



Comparing the porosity and surface areas of coal as measured by gas adsorption, mercury intrusion and SAXS techniques



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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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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.

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1. 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

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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% ≤ elemental carbon ≤ 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 (argon, carbon dioxide, ethane, helium, krypton, methane, nitrogen, water vapour, xenon, 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. Carbon dioxide and nitrogen 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 (WXRd), 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 carbon dioxide adsorption have been generally found to be much larger than the values from nitrogen adsorption [1,21,23,27]. This has been attributed to activated diffusion; the low thermal energy associated with nitrogen 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 h) 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 Å ≤ d_p ≤ 5 Å (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 Å ≤ d_p ≤ 3000 Å (higher micropore and entire mesopore range). Effective pore size distribution (PSD) analysed using MIP is in the range: 30 Å ≤ d_p ≤ 600,000 Å (60 μm) (meso- and macropore 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 Å ≤ d_p ≤ 17 Å are not readily picked up by any of these three widely used standard methods.

In recent times, Small Angle X-ray Scattering (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 (CO₂ and N₂) [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 CO₂ storage in coal seams, combustion, gasification, liquefaction, etc.

2. Experimental

2.1. 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.

2.2. 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 nitrogen gas, stored in a vacuum-sealed thick polyethylene container and kept in a desiccator. All sample characterisation

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