 10.6 kJ/mol; N₂: 8.5 - 8.8 kJ/mol (consistent with previous findings) indicating that physisorption was the more dominant sorption mechanism, while the adsorptives are store in the pores by structural or capillary trapping mechanism. The heat of sorption was also found to relatively increase with increasing sorption capacity and tend to be closely related to the gases' critical properties such as van der Waals' attractive constants and polarisability.
8. The proportionality constant, k , determined from the DR-HH isotherm model were generally low indicating that the accessible volume of coal penetrated by the adsorptive gases is not very different to that penetrated by helium, from that it can be concluded that processes such as swelling and imbibition were minimal during the sorption process, and decreases with increasing vitrinite reflectance. The proportionality constant, k , was also found to be fairly peculiar to each coal samples and relatively decreases in the order: CO₂ > CH₄ > N₂, suggesting that CO₂ penetrates more volume of the coals than both CH₄ and N₂.
9. For all three adsorptives, the maximum sorption capacities of the four investigated samples decreased with increasing vitrinite reflectance (rank) and elemental carbon content. The microlithotype (intermediate macerals) abundance of the samples was also found to impact the sorption capacity of the samples. The micropore properties of the coal samples were found to significantly influence the sorption processes of the adsorptives more than the mesopore and macropore properties; this supports the observation that the micropores are the primary fluid storage locations in coals. Hence, micropore properties of coals can give insightful information on the storage capacities of coal seams as candidate geological site for CO₂ sequestration.
10. Critical properties of the gases such as critical temperature, van der Waals' attractive constant and molar polarisability influenced the sorption properties of the samples. Under the experimental conditions used in this study, only pyrite and calcite were found

to exhibit a systematic trend with the sorption capacities of the samples, which arguably may be related to the rank of the samples.

6.3 Contributions to the knowledge base of coal science and technology

The main contributions of this study to the knowledge base of coal science and technology is presented in this section:

1. Significant insight and understanding of the porosity in coals has been highlighted in this study. This study has demonstrated that because the different techniques used to probe the surface areas and porosity properties of coals are restricted to different pore size ranges one technique is insufficient to completely describe the porosity properties of coal. While CO₂ LPGA examines the micropore properties, the N₂ LPGA is more suited for the analyses of the mesopore properties, and the MIP measurements can be used to study the macropore features of the coal. Furthermore, SAXS analytical technique, which was used to study these coals for the first time, returned higher values than the sum of values from the three other widely used techniques, arising from the fact that SAXS methods probe a wider range of pores, as well as pores not penetrated using the other methods.
2. Because coal is compressible, especially at high pressure, the compressibility effect due to mercury intrusion at high pressure was also demonstrated in this study to account for 20 – 25% of reported surface areas and pore volume during MIP measurements. This will introduce huge systematic error or uncertainty in the reported data from MIP if uncorrected. Methods of determining and correcting for this compressibility effect has also been detailed in the study.
3. The chemical structural properties of coal has been elucidated in this study using various advanced analytical tools including WAXRD-CFA, solid state ¹³C NMR, ATR-FTIR, and HRTEM. Significant preferential alignment was observed for the carbon crystallites which increases with increasing vitrinite reflectance (rank).

4. The similarities of the physical- and chemical-structural properties of the bituminous medium rank C (iso-rank) coals examined in this study originating from both the Highveld and the Witbank coalfields indicate that the Permian-aged coals of these two coalfields are of similar maturity, which is entirely different from that of the Tshikondeni sample. The vitrinite reflectance or rank of the samples significantly influenced the both the physical- and chemical-structural properties of the samples than maceral compositions or abundance.
5. For the first time, the CO₂, CH₄, and N₂ sorption properties of sample from the underground coal seams of South African has been studied at supercritical conditions similar to in-situ coal seam conditions at 55 °C and up to 16 MPa. Previous studies although limited to only two studies [1, 2], have been conducted at < 27 °C and 35 °C and at maximum pressures of 6 MPa and 8.5 MPa respectively. While the former [1] represented subcritical conditions with regards to CO₂, the later [2] got up to supercritical conditions, but reported increasing CO₂ excess sorption with increasing pressure up to 8 MPa. This may be due to uncertainty in the saturation vapour pressure used in their calculations or due to errors in coal volume or density during the experiments.
6. The coal samples examined were found to be able to hold up to 4.1 – 8.7% CO₂, 1.0 – 1.8% CH₄, and 1.0 – 2.2 % N₂ relative to their weights. With respect to the three adsorptive gases studied, sorption capacities of the samples decreased in the order: CO₂ > CH₄ ≈ N₂ by weight and CO₂ > CH₄ > N₂ by volume.
7. Coal properties such as rank characterised by the vitrinite reflectance of the samples and the intermediate maceral (microlithotype) abundance impacted the sorption capacities of the samples, while maceral composition and abundance did show a systematic trend with the sorption capacities of the sample in all three adsorptives. It has also demonstrated that the critical properties of the gases, especially molar polarizability and van der Waal's attractive constant influenced the sorption properties of the samples.
8. Results from this work can be used as a rough or relative estimate of the CO₂ storage capacities and the CBM contents of the bituminous coal seams of South Africa,

assuming 100% CO₂ or CH₄ saturation of the coal seams. However, other factors such as storage efficiency factor, and displacement efficiencies (vertical, horizontal, and gravitational) need to be considered for a more accurate assessment on a coal seam scale.

6.4 Recommended future research

Following the finding reported in this thesis, the following are recommended as value-added future research directions.

1. Investigation further a wider range of coals of various ranks that will include semi-anthracites and anthracites. Results from such wide variety in coal rank can help develop a predictive model for the sorption capacities of South African coals, and further help in identifying parameters that significantly influenced the sorption properties of the samples.
2. The experiments conducted in this study were undertaken on dry coal samples. It will be necessary to determine high pressure sorption behaviour of the moisture-equilibrated samples, as this is more representative of the in-situ condition in underground coal seams.
3. Apart from adsorption experimentations, desorption experiment can be carried out on the coal samples and other samples from South African coalfields to ascertain if all adsorbed species are fully desorbed and thus, be able to quantify imbibition and or dissolution of some gases into coal.
4. Studies on the volumetric swelling of these coals in the presence of these adsorptive gases at high pressure need to be undertaken to quantify the magnitude of swelling, if any, on these coals and its influence on both the sorption capacities and the bulk fluid transport processes and permeability within the coal seam.
5. It may be necessary to design and conduct experiments with the necessary volumetric and gravitational stress and strain often experienced in real injection scenarios in coal seams and study the possibility of permeability damage with increasing injection pressure.

6. Design and conduction of high pressure sorption experiments on these coals at varying temperatures to study the kinetics of the sorption process and the impacting factors.
7. The vast characterisation data (Chapters 3 and 4) arising from this thesis can be used to construct a coal model and possibly, simulate high pressure sorption of the three investigated gases on the coal models. These results can be compared with and / or validated with the experimental data and can be used further for predictive purposes.

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Appendices

Appendix A: Supplementary data on the petrographic properties of the coal samples.

Appendix A-1: Coal vitrinite and maceral scan random reflectance histograms of the coal samples.

The histograms of the random reflectance readings used to determine the vitrinite and maceral reflectance of the coal samples are presented in Figures A-1 and A-2.

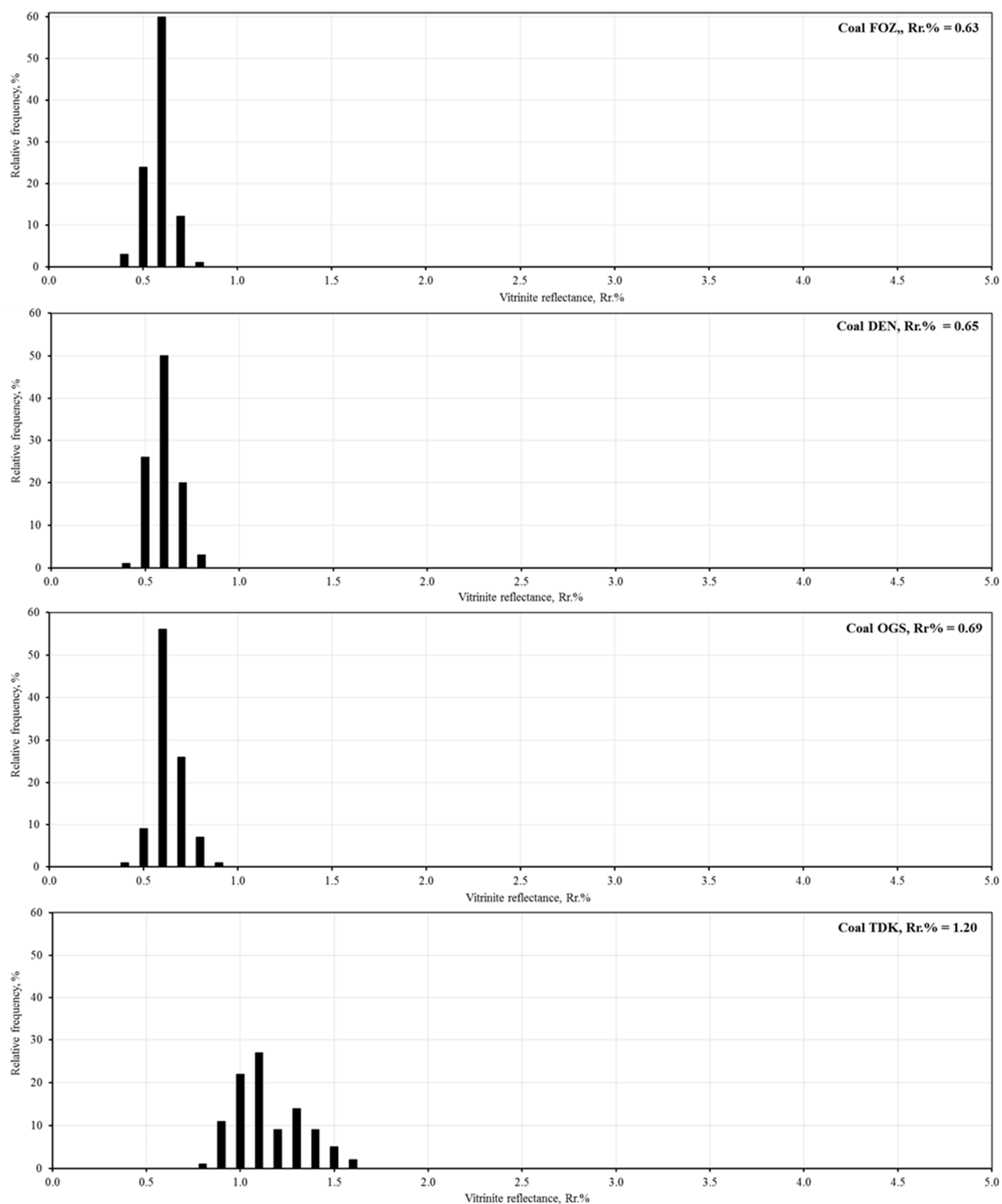


Figure A-1: Coal vitrinite random reflectance histograms of the coal samples.

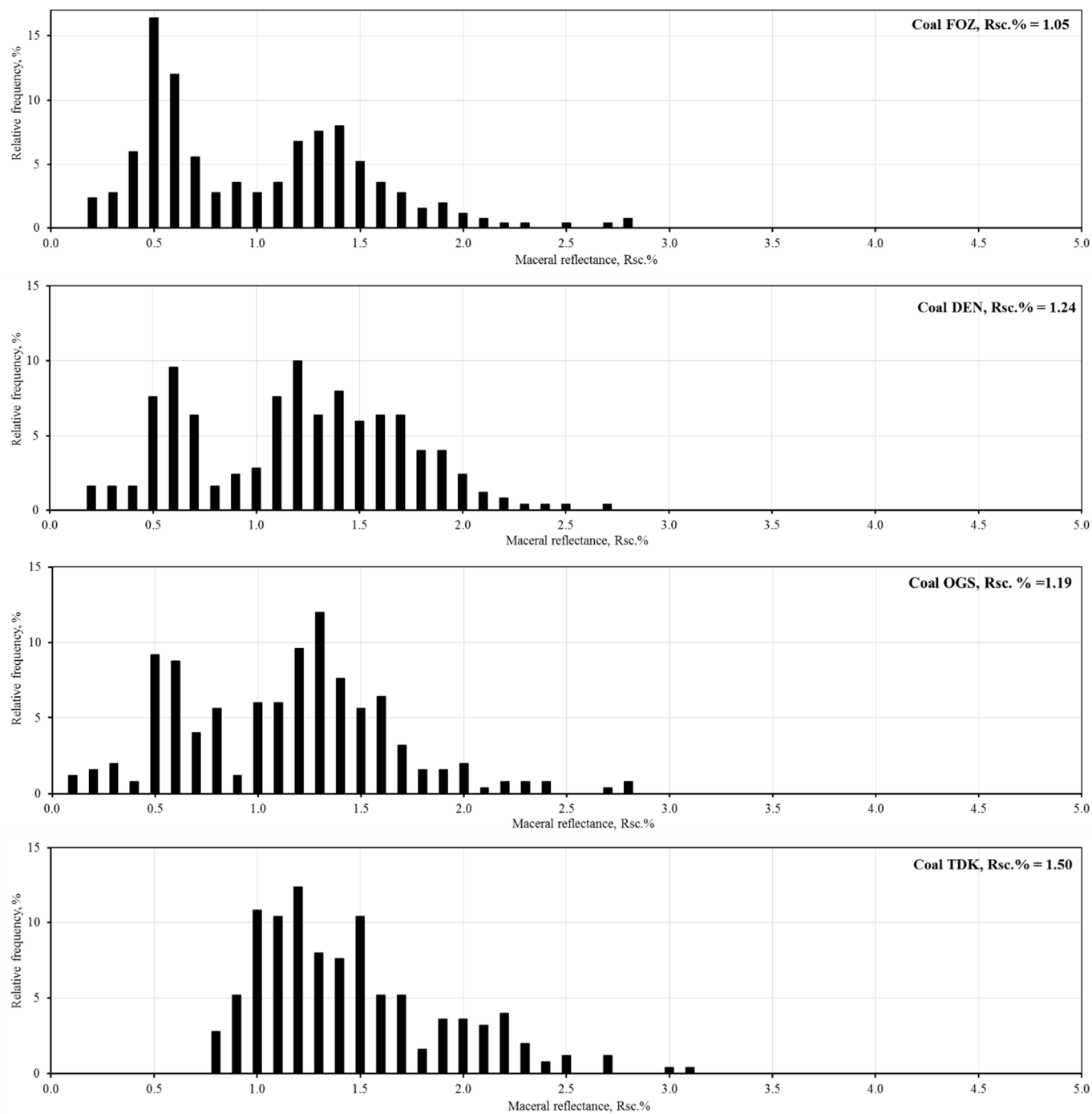


Figure A-2: Maceral scan random reflectance histograms of the coal samples.

Appendix B: Supplementary data on Sample Characterisation I: Physical-structural properties of the coal samples.

Appendix B-1: BET Surface area of samples from CO₂-LPGA

The BET surface area plots used to determine the CO₂ BET surface areas of the samples are given in Figure B-1, following the method proposed by Brunauer et al. [3], with correlation coefficients, $R^2 \leq 0.98$. The R^2 obtained from the BET surface area plots were lower than the R^2 returned by the D-R method [4], with relatively wider scatter than the D-R transformed plot presented in Figure 3.2, Section 3.4.2.1. The resulting BET surface areas of the samples are presented in Table B-1.

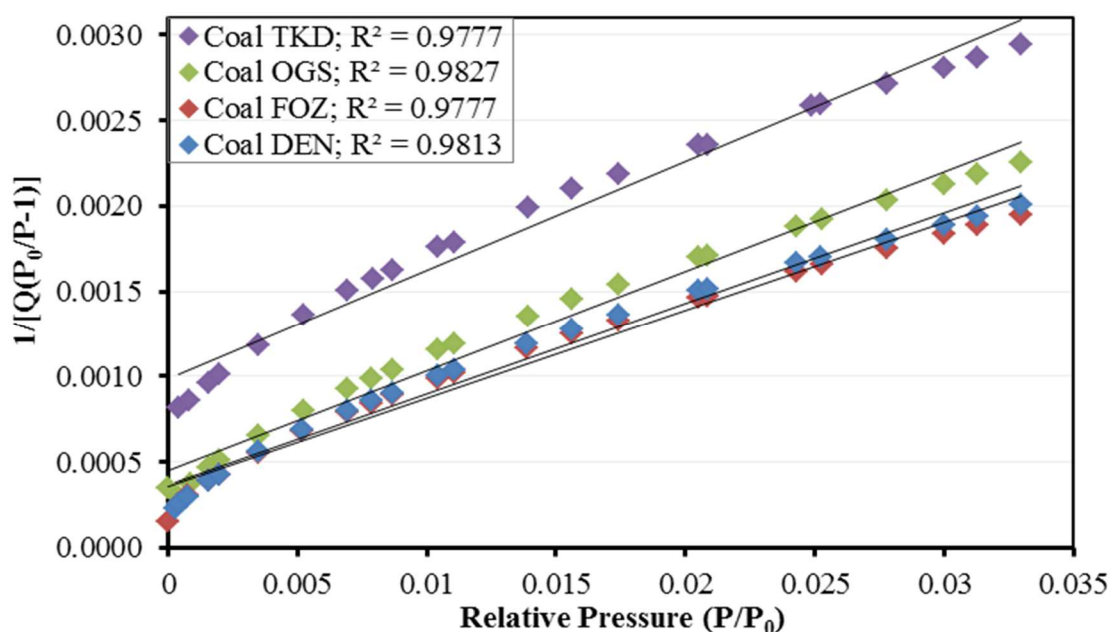


Figure B-1: CO₂ BET surface area plots of the coal samples.

Table B-1: BET surface area of coal samples from CO₂ LPGA

CO ₂ BET surface area					
Method / Sample ID	Method used	Coal DEN	Coal FOZ	Coal OGS	Coal TKD
BET surface area (m ² /g)	BET	85 ± 3	88.0 ± 3	77.6 ± 2	70.5 ± 2

It is clear from Table B-1 that the BET surface areas based on multi-layer adsorption on flat regular surfaces [3], are substantially lower than the D-R surface areas reported in Table 3.2, Section 3.4.2.1, based on Dubinin's theory of volume filling of micropores (TVFM) [4-6] and the Polanyi's potential theory [7]. Thus, the D-R isotherm model is more suited in describing the micropore properties of relatively highly microporous coals than the BET isotherm model [8-12].

Appendix B-2: SAXS diffractograms of the raw and demineralised coal samples

The double logarithmic plots of the SAXS data of the raw coal and demineralised coal samples are shown in Figure B-2.

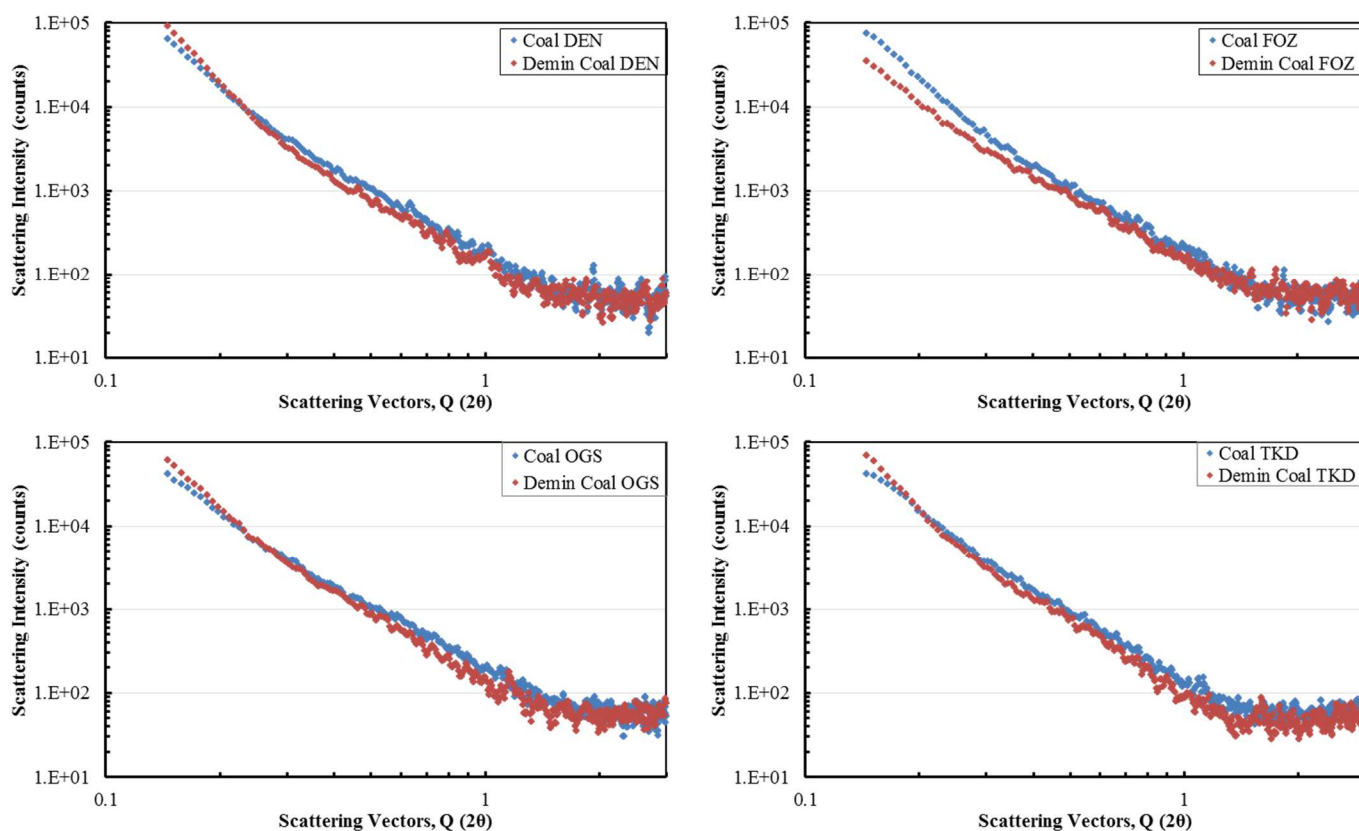


Figure B-2: Double logarithmic plots of the SAXS data of both the raw and demineralised coal samples.

The summary of the SAXS-determined physical structural properties of the coal and the subsequent demineralised coal samples are reported in Table 3.3, Section 3.4.2.4 and in the published report of Okolo et al. [8].

Appendix B-3: Graphical comparison of the surface areas and porosity properties of the coal samples determined from SAXS, CO₂- and N₂- LPGA, and MIP.

Graphical comparisons of the surface areas and porosity properties of the coal samples determined from SAXS data and the results obtained from three other conventional techniques (CO₂- and N₂-LPGA and MIP). Compared data were collated from Tables 3.2 and 3.3, Section 3.4.2. It should be noted that compared SAXS data were based on the results from the raw coals. These comparisons are presented in Figure B-3 (surface areas) and Figure B-4 (porosity properties).

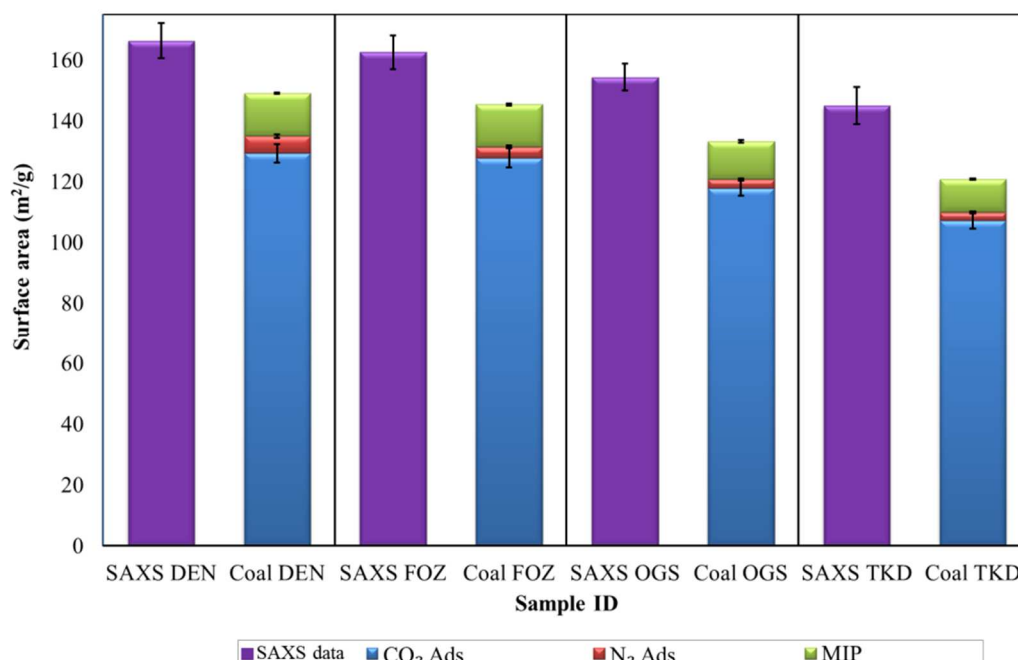


Figure B-3: Graphical comparison of the surface areas determined from SAXS and the other three standard methods.

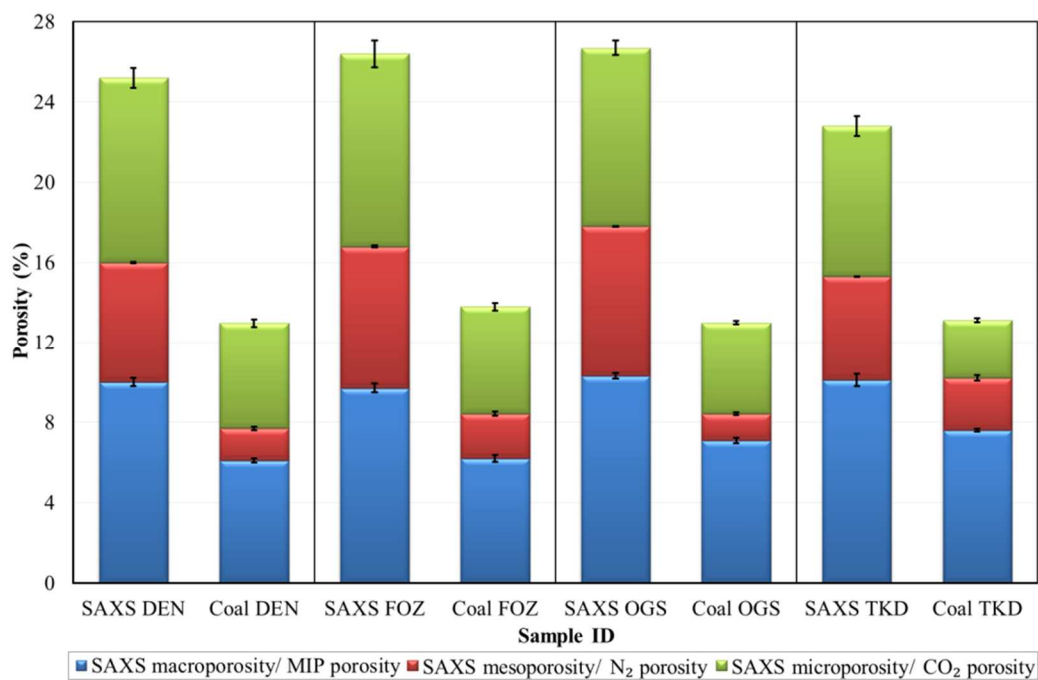


Figure B-4: Comparison plots of the porosity results from extrapolated SAXS data and the other techniques.

Appendix C: Supplementary data on Sample Characterisation II: Chemical-structural properties of the coal samples.

Appendix C-1: Graphical comparison of the aromaticity of the coal samples obtained from WAXRD-CFA and solid state ^{13}C NMR.

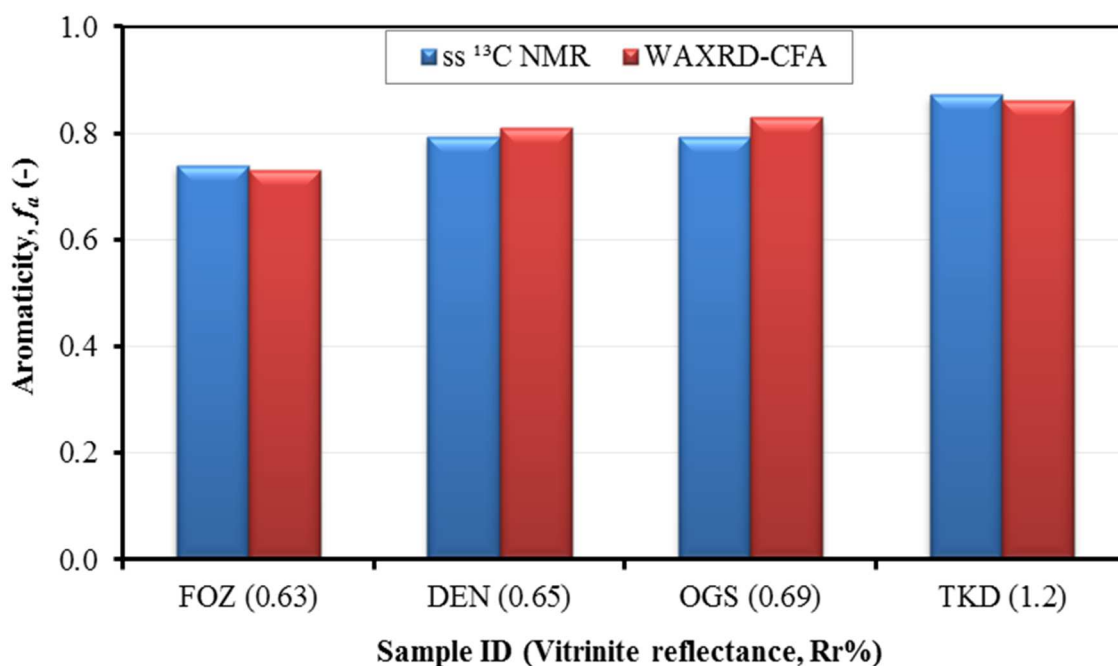


Figure C-1: Graphical comparison of the samples' aromaticity determined from WAXRD-CFA and solid state ^{13}C NMR analyses.

Appendix C-2: Detailed algorithm for HRTEM image processing using Photoshop CS5 and IPTK 5.0 plug-in.

Following the method proposed by Sharma et al. [13], a detailed algorithm for the HRTEM image analysis was developed on the platform of Adobe Photoshop CS5 in combination with an image processing tool kit (IPTK 5.0) plug-in (developed by Reindeer Graphics, USA). The detailed algorithm is presented in Figure C-2, with the relevant processed image obtained at every step of the image processing for coal TKD. A summarised algorithm was given in Figure 4.9, Section 4.4.3.4.

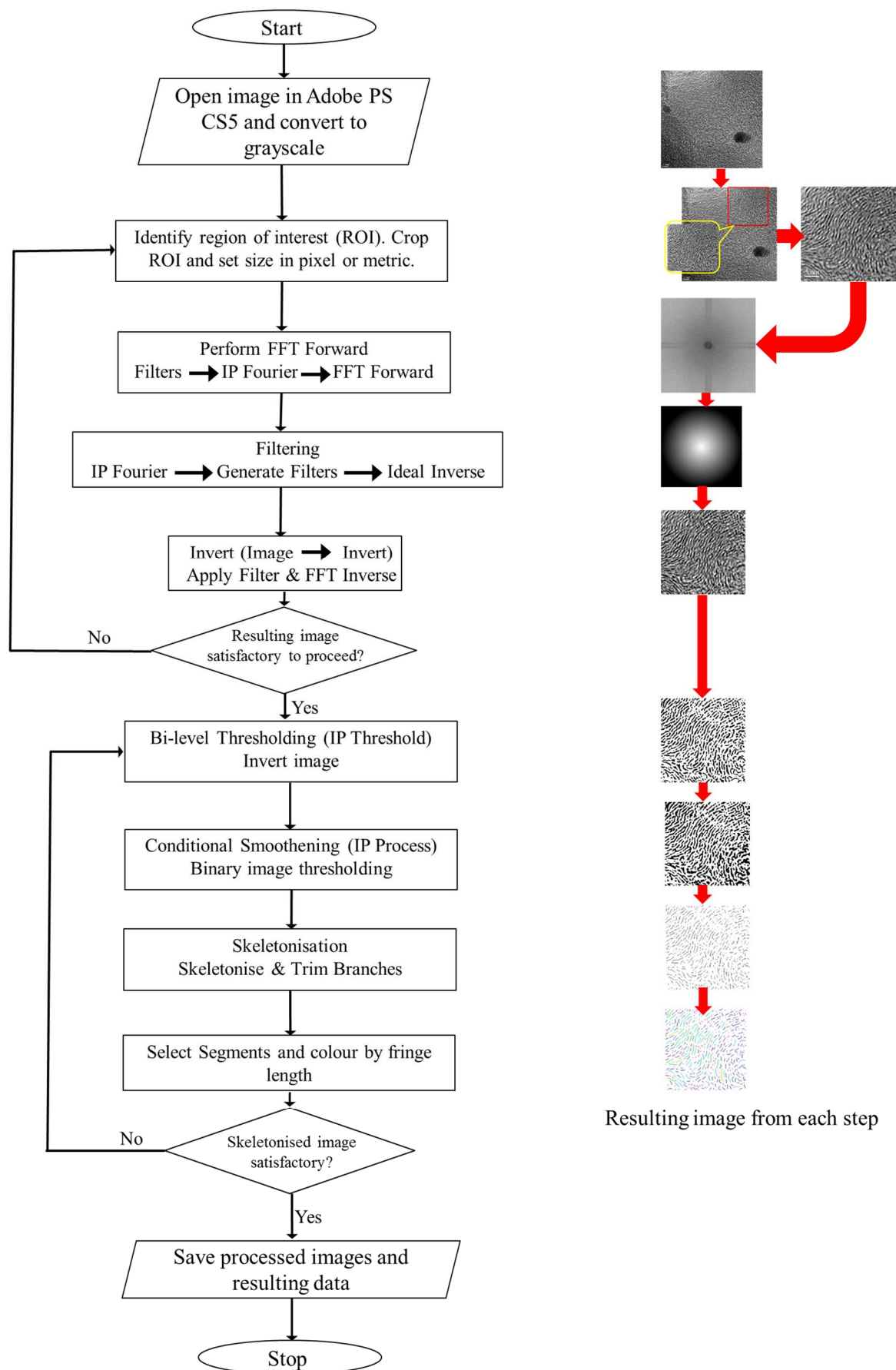


Figure C-2: Detailed algorithm for HRTEM fringe image processing for coal TKD micrograph.

Appendix C-3: Distribution of aromatic fringe lengths in the coal samples from HRTEM fringe image analysis.

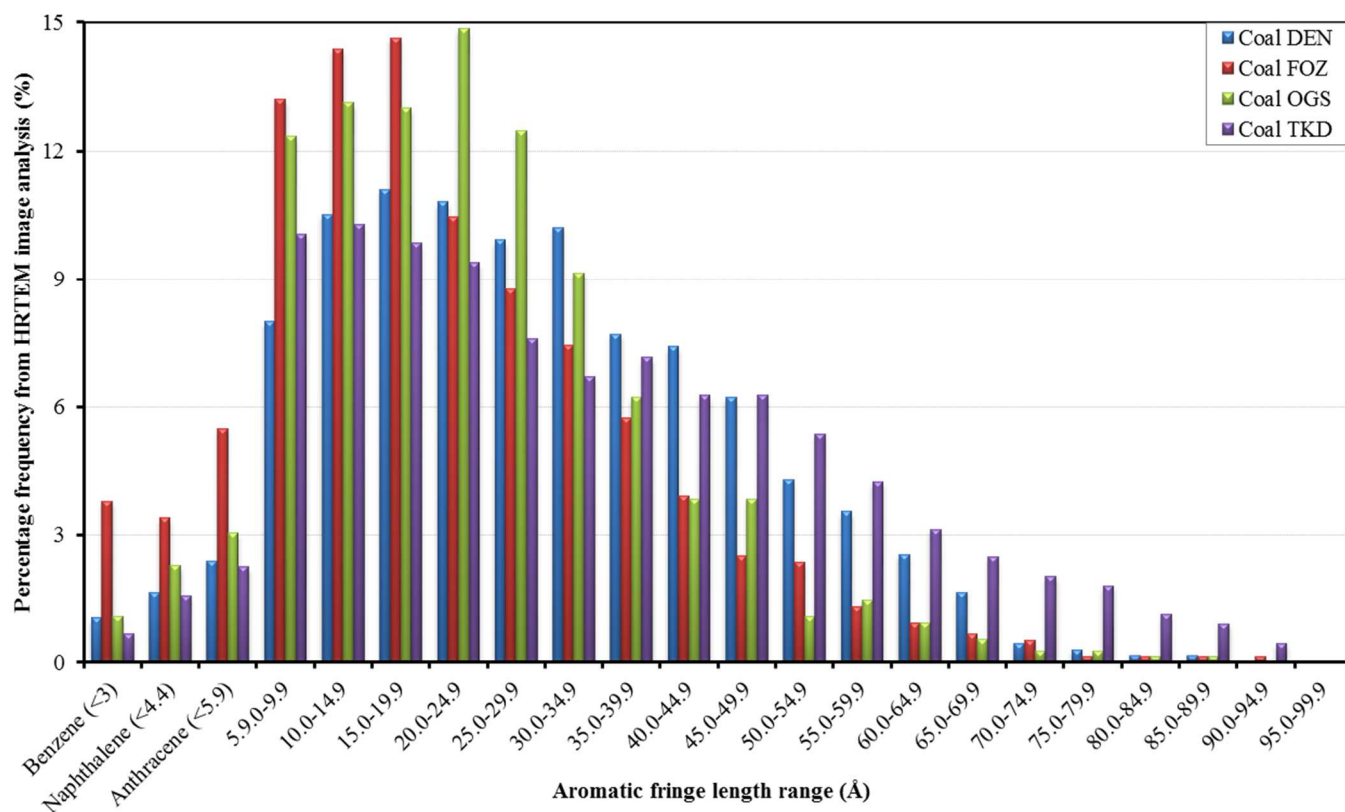


Figure C-3: Distribution of aromatic fringe lengths in the coal samples from HRTEM fringe image analysis

Appendix C-4: Distribution and contribution of HRTEM aromatic fringes to the average molecular weight of the coal samples.

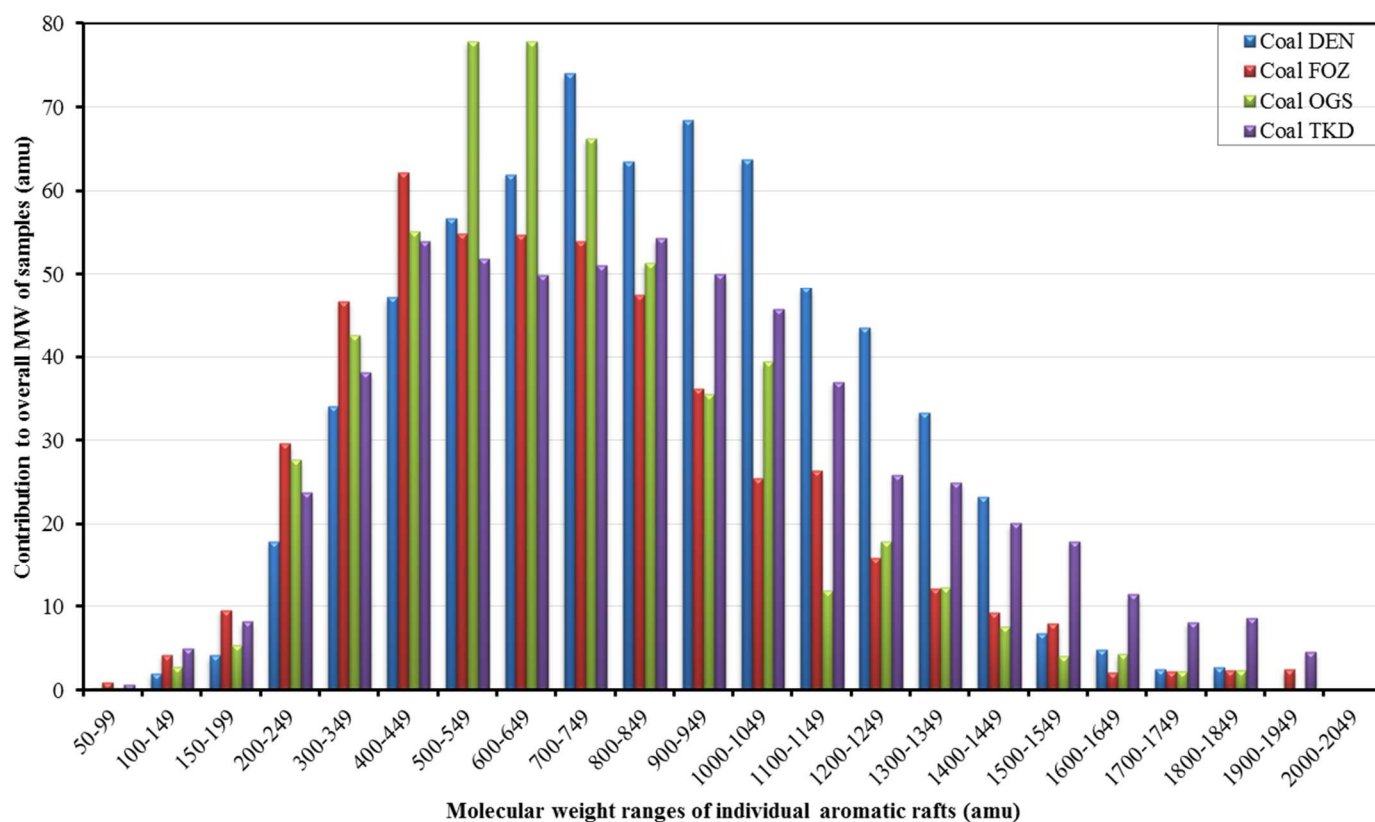


Figure C-4: Contribution of individual molecular weights of aromatic fringes to the overall average molecular weights of the aromatic fringes of the samples from HRTEM image analysis.

Appendix C-5: Comparison of the average molecular weight of the coal samples determined from HRTEM image analysis and solid state ^{13}C NMR spectroscopy.

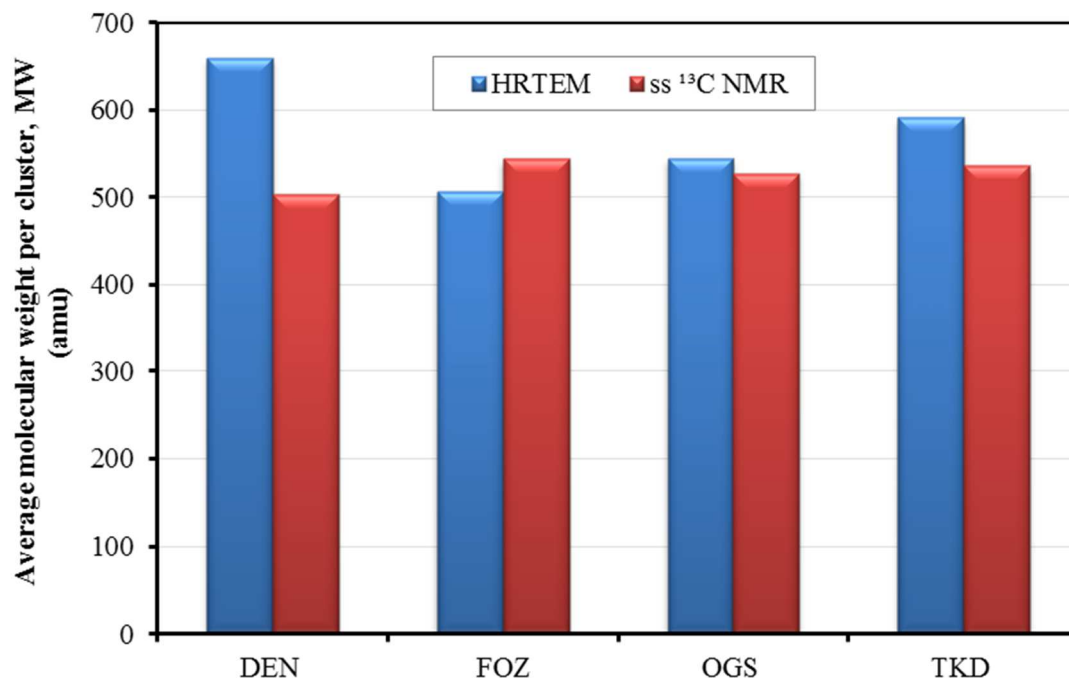


Figure C-5: Comparison of the aromatic fringe average molecular weight of the samples determined from HRTEM and solid state ^{13}C NMR analyses.

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