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Pore development during gasification of South African inertinite-rich chars evaluated using small angle X-ray scattering

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ABSTRACT

Pore development arising from steam and CO_2 gasification of a char, prepared from an inertinite-rich Witbank Seam 4 coal, was investigated using small angle X-ray scattering. The char, ~75 μm, was gasified to specific conversions (10, 25, 35 and 50%) using two gasification reagents, CO_2 and steam. A novel ratio analysis technique was developed to study the pore development from experimental data. Differently sized pores grow at different rates with the difference not being simply due to gas accessibility. In particular, the pores between 1 and 40 nm in size showed more pore growth than larger or smaller sizes. Steam gasification created a more porous char with increased pore growth of pore sizes between 1 and 40 nm than CO_2 gasification. The pore growth rate of steam was up to a factor 7 times faster than CO_2, compared at the highest gasification temperatures. For the smaller pores, <1 nm, it was found that the rate of pore generation was slower compared to larger pores, though pore growth was still evident with the critical cross over pore size for CO_2 to be 1 nm compared to 0.6 nm for steam. This may be a direct consequence of CO_2's greater kinetic diameter.

1.. Introduction and background

The conversion of coal with oxidising media such as CO_2 and steam is used to increase the economic potential of feedstocks, generating products including: syngas, electricity and activated carbon. During gasification, coal undergoes several stages of transformation such as dewatering, pyrolysis, gasification, and combustion resulting in physical and chemical changes. A fundamental understanding of these changes is key to the design of coal gasifiers [1]. For the gas–solid reactions, it is reported that the reaction rate is dependent on the change in physical char structure as conversion progresses [2–5], and has widely been studied for coal chars [6–10]. The physical changes that are observed during gasification can also be directly used to describe the surface area development in the production of activated carbon from waste material [11–16]. In general, pore structure development during steam and CO_2 gasification under comparable conditions is different. Steam gasification yields an increase in all pore sizes from the onset of gasification, and increases the mesoporosity to a greater extent than CO_2. While CO_2 tends to produce a relatively narrow micropore structure with broadening of microporosity only after extensive activation [6,7,12,13]. However, contradictory trends are reported regarding which gasification agent results in maximum micropore development (maximum reported for CO_2 [11,13,14] and for steam [17–19]), with the deviations being attributed to the diversity of the char structures used. These findings are based on combining measurements made by gas adsorption (typically, CO_2 at 273 K and N_2 at 77 K), mercury porosimetry, and also adsorption of organic vapours with differing molecular diameters. While useful, the influence of time-temperature histories on the char behaviour and differences between techniques complicate using a combination of different methods to determine pore size variations due to gasification [20].

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Small Angle X-ray Scattering (SAXS) can be used to evaluate pore sizes over a wide range using a single measurement. The intensity of the X-ray beam is determined as a function of scattering angle. The scattering angle is converted to the scattering vector Q, which can be used to determine pore radius R by the approximate relationship R ~2.5/Q [16]. If the pore size distribution follows fractal behaviour, the Porod plot (log (Intensity(Q)) versus log (Q)) results in a straight line, and the pore size distribution follows strict scaling laws. However, if the slope varies with Q, the material is not fractal and more complex modelling is required. In this case models require estimation of fixed input parameters (electron density difference and form factor) and variable fitting parameter (pore number or volume distribution) [21]. SAXS has been used to investigate coal pore structures [21–26], with the recent SAXS studies focused on how gas is sorbed and released from the coal structure [27–31]. SAXS data show that there is a wide distribution of pore sizes in chars. A summary of the research conducted on pore development during gasification using Small Angle Scattering (SAS) is shown in Table 1.

Although the pore development during carbon conversion has been studied previously using SAXS, the authors have found no systematic study comparing the pore development during steam and CO_2 gasification using this technique. The comparison of pore development from CO_2 and steam using SAXS will combine the effects observed using established techniques (gas adsorption and porosimetry) with the added benefits of SAXS [32–39]. Here the pore development during gasification of char made from an South African inertinite-rich, Witbank seam 4 coal, using steam and CO_2, is evaluated using SAXS.

2. Experimental section

2.1. Sample preparation and characterisation

The bulk coal sample (300 kg) was +30 mm particle size, Witbank seam 4 export steam coal (washed at specific gravity <1.5). Witbank seam 4 coal is inertinite-rich, see Table 2, which exhibits different properties to most Northern Hemisphere coals. The sample was cone-and-quartered 4 times and the representative sample crushed to −5 mm. Char preparation was carried out in a nitrogen atmosphere controlled oven at 1000 °C (heating rate of 10 °C/min) with a holding time of 1 h (flow rate of 2 L/min, STP). The sample was obtained by, crushing the char sample and collecting a narrow size fraction (−75 + 38 μm). The parent coal and char characterisations are shown in Table 2.

The char was gasified in a TGA (details in Coetzee et al. [40]) using either steam (20 mol%) or CO_2 (10 mol%) with an Argon balance. The converted char preparation was carried out using two gasification temperatures (800 and 950 °C for steam, 850 and 1000 °C for CO_2). The particle size and gasification temperatures were chosen to reduce external mass transfer limitations and to allow acceptable reactivity times (50% conversion within 3 days). The TGA was pre-heated to the set gasification temperature, using inert conditions, after which the char sample was inserted and the gasification reagent was introduced once isothermal conditions were reached.

Table 2
The characterisation results of the parent coal and char.

	Parent coal	Char
Proximate analysis (wt% db)		
Ash	13.7	17.6
Volatile matter	26.3	2.2
Carbon	60.0	80.2
Ultimate analysis (wt% daf)		
Carbon	83.5	95.9
Hydrogen	4.5	0.2
Nitrogen	2.0	1.9
Sulphur (total)	0.9	0.8
Oxygen	9.3	1.3
Petrography		
Macerals (vol% mmf)		
Vitrinite	29	
Liptinite	4	
Inertinite	67	
Rr (%)	0.78	
Rsc (%)	1.38	
Rank:	Medium rank C	

2.2. SAXS measurement

The SAXS measurements were performed at the Australian Synchrotron in Melbourne; a detailed discussion on the beamline is discussed in Kirby et al. [41]. The beam energy, -wavelength and -size used was 11 keV, 1.127 Å and 250 × 150 μm, respectively. A Pilatus 1 M detector was used for data acquisition, with exposure time of 1 second and two detector positions (denoted as short and long SAXS). The two positions resulted in a Q-range probed from $1.698 \cdot 10^{-3}$ to 0.8333 $Å^{-1}$, which corresponds to assumed pore diameter between 0.25 and 147 nm.

The gasified samples were mounted in a washer (inner diameter of 10 mm and a thickness of 300 μm) using M3 Scotch® transparent tape. The weight and thickness of the mounted char samples was measured. Two secondary standards, glassy carbon (300 μm thick), were used for absolute intensity calibration of the SAXS datasets. A raster grid of ~0.7 × 0.7 mm was collected using 18 scans (3 × 6) for each sample and both detector positions.

The experimental repeatability of the measurements was calculated using a repeat scan (18 mapped scans) of the short SAXS setting. The average 95% confidence interval experimental error over the full Q-range was calculated as <1%. The sample variance for the char (over the entire Q-range, after merging camera position data) was determined as <8%. Larger errors were observed at the extreme ends of the Q-range. The statistical difference between

Table 1
Summary of research on the pore development during carbon conversion using SAS.

Reference	Source	Reagent	Temperature (°C)	Analysis
Bale et al. [32]	Lignite	O_2	240	SAXS
Calo et al. [33]	Subbituminous coal & Phenolic resin char	O_2	400, 470	SANS[a] with contrast matching
Calo et al. [34]	Saran char, raw and calcium-loaded cellulose	O_2	340, 425, 560	SAXS
Antxustegi et al. [35]	Argonne Premium Pittsburgh No. 8	O_2	400	SANS with contrast matching
Diduszko et al. [36]	Activated carbon (hard coal)	Steam	–	SAXS, benzene adsorption
Foster and Jensen [37]	Anthracite	CO_2	825	SAXS
Foster and Jensen [38]	Carbosieve-S	CO_2	825	SAXS
Pfeifer et al. [39]	Olive stone	Steam	750	SAXS

[a] Small Angle Neutron Scattering.