STRUCTURE AND COMBUSTION REACTIVITY OF INERTINITE-RICH AND VITRINITE-RICH SOUTH AFRICAN COAL CHARS: QUANTIFICATION OF THE STRUCTURAL FACTORS CONTRIBUTING TO REACTIVITY DIFFERENCES

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ABSTRACT

South Africa has large reserves of Permian-aged, high-ash bituminous coals. Although these coals are of great economic importance, their behavior has not been well studied. This study compares the devolatilization and subsequent combustion behavior of an inertinite-rich (87.7% dmmf) and a vitrinite-rich (91.8% dmmf) South African coal, wet-screened to a narrow particle size distribution of 200 x 400 mesh. Pyrolysis chars were generated under rapid-heating conditions ($10^4$–$10^5$°C/s) in a drop-tube reactor to closely resemble chars generated in pulverized combustion conditions. The inertinite-rich coal took 400ms to devolatilize in the drop-tube, compared to only 240ms for the vitrinite-rich sample. The longer residence time in the drop-tube reactor is expected to contribute to reactivity differences. The combustion reactivities of the chars were correlated to a range of chemical, physical, and optical characteristics including the maceral differences and high ash yields. To evaluate the combustion reactivity, isothermal and non-isothermal thermogravimetical analyses (TGA) were utilized. The vitrinite-rich char had on average 20% higher reaction rates than the inertinite-rich char under the various combustion conditions. To verify these results, temperature programmed oxidation was used and confirmed the higher reactivity of the vitrinite-rich char, where the vitrinite-rich char reached a higher maximum carbon dioxide signal at 590°C compared to 650°C for the inertinite-rich char. The char samples were de-ashed with HCl and HF acid which resulted in an increase in combustion reactivity. The maximum reaction rate of the high-ash (36%) inertinite-rich char increased with 80% after de-ashing. This suggested that the ash acted as a barrier, and the removal of ash most likely increased the access to reactive surface area.

The chemical and physical structures of the chars were characterized through a range of different analytical techniques to quantify the factors contributing to reactivity differences. The morphologies of the chars were characterized with SEM and optical microscopy, while quantitative information on the ordered nature of chars was obtained through XRD on de-ashed chars. The inertinite-rich coal experienced limited fluidity
during heat-treatment, resulting in slower devolatilization, limited growth in crystallite height (11.8 to 12.6 Å), only rounding of particle edges, and over 40% of mixed-dense type chars. The vitrinite-char showed more significant structural transformations; producing mostly (80%) extensively swollen crassisphere, tenuisphere, and network-type chars, and XRD showed a large increase in crystallite height (4.3 to 11.7 Å). Nitrogen adsorption and small-angle X-ray scattering (SAXS) were utilized to compare the nitrogen surface areas and pore size distributions of the two chars. Both chars were mostly mesoporous but the inertinite-rich char had double the average pore size, which also resulted in a larger nitrogen surface area since nitrogen can only access surface areas in larger pores. The BET surface area was 3.9 and 2.7 m²/g for the inertinite- and vitrinite-rich chars respectively. SAXS data showed that the vitrinite-rich char had 60% higher frequencies of pores in the micropore range. Helium porosimetry indicated that the inertinite-rich coal and resultant char had higher densities than the vitrinite coal and char; 1.6 and 2.0 g/cm³, compared to 1.3 and 1.9 g/cm³ (dry basis). It is difficult to determine the extent to which the above mentioned factors contribute to the combustion reactivity differences.

HRTEM was utilized for further characterization since it allows the direct observation of the distribution of structural features (layer size and stacking) of the chars. A new semi-automated approach for HRTEM image analysis and a new technique for quantifying distributions were developed in Photoshop and Matlab respectively, which enabled the quantitative characterization of the crystalline char structure. Distributions of layer size, interlayer spacing, stacking number, and layer orientation were obtained. By developing this computerized approach for image processing and statistical analysis, it is now possible to analyze more micrographs (larger sample size) in a shorter period of time with less user bias. Therefore, the usefulness of HRTEM to analyze carbonaceous structures is greatly improved.

The shrinking core and random pore models were fitted to the reactivity data. These mathematical models, used for predicting the effect of process variables on the reaction
rates of chars and carbons in various environments, are not able to predict behavior at conditions higher than 550°C. Consequently, there is a need for improved reactivity modeling approaches which would enable the incorporation of the multiple competing structural factors. Current molecular modeling tools and approaches do not allow testing of our understanding of char structure-behavior relationship since most of the above-mentioned structural features cannot be incorporated. Here, a new tool for the construction of molecular models was developed which enables the construction of large scale atomistic representations based on the distribution of structural features such as stacking. This novel approach was able to generate structures which capture some of the structural differences seen in experimental data between the inertinite-rich and vitrinite-rich coal chars. To explore reactivity differences between these two char models, a rules-based simulation approach was developed utilizing Material Studio and Matlab. Oxygen atoms were diffused through the char structure, and if an oxygen atom was within a critical distance of an edge carbon atom, it was assumed that they will react and consequently the carbon atom was deleted. These steps were repeated 15 and 18 times for the vitrinite-rich and inertinite-rich char structures, respectively. After these steps, 80% of the initial char structure was ‘combusted’. Although a simplified approach, it agreed with experimental data where the vitrinite-rich char combusted slightly faster than the inertinite-rich char. Increased automation and further enhancements to this approach would enable us to explore structure-reactivity relationship in a less time-consuming fashion.
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Chapter 1

Introduction

Coal is the most abundant fossil fuel in South Africa and is a major commodity since it supplies 79% of the country’s energy needs.\textsuperscript{1} Even though South Africa uses coal in their highly developed petrochemical industry (40 million tons annually), coal is primarily utilized in pulverized combustion for the generation of electrical power (110 million tons). The International Energy Agency has forecasted that by 2030, coal will supply 38% of the world's electricity.\textsuperscript{2} South African coal reserves are mostly high-ash bituminous\textsuperscript{3, 4} and although inertinite is the dominating maceral, there is also a large fraction of vitrinite-rich coal which are of economic importance.\textsuperscript{1} It is mostly the lower grade coals that are available for domestic utilization. The quality is expected to even further decrease since seams with lower grade coal containing higher ash yields are mined, and environmental regulations limits the beneficiation (washing) of coal. Current technology for coal utilization in South Africa is limited to mainly fixed-bed gasification and pulverized fuel combustion.\textsuperscript{4} New technologies are required in order to utilize the high-ash, lower quality coal. Understanding coal to char transformations and resulting reactivity, is essential for designing/developing new utilization technologies.

Due to its depositional environment, Permian-aged Gondwana coal differs in petrographic composition from Northern hemisphere Carboniferous coals and are typically inertinite-rich and less reactive.\textsuperscript{1} South African inertinite also differs from inertinites from other regions since it contains considerable amounts of semifusinite.\textsuperscript{3} These are often referred to as ‘reactive semifusinite’ regionally as it has been reported to have a relatively high reactivity during coking and liquefaction.\textsuperscript{5} A recent study\textsuperscript{1} investigated the structural variations between two maceral-diverse South African coals. The vitrinite-rich Waterberg and inertinite-rich Highveld coal, were found to be surprisingly similar in bulk properties.\textsuperscript{1} The coals had similar carbon content (dmmf), vitrinite reflectance (mean max) and average aromatic cluster sizes (NMR derived). The main differences between the coals were the higher aromaticity, lower hydrogen content, more ordered structure (X-ray and HRTEM), and the larger degree of crystal stacking (X-
ray scattering) of the Highveld coal. Since the coal structure has been characterized, and
there are many similarities, it presents a good opportunity to explore maceral influences
on char morphology and burnout without the need to employ maceral separation
approaches. Although maceral separation techniques have improved over the years, it still
remains a tedious and time-consuming process that yields relatively small amounts of
single macerals.6-8

Both gasification and combustion occurs as complex heterogeneous gas-sold reactions9
with reaction rates proportional to the total accessible surface area of the char.10 Interplay
between surface reactions and mass transfer by diffusion influences the rate at which the
reactions take place. Reactivity can be used to describe the relative degree of ease with
which coal will undergo conversion reactions.11 According to Walker12 the ease of
conversion is dependent on three parameters; the concentration of the carbon active sites,
the concentration and dispersion of inorganic species (which can act as catalysts for the
reactions) and the transfer of reactive gases through the pore system of the char. These
parameters are affected during devolatilization due to evolution of surface area,13
effective oxygen diffusion through the changing porous char,14 developing regions of
anisotropy,15 maceral reactivity differences,7 mineral matter influences (includes
increased reactivity due to catalysis as well as decrease due to obstruction of reactive
sites and energy loss due to phase change),16 changes in functional groups (e.g. hydrogen
loss), and alterations to the aromatic layers (due to rearrangement and oxygen
reactions).17
Chapter 2
Comparison of the Combustion Reactivity of TGA and Drop-tube Generated Chars

2.1 Abstract

Thermogravimmetrical analysis (TGA) is the most convenient, rapid and widely used methods for studying coal and char reactivity.\textsuperscript{18-20} Due to limitations in heating rates and maximum temperature the extrapolation of reactivity parameters to industrial systems remains controversial. Here, a TGA was used to generate chars from inertinite-rich and vitrinite-rich South African coals, under slow heating conditions (10°C/min) to a temperature of 950°C. Prior to devolatilization, the coals were wet screened to obtain an narrow particle size distribution between 37 and 74µm. Combustion reactivities of the resulting chars were determined isothermally in the TGA, and showed a slightly higher reactivity for the vitrinite-rich char compared to the inertinite-rich char, with maximum reaction rates of ~0.139(±0.01) and 0.121mg/mg.s, respectively. Reactivity differences under these conditions motivated further investigation of combustion reactivity at more industrially relevant conditions. Chars were generated in a drop-tube reactor (DTR) under rapid-heating conditions at 1400°C. Burnout profiles of DTR-generated chars were measured in a TGA and compared to those of the TGA-generated chars. The difference between the maximum reaction rate of the two DTR chars, were 4 times larger than the difference between the rate maximum observed in the TGA chars. Although both DTR chars displayed a maximum in reaction rate at lower conversion (around 30% conversion), the DTR chars from the two coals showed opposing trends when compared to the TGA chars. While the TGA char from the inertinite-rich coal was more reactive than the DTR char from the same coal, the DTR char from the vitrinite-rich coal was more reactive than its TGA char. The DTR chars of the inertinite- and vitrinite-chars had maximum reaction rates of 0.085 and 0.159mg/mg.s, respectively. These differences are
most likely due to chemical and physical structural differences in the chars but further structural analysis of the chars is necessary to corroborate this. Therefore, char samples were collected at various residence times in the DTR, prior to full devolutilization, to allow investigation of structural transformations during heat treatment to aid in better understanding of the final char structure. These chars were characterized through proximate and ultimate analyses, and followed the expected trends of decreasing volatile matter, oxygen and hydrogen. Solvent (THF) extraction was used to remove the tar fraction present in the Waterberg (vitrinite-rich) samples collected at early intermediate residence times. The presence of tar can influence the devolatilization and combustion behavior.

2.2 Background

In coal utilization processes, such as pulverized fuel combustion, the heterogenous oxidation reactions of char play an important role in the overall conversion, which determines the total residence time required. Char combustion can be limited by gas-phase diffusion and the rate of chemical reactions, depending on parameters such as temperature, reactor size, and particle size distribution. The degree of thermoplasticity during coal to char transition is dependent on the maceral composition, rank, and heating rate. These factors affect the transformations to chars producing various char structures, morphologies, and hence reactivity. Macerals are the individual organic components that reflect differences in original plant material, depositional environment and the degree of coalification. Vitrinite is mainly from deposition of woody plant material (e.g. bark, wood, leaves, and roots) while inertinite is formed from plant material that have been oxidized prior to burial (e.g. decomposition caused by fire or aerobic bacterial decomposition). The maceral composition of a coal will influence reactivity since each maceral group has differences in chemical properties such as structural order of the aromatic structure, oxygen content and cross-linking that influences the degree of plasticity during heat treatment for the bituminous coal rank range. The distribution of the
macerals within a particular coal can vary, which results in different structural parameters, and as a consequence, different combustion behavior. Combustion of vitrinite-rich coals has been well studied but less is known about the combustion behavior of inertinite-rich coals, that is often the major maceral in Southern hemisphere, Permian aged coals.

Jones et al. 22 studied the influence of the rank and maceral composition on char. They compared the porous structure of char produced from an inertinite-rich coal with the char from a vitrinite-rich coal. By using reflective light microscopy it was found that chars derived from vitrinite produce cenospheric chars (as classified by Cloke and Lester 23), while inertinite derived chars were mainly honeycomb (dense) and unfused chars. Similar trends were found by work done by Benfell et al.[14] Image analysis was also used to measure the particle volume and pore size distribution. This showed that both the char porosity and pore size decrease in the order cenosphere > honeycomb > unfused char. The influence of increasing coal rank was also studied and found that the porous structure of inertinite-derived chars stayed relatively unchanged, while vitrinite-derived chars was found to decrease in porosity. Consequently the structure of vitrinite and inertinite chars converges at a higher rank and predicts that high-rank coals with different maceral contents might behave similarly. Other work suggest that concluding to relationships like these appear equivocal considering the diverse and complex nature of coal.24

South Africa’s energy economy is dominated by coal, where it accounts for approximately 79% of the total energy production. Whilst the country has large reserves of inertinite-rich and vitrinite-rich bituminous coals,1, 3 to date no research has been published comparing the devolatilization or combustion behavior of these maceral diverse South African coals. Since the coal structure of an inertinite-rich and vitrinite-rich South African coal have recently been well characterized,1 and since they have the same depositional environment and rank, it presents a good opportunity to explore maceral
influences on char morphology and burnout without the need to employ maceral separation approaches.

There has been continuing efforts in the area of maceral separation by utilizing methods such as density gradient centrifugation but these methods can be extremely time-consuming.\textsuperscript{25} It is mostly effective with demineralized samples and unrealistically small particle size for combustion studies due to particle size vs. maceral liberation problem.\textsuperscript{8, 26, 27} Still, not a lot of work has concentrated on the combustion characteristics of single coal macerals, partly due the limited availability of sufficient amounts of individual macerals from density separation techniques.\textsuperscript{6, 22} Trace amounts of the alkali metal salt (CsCl) used for density separation remain on the samples after washing and could slightly increase combustion reactivity, due to the catalytic effect of CsCl.\textsuperscript{6} In addition, standard characterization techniques such as X-ray diffraction and electron microscopy cannot be used to identify macerals, which further complicates the study of individual macerals.\textsuperscript{7}

Intrinsic char reactivity has been recognized as an important factor affecting char burn-out under pulverized fuel combustion conditions. Methods to determine char reactivity are therefore of importance not only for fundamental research purposes but also to coal-fired utility plant operators and designers. TGA is a widely used approach that provides a convenient, inexpensive, and reasonably rapid means of evaluating combustion kinetics of char. Thermogravimetical analysis allows mass and heat transfer effects to be decoupled from intrinsic reactivity.\textsuperscript{18, 28} It offers the ability to control heating rate, temperature, and gas environments, which allows the calculation of intrinsic rate parameters. Rate parameters can be determined at either a constant temperature (isothermal) or during combustion at a constant heating rate (non-isothermal).

The effect of heat treatment on reactivity has been studied, and generally disordered carbons become less reactive as heat-treatment temperature increases.\textsuperscript{17} Conversely,
Chars generated at higher heating rates are expected to achieve higher reaction rates since rapid-heating can enhance thermoplasticity and porosity which provides larger available surface areas.\textsuperscript{18,29} A drop-tube reactor is a medium scale device that is able to create an environment that more closely simulates industrial conditions by providing high temperatures, short residence times, and a high heating rate (~10\textsuperscript{5}\textdegree C/s). Since these operating conditions affect char structure and consequently combustion reactivity, chars were generated in the DTR. The reactivity of the chars generated under these conditions can then be determined. A TGA provides an accurate means of evaluating the inherent reactivity at low combustion temperatures, where no diffusion limitations are present (<500\textdegree C). It has also been shown to be effective in measuring reactivity at higher temperatures (>800\textdegree C), where diffusion of products and reactants to surfaces has a significant effect on reaction rate.\textsuperscript{30}

2.3 Experimental

2.3.1 Coal Preparation

Two coal samples collected in South Africa: (1) Run-of-mine Highveld coal, and (2) commercially cleaned (density separated) Waterberg coal, were used in this study. The coal samples were pulverized with a laboratory scale ball mill and wet-sieved into a narrow size cut of 200 x 400 mesh, (37 – 74\textmu m) which is similar to that of commercial pulverized combustion. Wet screening was performed to achieve a much narrower size fraction than the more common dry sieving approach. Coal was placed on the top sieve and carefully rinsed with a water spray nozzle capturing the water/particles passing in a bucket. Rinsing was performed until the liquid leaving each sieve is no longer turbid. The fractions remaining on each sieve is then rinsed off on to a paper filter and dried in an oven overnight (100\textdegree C). A Microtrac dynamic laser light scattering device (S3500) was used to determine particle size distributions of the dry- and wet-screened coals.
2.3.2 Char Generation in TGA

Wet screened samples of the vitrinite-rich Waterberg and inertinite-rich Highveld coals were used to generate chars under slow heating conditions. A Perkin-Elmer-7 TGA was used to generate small amounts of char (15mg), in a nitrogen atmosphere at a heating rate of 10°C/min to 900°C.

2.3.3 Char Generation in Drop-Tube Reactor

Char samples were generated in a drop-tube reactor heated to 1400°C. An atmosphere of 1% oxygen in nitrogen was maintained to aid in the combustion of tars. Char samples were collected at different residence times by varying the height of the water-cooled sampling probe. Approximate residence times were estimated mathematically by using gas flow rates, gas and coal densities, particle size, and reactor specifications. For these calculations it was assumed that all particles fall at the same velocity. Temperature profiles have been calculated for the drop-tube reactor which indicated that particles will only reach the desired furnace temperature a few centimeters away from the injector. All the char samples were collected at residence times where the gas would have reached the desired furnace temperature of 1400°C. Pre-screening experiments indicated that the vitrinite-rich coal devolatilized more rapidly and so samples spanned the 240ms and 400ms residence times for the vitrinite-rich and inertinite-rich coals, respectively. Table 2-1 shows the location, and corresponding residence time, where four char samples for each coal was collected. These sampling locations were chosen to represent different stages of devolatilization.
Table 2-1: Sampling collection scheme for DTR-generated chars

<table>
<thead>
<tr>
<th></th>
<th>Highveld coal</th>
<th></th>
<th>Waterberg coal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corresponding</td>
<td>Residence time</td>
<td>Corresponding</td>
</tr>
<tr>
<td></td>
<td>probe height</td>
<td>(ms)</td>
<td>probe height</td>
</tr>
<tr>
<td>(inches from top)</td>
<td></td>
<td></td>
<td>(inches from</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>top)</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>6</td>
<td>120</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>8</td>
<td>160</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>20</td>
<td>400</td>
<td>12</td>
<td>240</td>
</tr>
</tbody>
</table>

2.3.4 Proximate and Ultimate analyses

Proximate analyses were performed in a Perkin-Elmer-7 TGA in accordance with ASTM D-3172, but with a slightly slower heating rate than the required 50°C/min. The carbon, hydrogen and nitrogen content were determined using a LECO 600 CHN analyzer following the ASTM D5373. The results were corrected for moisture and mineral matter/ash yields.

2.3.5 Tar Extraction

Tetrahydofuran (THF) was used to extract tars from the char samples. Some of the char samples had a very strong tar odor that would “contaminate” the char data. Unger et al. showed THF was an effective solvent for solvating pyrolysis tars. Semi continuous, Soxhlet extraction was used which allows the buildup and then flushing of the solvent in the extraction chamber. After each cycle, ~30mins, the extract-containing THF was siphoned back into the boiling flask. A 1g char sample was put in a thimble, secured with glass wool and the extraction was performed for 24hours. Multiple runs produced the desired quantity of tar-free char.
2.3.6 Char Combustion Reactivity by TGA

A TGA was used to determine combustion reactivities of the chars in air, isothermally, at 550°C. The samples were heated in nitrogen until the weight stabilized at the desired temperature, the nitrogen flow was then switched to air and the weight loss was monitored at constant temperature. The sample mass was normalized with respect to the moisture and ash yield. The reaction rates were calculated, and plotted versus the total conversion with the maximum rates being compared.

2.4 Results and Discussion

2.4.1 Char Properties

A narrow time-temperature history is desirable for generating chars in a drop-tube reactor. For this work a narrow range of particle sizes 37 – 74 µm was chosen since this is comparable to commercial pulverized combustion. As seen in Table 2-2, dynamic laser-light scattering determined with a Microtrac S3500 indicated that dry-screening of the two coals failed to produce the desired narrow distribution. Both dry-screened coal samples had an mean volume based particle size (Dv50) much larger than the preferred range (115µm and 130 µm for the Highveld and Waterberg coal respectively), as well as a high standard deviation (>50 µm). Pulverized coal particles have a sharp, elongated shape which can prevent particles from passing through a specific mesh opening if the long side is larger than the mesh opening. For this reason wet-screening was employed since it increases the probability of long, narrow particles passing through the mesh opening. Fine particles tend to stick to coarser particles and do not pass the screens, and wet screening can achieve a better degree of separation between individual fractions. Table 2-2 shows that the wet-sieving approach provided significantly narrower size distributions. The average particle sizes of the coals are effectively the same (63 and 62
µm) and are within the desired range. The standard deviation is also significantly smaller indicating a more appropriate distribution for narrow time-temperature histories. Even though wet screening is time-intensive, it was necessary for obtaining an accurate size distribution.

Table 2-2: Particle size determined by Dynamic laser-light scattering (volumetric basis)

<table>
<thead>
<tr>
<th></th>
<th>Dry-screened</th>
<th>Wet-screened</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Highveld</td>
<td>Waterberg</td>
</tr>
<tr>
<td>Avg. particle size (µm)</td>
<td>115</td>
<td>130</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>55</td>
<td>69</td>
</tr>
<tr>
<td>D₅₀ (µm)</td>
<td>113</td>
<td>125</td>
</tr>
</tbody>
</table>

Table 2-2 shows the proximate analyses determined at different estimated residence times for both coals at different stages of devolatization. As expected, the volatile matter and hydrogen content decreased with residence time. The final char samples are almost fully devolatilized with residual volatile matter of 2.7 and 4.4% for Highveld and Waterberg respectively. The Waterberg (vitrinite-rich) coal devolatilizes much faster than the Highveld coal as expected. After 200ms in the DTR, the inertinite-rich char contains 12% volatile matter by mass (according to TGA determined ASTM proximate analysis) and the vitrinite-rich char has 10% volatile matter, which is a significant difference if the initial higher volatile matter of the vitrinite-rich coal (36.5%) is taken into account. The hydrogen, carbon, and nitrogen content in are shown on a dry, ash-free basis. The atomic hydrogen to carbon (H/C) ratio was also calculated and is presented in the table.
Table 2-3: Char proximate and ultimate analyses

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Inertinite-rich Char</th>
<th>Coal</th>
<th>Vitrinite-rich Char</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>H1</td>
<td>H2</td>
<td>H3</td>
</tr>
<tr>
<td>Residence time</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ms)</td>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% dry)</td>
<td>24.4</td>
<td>22.1</td>
<td>12.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% dry)</td>
<td>47.5</td>
<td>47.7</td>
<td>52.4</td>
<td>57.9</td>
</tr>
<tr>
<td>Ash yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% dry)</td>
<td>28.1</td>
<td>30.2</td>
<td>35.2</td>
<td>38.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% daf)</td>
<td>4.4</td>
<td>4.2</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% daf)</td>
<td>83.7</td>
<td>78.0</td>
<td>82.3</td>
<td>91.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% daf)</td>
<td>2.0</td>
<td>2.1</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Oxygen+Sulfur</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% daf)**</td>
<td>9.9</td>
<td>5.7</td>
<td>2.4</td>
<td>5.4</td>
</tr>
<tr>
<td>H/C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(% dry)</td>
<td>0.65</td>
<td>0.65</td>
<td>0.45</td>
<td>0.19</td>
</tr>
</tbody>
</table>

** The original sulfur content of the Highveld and Waterberg coals were 1.99% and 1.13% respectively.

As devolatization progresses, the H/C ratio of both chars decreased and the final inertinite-rich char has a slightly lower H/C compared to the final vitrinite-rich char. A lower H/C ratio can be associated with a higher degree of order, that is expected to result in a lower reactivity.17, 29, 39 Further characterization is necessary to study differences in the structural ordering of the generated chars.
2.4.2 Tar Extraction

Even though 1wt% O\textsubscript{2} was included in the drop-tube atmosphere (99% N\textsubscript{2}) to combust undesired tar. The tar overwhelmed the oxygen available in the early Waterberg vitrinite-rich chars only. The chars also had a strong tar odor. The large quantity of tar caused problems during operation of the drop-tube and sampling. Since tar is essentially volatiles that are condensed at room temperature\textsuperscript{40} it will contribute to the volatile matter yield during proximate analysis, which is the likely cause of the higher volatile matter yield for the WB2 sample: 23.4% volatiles at estimated residence time of 160ms compared to 20.8% at 120ms. THF can be used to extract the tar.\textsuperscript{37, 41, 42} Therefore, THF soxhlet extraction was used to extract the tar from the char samples. Proximate analysis of the residue was performed to evaluate the change in volatile matter yield. During Soxhlet extraction of the Highveld chars, the extract did not change color and the subsequent proximate analysis did not change indicating that no tar was present in the inertinite-rich char samples. For the vitrinite-rich Waterberg chars, the extract changed to a brownish yellow color for the WB1 and WB2 samples. A total weight reduction of 14.1 and 16.4% for the WB1 and WB2 samples, respectively, were obtained after the THF extraction. No change was observed for WB3 and WB4. Figure 2-1 shows the volatile matter (dry ash-free basis), as determined by proximate analysis, for the Waterberg chars before and after THF extraction.

For the WB1 and WB2 samples (sampled at 100ms and 200ms respectively) there is a decrease in volatile matter after extraction, while there is no change in composition for WB3 and WB4 samples. The oxygen could have combusted the tar after longer residence times, which will explain the absence of tar after 300ms in the drop-tube. It is also possible that cracking of tar molecules occurred after longer residence times, producing volatiles and char. The subsequent chapters will focus on the behavior of the ‘final chars’, therefore the presence of tar in the char at earlier residence time does not affect those
chars. The presence of liquid tar at early stages of devolatization in Waterberg coal could have an effect on the evolution of char structure and therefore influence the final structure.

2.4.3 Combustion Reactivity Differences of Chars Generated in Different Equipment

Chars generated from inertinite- and vitrinite-rich coals are expected to have different combustion reactivities due to macerals producing different chemical and physical structures. Prior to generating chars in the DTR, chars were generated from the two coals in a thermogravimetrethical analyzer (TGA) to determine whether there are any (inherent) reactivity differences between the two coals and to examine the influence of heating conditions on char reactivity. Chars from each coal were generated by slow heating (10°C/min) in the TGA at 900°C in nitrogen. After devolatilization in the TGA, the chars were combusted isothermally in air at 550°C. The burnout profiles of the TGA-generated chars, shown in Figure 2-2, have similar shapes but the Waterberg char has a slightly higher maximum reaction rate compared to the Highveld char (~0.015 mg/mg.s larger).
The vitrinite-rich coal was expected to undergo more thermoplastic transformations resulting in a more porous char, which should increase the access of reacting gases to the reactive surface area. Competing factors include; the low heating rate in the TGA not allowing the development of a highly porous structure in the Waterberg coal, and the thermoplastic transformations during heat-treatment resulting in a more ordered carbon structure, which is usually associated with a lower reactivity. To further investigate the combustion reactivity differences, chars were generated under different conditions in a drop-tube reactor.

The higher temperature and faster heating rates in the drop-tube reactor (DTR), as compared to a TGA, was expected to produce chars with greater differences in physical and chemical structures, resulting in different combustion reactivities. To evaluate this, combustion reactivities of the final DTR chars were determined isothermally in a TGA at 550°C. Figure 2-2 compares reaction rates measured at 550°C in the TGA, for Waterberg and Highveld chars generated in the TGA with those generated in the DTR.

![Figure 2-2: Comparing reactivity of DTR generated chars with TGA generated chars](image)

The shape of the DTR-generated char profiles differs from the TGA-char profiles; where a more prominent maximum in the reaction rate is observed at lower conversions. The
occurrence of such a maximum was investigated by Naredi et al.\textsuperscript{20}, who attributed the maximum to the transition from diffusion control regime to kinetically controlled regime. This study used one coal and therefore only observed a single trend of increasing reaction rates associated with an increase in devolatilization temperature and heating rate (obtained in the same DTR used here). They, among others also found that a maximum in the rate profile strongly depends on the time-temperature history as well as the combustion conditions. Figure 2-2 shows that the Waterberg DTR generated char (W DTR-char) reaches a maximum combustion rate of \(~0.16\text{mg/mg.s}\), which is almost double maximum rate achieved by combustion of the Highveld DTR char (H DTR-char). For the Waterberg coal, higher reaction rates were achieved for chars generated in the DTR, than for those generated in the TGA. The Highveld samples however attained higher reaction rates for the TGA-generated chars than for the DTR-generated chars; 0.12mg/mg.s compared to 0.09mg/mg.s. Chars generated at higher heating rates are generally expected to achieve higher combustion rates since rapid-heating can enhance thermoplasticity and porosity which often will produce larger available surface areas.\textsuperscript{18, 29} Furthermore, the more porous structure will improve oxygen pore diffusion, resulting in an overall higher combustion rate during regime II conditions. The thermoplastic behavior of the coals is however rank dependent and in the simplest sense the inertinite-rich coals are rank displaced to a higher relative rank than the vitrinite coals at similar maturation (as used here). The Highveld DTR-chars are not expected to swell to the same extent as the Waterberg DTR-chars and due to limited plasticity should not form highly porous chars. This will contribute to Highveld chars, generated under a high heating rate, will have a higher reactivity.

Additionally, the DTR chars were exposed to a higher maximum temperature (\(~1,400°C\)) than the TGA chars (900°C) possibly causing a higher degree of ordering or thermal annealing. This will result in the loss of carbon active sites which could decrease the overall reactivity.\textsuperscript{20, 43} A higher reactivity could also be due to incomplete devolatilization of the DTR chars, where any unreleased volatile matter will react upon onset of combustion. Even though the proximate analysis of the Highveld DTR char (HV4)
indicates unreleased volatiles (2.7% volatile matter (dry basis)), the Waterberg DTR char (WB4) has slightly more unreleased volatiles (4.5% volatile matter (dry basis)) which could also have an influence on behavior.\textsuperscript{44} When volatiles are released, a volatile ‘cloud’ can form which limits the access of oxygen to the char. Although residual volatiles influence the combustion behavior, La Manquais et al.\textsuperscript{18} indicated that only a 10-fold volatile increase would cause an appreciable change in the char’s combustion reactivity. Therefore, the difference in residual volatile matter between the Waterberg and Highveld char is not expected to have a major impact on reactivity. Establishing good correlation between these chars and their behaviors is not possible since there are too many influencing factors (devolatilization temperature, heating rate, coal, and char properties). To draw better correlations, some of the factors should be isolated.

\subsection*{2.5 Conclusion}

Chars from inertinite-rich and vitrinite-rich South African coals were generated in a thermogravimectrical analyzer (TGA) at slow heating rates (10°C/min) to 900°C. Subsequent combustion reactivities, also measured in a TGA, indicated that the vitrinite-rich char was slightly more reactive than the inertinite-rich char. To further explore the reactivity differences associated with these maceral diverse coals, chars were generated under rapid-heating conditions (~10^5°C/s) in a drop-tube reactor (DTR) at 1400°C, since it provides chars more comparable to industrially generated char (pulverized coal combustion). Vitrinite char devolatilized at a more rapid rate than the inertinite-rich chars. Vitrinite char was more reactive in both cases of TGA slow heating and drop-tube high-heating rate chars.

For the inertinite-rich Highveld coal, the DTR-generated char had a lower maximum combustion rate than the TGA-generated char; ~0.09mg/mg.s compared to 0.012 mg/mg.s (±0.01). The vitrinite-rich Waterberg coal showed the opposite trend, with the DTR-generated char reaching a higher maximum rate (0.16) than the TGA-generated
Differences between the reactivity of DTR- and TGA-generated chars can be attributed to varying contributions of factors such as the accessible surface area that relates to the porous structure, and the degree of structural order that relates to the carbon active sites. Further investigation of the contributing factors is necessary to correlate the behavioral differences to specific devolatilization conditions, coal, or char properties.

At short residence times, a notable amount of tar was observed in the collected vitrinite-rich chars. Solvent extraction (THF soxhlet extraction) was used to remove the tar fraction, and subsequent proximate analysis confirmed the presence of tar. The presence of tar can cause agglomeration of particles and shows up as volatile matter during a proximate analysis, which affects characterization results. Structural characterization of the chars are necessary to evaluate the contributions of different chemical and physical properties to the overall reaction rate.
Chapter 3
Quantifying Combustion Reactivity Differences Between Inertinite-Rich and Vitrinite-Rich South African Coal Derived Chars

3.1 Abstract

Determining the kinetics of char combustion is important for combustor design and modelling of industrial, combustion processes. It is also a useful measure for quantitatively comparing different coals and predicting process performance. Here the combustion reactivity of two South African coal chars generated in a drop-tube reactor from narrow cuts are compared: a vitrinite-rich and an inertinite-rich South African coal after pyrolysis to simulate devolatilization in pulverized coal combustion. The intrinsic rate parameters were investigated using TGA isothermal and non-isothermal approaches, and reactivity was also evaluated using TPO. The results obtained from all three methods, indicated that the char from the vitrinite-rich coal has higher combustion reactivity than the inertinite-derived char. The vitrinite-derived char reached higher maximum combustion rates than the inertinitie-derived char during all isothermal combustion runs. Non-isothermal TGA burnout profiles showed the inertinite-rich char had a burnout temperature of 680°C, slightly higher than the vitrinite-rich char’s 650°C. The temperature at the maximum rate of weight loss was reached at 480°C for the vitrinite-rich char and at 530°C for the inertinite-rich char indicating significant reactivity differences. The role that the large ash yields have on reactivity was quantified by comparison of raw and demineralized chars. Results indicated that ash removal (or demineralization) increases combustion reactivity under the studied conditions. The governing phenomenon of inorganic material on reactivity is most likely the hindrance effect the presence of ash has on the accessibility of oxygen to the active surface area. The ability of the shrinking core and random pore models to predict combustion behavior of these chars was evaluated by fitting the models to the TGA combustion reactivity data. At lower combustion temperatures, both models were able to predict combustion
behavior with reasonable confidence. At higher temperatures however, the models failed to predict behavior and there was a significant variance between the predicted and measured values.

3.2 Background

The combustion of coal is the process of utilizing the inherent energy within coal. Coal combustion is preceded by a pyrolysis step in which the volatiles are driven off and a residual carbonaceous solid, referred to as char is formed and subsequently combusted.$^{43, 45, 46}$ Both the physical and chemical structure of char play a role in the overall combustion reactivity under zone II conditions relevant to pulverized coal combustion.

Imperative to understanding combustion reactivity of coal chars is the knowledge of macroscopic structural changes during combustion. To this end, two mathematical models are commonly used: the shrinking core model and random pore model. This shrinking core model$^{47}$ is applicable to chars with low porosities, such that the combustion reagent (oxygen) is mostly restricted to the inner particle. The reaction will therefore occur predominantly at the surface of the char or at the interface between the unreacted char and, if present, the ash layer. Conversely, for chars with a more porous structure whereby reacting gases are free to diffuse throughout the inner particle, the shrinking core model fails to accurately predict the conversion behavior.

The random pore model, proposed by Bhatia and Perlmutter$^{48, 49}$ and Gavalas$^{50}$ takes into account the porous nature of the char by assuming reactions take place on the surface of growing and collapsing pores within the particle. This is achieved through calculating a structural parameter which is unique to a specific char and dependent only on the initial properties of the char like pore length, porosity, and surface area. The appropriateness of these reactivity models will be evaluated.
3.2.1 Factors Influencing Reactivity

According to Walker\textsuperscript{12} the rate of char conversion is dependent on three factors; the concentration of carbon active sites, the concentration and dispersion of inorganic species and the transfer of reactive gases/products through the pore system. The contribution of these factors depends on the thermal (time-temperature) history of the char, coal rank, mineral matter quantity/type/dispersion, and maceral composition.\textsuperscript{28, 51} The thermal history of char includes the heating rate as well as the maximum temperature at which devolatization occurs.\textsuperscript{52} It is well known that deactivation occurs when char is exposed to high temperatures and as the maximum temperature increases, the combustion reactivity is expected to decrease.\textsuperscript{53, 54} Deactivation associated with severity of devolatization could be attributed to the loss of total carbon active sites, as structural alignment of carbon layers increase and hydrogen decrease.\textsuperscript{52, 53} The reactivity will also be influenced by the heating rate during devolatization, since heating rate affects thermoplastic behavior which in turn affects chemical and physical properties of the char.\textsuperscript{24} Generating char in slow heating rates limits the evolution to a porous structure.\textsuperscript{18}

The inorganic portion of the coal contributes to combustion behavior, particularly in the low-quality (high mineral matter) coals of South Africa and other Gondwana coals that can contain >20% mineral matter by mass. In comparison N. American coals are typically <15% by mass. The presence of mineral matter generated ash in the char may reduce reactivity because of a hindrance or blocking effect by the ash layer. Therefore, upon demineralization, the total accessible surface area and porosity is expected to increase in most cases, which consequently increases reactivity.\textsuperscript{55}

Selecting an appropriate demineralization method is important since the process may result in oxidation of the sample, likely decreasing the reactivity, or in the case of certain chemicals, e.g. nitric acid, alter the chemical structure.\textsuperscript{26, 56} Depending on the amount, extent of dispersion and chemical composition of the inorganic fraction, it could also
have a catalytic effect on the reactions. Different metals, metal oxides and salts present in coal have been shown to increase the catalytic activity. High concentrations of iron, calcium and magnesium are most significant to gasification reactivity. The presence of ash could also influence the thermal behavior since ash consumes energy to be heated, and the radiative properties of ash differ from the char. The aforementioned effects play a vital role in the operation of practical combustion systems where it affects the overall heat transfer, fouling and slagging on reactor walls, corrosion, sulfur pollutant formation, and formation of fly ash.

Depending on temperature, the oxidation rate of char could be limited by chemical steps like adsorption of the reactants, reaction and desorption of products, or by the diffusion of the reactant and product gases. As a result, three different rate-controlling zones or regimes can be identified which indicates whether diffusion, chemical control or a contribution of both are dominant at a specific temperature. Figure 3-1 qualitatively represents these rate-controlling zones in a logarithmic rate versus inverted temperature graph.

Figure 3-1: Different reaction regimes
In the lower temperature regime I, the chemical reaction is the rate-determining step, the oxidizing gas diffuses through the particle fast enough to reach the internal surface.\textsuperscript{58} The only factor affecting the overall rate under these conditions is the rate at which the surface reaction takes place (inherent reactivity).\textsuperscript{28} The total accessible surface area and amount of active sites are therefore important in this regime. This occurs at low temperatures and usually with larger particles.\textsuperscript{11} When reaction temperatures increase, the effect of pore diffusion becomes prominent and will be a rate limiting factor (regime II).\textsuperscript{11, 46, 58, 59} As the temperature increases even more, the surface reactions are so rapid that the reaction takes place on the outside of the particle. It is therefore only the rate at which diffusion occurs that determines the overall apparent reaction rate in this zone. Consequently, the apparent activation energy will be zero in this regime \textsuperscript{46, 58} which is commonly referred to as regime III. The porous network of char will especially be important during regime II conditions since it controls the intra-particle diffusion.

Different mechanisms of diffusion exist,\textsuperscript{46} depending on the shape and size of pores. When operating under regime III conditions, diffusion occurs primarily through larger macropores\textsuperscript{43, 58} and is based on molecular collisions, similar to the bulk gas phase. For bulk diffusion, diffusivity can be calculated as the product of the velocity of the molecules and their mean free path. When the size of the pore is smaller than the mean free path of the molecules, the mechanism of diffusion changes. Instead of colliding with each other, the molecules will now also collide with the pore walls. This is referred to as Knudsen diffusion. It is this type of diffusion that plays a controlling role in the observed reaction rate during regime II. Consequently, the activation energy in this region is given as only about half of the activation energy of region III.\textsuperscript{46, 58}

\subsection*{3.2.2 Determine Intrinsic Combustion Reactivity}

Determining kinetic parameters for coal combustion is complex since the chemical reactions can be obscured by pore and boundary layer diffusion. To keep diffusion
limitations to a minimum, reaction kinetics should be determined at low temperatures. Russel et al.\textsuperscript{60} suggested that if the Arrhenius plot is almost linear, the reactivity for that char could adequately be described by simple first-order kinetics. Pseudo-first order kinetics were applied between 10 and 90\% carbon burnout at low combustion temperatures (450 - 550°C) to allow for the calculation of a composite rate constant ($k$) using Equation 3-1\textsuperscript{18,30}

$$\frac{da}{dt} = k(1 - \alpha) \quad \text{Equation 3-1}$$

Where $\alpha$ is the fractional weight conversion ($1-m/m_o$). The data used for calculations were limited to data after 10\% conversion to limit scatter associated with release of residual volatile matter, and up to 90\% as this is generally consider to be a reliable upper bound for thermogravimmetrical data.\textsuperscript{20,61} Integration of Equation 3-1 and using exploiting the fact that the fractional conversion at the start of the experiment is zero ($\alpha = 0$ at $t = 0$) as initial condition, yields Equation 3-2:

$$-\ln(1 - \alpha) = kt \quad \text{Equation 3-2}$$

The rate constant at a specific temperature can therefore be determined graphically from the gradient of plotting $-\ln(1 - \alpha)$ versus $t$.

The rate constant, $k$ is also related to temperature through the Arrenhius expression:

$$\ln k = \ln A - E/RT \quad \text{Equation 3-3}$$

Where $A$ is the pre-exponential factor and $E$ the global activation energy. These values can be determined by plotting the logarithm of the rate constant determined at different temperatures versus inverted temperature ($1/T$). According to Equation 3-3, this type of plot is linear with a slope of $-E/R$ and a y-intercept of $\ln A$. 

24
Temperature-programmed oxidation (TPO) is a technique that provides information on structure (degree of crystallinity) as well as reactivity of carbonaceous material. Characterization is based on the oxidation of different carbon domains as the structural order directly relates to reactivity.\(^5^3\) The technique involves heating the sample from near-ambient temperatures at a specific heating rate in an oxygen-rich atmosphere. The amount of carbonaceous material oxidized is determined through monitoring the exit gas (CO\(_2\)). The position and size of the peaks in the resulting CO\(_2\) profile provides valuable information on the oxidative reactivity and the distribution of structural order.\(^6^2\) Low-temperature peaks correspond to less-ordered (more reactive) carbon, whereas the high-temperature peaks in the profile are attributed to structurally more-ordered (less-reactive) carbon. Even though TPO results ought to be in good agreement with reactivity trends obtained in thermogravimetric analysis (TGA), TPO has the advantage of directly measuring the reacted carbon, not inferring it from the sample mass change. It has successfully been used to characterize carbon nanotubes,\(^6^3\) nanofibers,\(^6^4\) coal,\(^6^5\)\(^ ,^6^6\) cokes,\(^6^7\) and other carbonaceous materials.\(^6^2\),\(^6^8\),\(^6^9\)

### 3.2.3 Mathematical Modeling of Reaction Kinetics

Reactivity can decrease with a decrease in pore volume and surface area\(^7^0\), and with increased structural ordering.\(^5^4\) Correlating reactivity with structural features like these can be complex. Several mathematical models have been proposed to model or predict coal reactivity; each with its own set of assumptions and degree of complexity and only some attempting to incorporate structural features.\(^1^0\),\(^7^1\),\(^7^2\) Molina & Mondragón\(^7^3\) have stated that, depending on the purpose of the study, i.e. calculating reaction kinetics data or modeling conversion-time data, a particular model may be more suitable than another.\(^7^3\) Some of the most widely used models are the random pore model and the shrinking core model which will be briefly discussed here.
The shrinking core model, as proposed by Székely and Evans\textsuperscript{74}, assumes that a porous char consists of a network of uniformly distributed, nonporous grains, and that the reaction takes place on the surface of these grains. In the shrinking core model the reactions take place mostly on the surface and therefore it burns out at a near constant density with a decreasing particle diameter.\textsuperscript{73} Figure 3-2 shows the sequential operation of three rate controlling phenomena; diffusion through the gas film, diffusion through the ash layer and surface reactions at the central core.

If the diffusion through the gas film controls the overall reaction rate, the shrinking core model is defined with the expression in Equation 3-4:

\[
t = \tau_{GFD} \times X
\]  

\textbf{Equation 3-4}
Where $\tau_{\text{GFD}}$ is a constant for gas film diffusion (GFD) which is also equal to the time at complete conversion. Detailed derivations for the equation and $\tau$ are given in Levenspiel.\textsuperscript{75} The expression for GFD is defined in Equation 3-4:

$$t = \tau_{\text{GFD}} \times (1 - (1 - X)^{1/2})$$ \hspace{1cm} \text{Equation 3-5}

When the resistance of diffusion through the ash film controls the reaction rate, the shrinking core model is expressed in Equation 3-6:

$$t = \tau_{\text{AFD}} \times (1 - 3(1 - X)^{2/3} + 2(1 - X))$$ \hspace{1cm} \text{Equation 3-6}

Analogously to the case for GFD, $\tau_{\text{AFD}}$ is a constant equal to the time it takes for complete conversion when ash film diffusion (AFD) is rate controlling. Finally, the case where the rate is controlled by the chemical reaction, and assuming all the pores are spherical, the overall reaction rate can be expressed as in Equation 3-7:

$$t = \tau_{\text{CR}} \times (1 - (1 - X)^{1/3})$$ \hspace{1cm} \text{Equation 3-7}

Here, $\tau_{\text{CR}}$ is a complete conversion time constant where the chemical reaction (CR) is rate controlling. Everson et al.\textsuperscript{76} demonstrated that the shrinking core model with a controlling surface reaction successfully predicts char gasification behavior for inertinite-rich coal. The validity is attributed to inertinite-derived char particles having very low porosities which prevent gases from penetrating. During rapid-heating ($>10^5$C/s) reactions could also occur according to the shrinking core model since they are confined to a thin layer around the particle.\textsuperscript{58} A major shortcoming of the SCM is that it does not take into account the effects of pore diffusion and is therefore mostly applicable to highly non-porous chars.

The random pore model accounts for some structural changes to the char that may occur during the combustion reaction.\textsuperscript{48} It considers the effects of pore growth during the initial stages of combustion, as well as the merging of neighboring pores in the final stages.\textsuperscript{10}
To account for these structural changes, the random pore model\textsuperscript{48} contains an additional parameter, $\psi$, which is a measure of the physical structure of the unreacted particle, defined in Equation 3-8:

$$
\psi = \frac{4\pi L_0 (1 - \varepsilon_0)}{S_0^2}
$$

Equation 3-8

where $S_0$, $L_0$ and $\varepsilon_0$ represent the pore unreacted surface area, pore length, and solid porosity respectively. The random pore model (RPM) is then given by Equation 3-9:

$$
\frac{dX}{dt} = \frac{r_s (1 - X) S_0 \sqrt{1 - \psi \ln(1 - X)}}{1 - \varepsilon_0}
$$

Equation 3-9

According to Molina and Mondragon,\textsuperscript{73} the random pore model is useful when modeling the change in reaction rate as the reaction proceeds. Liu et al.\textsuperscript{77} measured the char surface area as a function of combustion conversion, and found the trend matched what can be predicted by the random pore model.

Calculations have been performed and plots have been generated on smooth part of curves $X$ vs $t$ data, i.e. after initial “burn-off” until the first point of complete conversion.

Equation 3-9 can be rewritten in terms of a warped time variable ($\tau = \frac{r_s S_0 t}{1 - \varepsilon_0}$), such that:

$$
\frac{dX}{d\tau} = (1 - X) \sqrt{1 - \psi \ln(1 - X)}
$$

Equation 3-10

Subsequently integrating of Equation 3-9 and Equation 3-10 yields Equation 3-11 and Equation 3-12, respectively:

$$
t = \frac{2r_s S_0}{(1 - \varepsilon_0) \psi} \left( \sqrt{1 - \psi \ln(1 - X)} - 1 \right)
$$

Equation 3-11
The constants preceding the bracket in Equation 3-11 can be lumped together into a single variable, the time factor ($t_f$):

$$t_f = \frac{r_s S_0}{1 - e_0} \quad \text{Equation 3-13}$$

For the sake of completeness, it is worth stating that Equation 3-12 can be written explicitly in terms of conversion:

$$X = 1 - \exp\left[-\tau \left(1 + \frac{\psi \tau}{4}\right)\right] \quad \text{Equation 3-14}$$

In determining the structural parameter for a specific char, it is assumed that the upper limit for reliable experimental results is at a conversion of 0.9 (occurring at time $t_{0.9}$). Using this upper limit for conversion and dividing Equation 3-11 by $t_{0.9}$ to eliminate the constants preceding the bracket, it follows that:

$$\frac{t}{t_{0.9}} = \frac{\sqrt{1 - \psi \ln(1 - X) - 1}}{\sqrt{1 - \psi \ln(1 - 0.9) - 1}} \quad \text{Equation 3-15}$$

The relationship in Equation 3-15 is valid for all conversions. The structural parameter can be solved by a least squares regression, i.e. finding a value for $\psi$ that minimizes the squared difference between the right hand and left hand side of Equation 3-15. Once the structural parameter is known, it is possible to solve for the time factor variable in Equation 3-11, again by a least squares regression between predicted values for $t$ and actual values for $t$ at a certain conversion.
Once reliable values for $t_f$ and $\psi$ are known at at least 3 temperatures, it is possible to calculate activation energy, reaction order and the apparent rate constant (Equation 3-3 in Everson et al.\textsuperscript{61}) through Arrhenius type plots.

From a modeling perspective there are three important parameters for making predictions with the evolution of the porous structure.\textsuperscript{78} These are the accessible porosity, the internal surface area (both the total accessible and the total active) as well as the transport coefficients of the char particles. Much research has been done to demonstrate that the type of models discussed previously can, by taking these parameters into consideration, make rate predictions that are in good agreement with the experimental data.\textsuperscript{10, 48, 50, 78-80}

### 3.3 Experimental

#### 3.3.1 Temperature programmed oxidation

Temperature programmed oxidation (TPO) was performed using a LECO RC 612 Multiphase Carbon Analyzer. Raw and demineralized samples (~0.003g) were oxidized to carbon dioxide by reaction with ultrahigh purity oxygen in a furnace over a CuO catalyst bed. The sample was heated at a rate of 30 °C/min in flowing oxygen at a rate of 750 mL/min to a maximum temperature of 900 °C. The resulting carbon dioxide was quantitatively measured as a function of the temperature in the furnace using a calibrated IR detector.\textsuperscript{62}

#### 3.3.2 TGA: reactivity and burnout

TGA experiments are usually carried out in two ways: (i) isothermal, where the sample is heated at a constant temperature,\textsuperscript{10, 19, 30, 81} and (ii) non-isothermal, where the sample is
heated at a constant rate. A thermogravimetical analyzer (TGA) was used to determine the combustion reactivity of the char, isothermally, at 450, 500, 550, 800, 900, and 1000°C. Each sample, of the same mass, was heated in nitrogen until it has stabilized at the desired temperature, the nitrogen flow switched to air and the weight loss monitored. To evaluate if the reaction rate was controlled by the intrinsic reactivity (hence regime 1) at the lower temperatures, runs at 500°C were repeated with differing amounts of sample (changing the bed depth). At 500°C, no significant rate change was observed with changes in bed depth, indicating that there is limited to no diffusional influences at this temperature.

The rate of the reaction is defined in Equation 3-16:

\[ Rate = \frac{1}{m_c} \frac{dm}{dt} \]  

Equation 3-16

where, \( m \) is the mass of the carbon on a dry, ash free basis at time \( t \). Conversion, \( X \) can be defined as Equation 3-17:

\[ X = \frac{(m_0 - m)}{m_0} \]  

Equation 3-17

Where \( m_0 \) is the initial mass. Rate can therefore be expressed as Equation 3-18:

\[ Rate = \frac{1}{(1 - X_c)} \frac{dX}{dt} \]  

Equation 3-18

To further evaluate reactivity, non-isothermal burnout profiles were also determined using thermogravimetical analysis. The non-isothermal approach has the advantage of achieving complete conversion in less time. However, the reactivity measured does not mean intrinsic reactivity, particularly at high temperature when the oxygen diffusion plays an important role. A char sample of 8±0.1mg was heated at a constant rate of 5K min\(^{-1}\) with airflow of 100 mL min\(^{-1}\). The burnout profile was used to determine temperatures of maximum mass loss rate, and final burnout. The non-isothermal option presents the advantage of studying the reaction in a single experimental run, and
achieving complete char conversion in a shorter period of time (the isothermal method at low temperatures could take up to 30 hours).\textsuperscript{30}

\subsection*{3.3.3 Demineralization}

Demineralization of the char samples were performed with HCl/HF as suggested by Strydom et al.\textsuperscript{56} to remove mineral matter and hence the disturbance of mineral matter on the X-ray scattering spectra.\textsuperscript{87} Previous research has shown this method of demineralization is the most effective without changing coal properties.\textsuperscript{88} Four grams of each char sample was mixed with 50ml of 6M hydrochloric acid (HCl) in a 300ml Nalgene beaker. The mixture was heated via the use of a water bath to 60$^\circ$C for one hour, whilst continuously stirring. The mixture was left undisturbed for 24 hours, after which the acid was centrifuged and decanted. The HCl-washed char was mixed with 60ml of 47 – 52 % hydrofluoric acid (HF) in the Nalgene beaker. The mixture was agitated for 24h (on a stirring plate with a plastic-covered stirring magnet). Following the HF treatment, the solution was again centrifuged and the acid decanted. The precipitate was washed with de-ionized water, vacuum filtered, and then dried in a vacuum oven.

\subsection*{3.4 Results and Discussion}

\subsection*{3.4.1 Isothermal Combustion Reactivity Comparison}

Combustion reactivity in air was determined using isothermal and non-isothermal TGA techniques. The following section presents the isothermal TGA profiles obtained at different combustion temperatures. Figure 3-3 shows the TGA profiles at different temperatures runs between 450 and 1000$^\circ$C for the raw inertinite-rich Highveld and vitrinite-rich Waterberg chars.
The maximum reaction rates for the Waterberg chars are higher than for the Highveld chars at all combustion temperatures. At a combustion temperature of 500°C, the Waterberg char reaches a maximum rate more than double the maximum rate obtained during combustion of the Highveld char. At this combustion temperature, there is also a large difference in the shape of the combustion profile. At lower temperatures (450 - 550°C), reaction rates for the Highveld char are low and they significantly increase at higher combustion temperatures. At low conversion, pore coalescence is low and the rate of reaction increases due to opening of formerly closed pores, resulting in the increase of surface area. As conversion increases, carbon is consumed, causing pores to grow and combine with neighboring pores resulting in decreased surface area, and therefore the rate decreases.

At higher temperatures (≥ 850°C), the shape of the combustion profile changes and there is only a slight increase in rate associated with temperature increase to 1000°C (Figure 3-3). The change in the profile shape and shift of the rate maximum toward a higher conversion agrees with the observations by Naredi and Pisupati for TGA combustion profiles of DTR generated coal chars. In this work, the maximum was attributed to limitations of gas diffusion, where the maximum indicated the beginning of the
kinetically controlled regime. At higher temperatures (≥850°C) where there is only a slight reactivity increase with temperature increase, it could indicate the transition from regime I to regime II or III. As combustion temperature increases, the rates of the reaction and of mass transfer (diffusion) increase. Small combustion temperature increases, results in a large change in inherent combustion reactivity (evident in Arrhenius plots), while the change in the rate of diffusion associated with a combustion temperature increase, is much less (possibly evident in Figure 3-3). Therefore, as combustion temperature increases, the reaction rate will become so rapid, that it will eventually be the diffusion that limits the overall combustion rate, instead of the inherent reactivity.

The vitrinite-rich Waterberg chars are more porous (mostly thick and thin walled cenospheres) and were expected to reach higher combustion reactivity rates. At the lower temperatures (450 - 550°C), the reaction rates for the Waterberg chars also increase with increasing combustion temperature (Figure 3-3). The shape of the Waterberg profiles is different from Highveld profiles at lower temperatures as it goes through a noticeable maximum combustion rate (~30% conversion). A maximum in a burnout profile could be due to the increased surface area associated with evolution of pore structure.20 Large pores then start to coalesce or collapse, resulting in a decrease in surface area hence decreasing reaction rate. At higher temperatures (≥ 850°C) the shape of the profile is similar to the Highveld profiles but even at these temperatures, there is still an increase in rate with increasing temperature. The difference could be the dense-type structure of Highveld chars (can be confirmed through optical and SEM microscopy) does not permit further development of pore structure as combustion temperature increase.

The difference in reactivity is attributed to differences in both chemical and physical properties, since both play an important role in reactivity behavior.89 At higher combustion temperatures, the higher reactivity could be due to larger surface areas associated with the more porous vitrinite-rich char particles. XRD should be able to
indicate that the Highveld inertinite-rich char has a higher stacking number than the Waterberg char, implying a more ordered structure, resulting in an increase of the ratio of basal plane to edge (active) surface sites. The lower concentration of carbon active sites will likely have a lower overall reactivity. 53

The enhanced reactivity at edge sites is presumed to be due to chemisorption (occurs at unpaired electrons). 43 Even among edge sites, there are reactivity differences between armchair and zigzag sites. 90 A higher reactivity is also expected at defects or dislocations due to geometric or charge imbalances. 43 Some functional groups promote reactivity since chemisorptions on these non-aromatic sites are favored over aromatic sites. 43 Oxygen sites, e.g. carbonyl, increase reactivity through electron exchange and hydrogen sites are preferentially oxidized relative to carbon. 43, 52

Figure 3-4 shows an Arrhenius plot (from the reactivity data shown in Figure 3-3), obtained by representing the logarithm of the maximum reaction rate determined at each combustion temperature vs. the inverse of the absolute temperature.
Two regions can be identified, which corresponds to the plot identifying different reaction regimes (Figure 3-1). This could indicate that kinetic control exists at lower temperatures, while the effect of diffusional limitations becomes evident at higher temperatures affecting the overall combustion rates.

3.4.2 Non-Isothermal Combustion Reactivity Comparison

Figure 3-5 shows normalized rate of weight loss profiles from final char samples (burnout profile), which is the plot of the instantaneous sample weight divided by initial sample weight versus sample temperature. The peak position is a relative reactivity measurement where the peak of Highveld char indicates a significantly lower reactivity. The temperature at the maximum rate of weight loss is at 480°C (±5°C) for the vitrinite-rich char and at 530°C (±4°C) for the inertinite-rich char indicating significant reactivity differences as expected. The Waterberg (vitrinite-rich) sample reached a higher
maximum rate of weight loss than the Highveld char, which also suggests a higher reactivity. The Highveld sample had a burnout temperature of 680°C, which was higher than the vitrinite-rich char’s burnout temperature of 650°C. It is not only the peak positions and intensities that differ but also the shape of the profiles. When comparing the profiles of the two char profiles, the Waterberg reaches a maximum faster than the Highveld char for both the raw and demineralized samples. After the maximum rate is reached, the Highveld samples burn off much faster than the Waterberg char. The profiles of the Waterberg char have longer tails, resulting in a larger peak width (analog to a longer total reaction time). This could be due to annealing during the initial reaction stages (at temperatures around 450°C). Hurt suggested that thermal deactivation could occur at the peak temperature and that an increase in structural ordering during heat treatment can cause the reaction rate to decrease.

Figure 3-5: Reaction rates for non-isothermal burnoff at 5°C/min for vitrinite-rich Waterberg and inertinite-rich Highveld coal chars
XRD indicated that Highveld char has a higher stacking number ($N = 3.52$) than the Waterberg char ($N = 3.26$) indicating a slightly more ordered structure, possibly resulting in a lower concentration of carbon active sites. If the burnout occurs in the chemical controlled regime, the lower concentration of carbon active sites will result in a lower reactivity. Depending on the temperature however, the difference in reactivity could be attributed to differences in both chemical and physical properties, since both play an important role in reactivity behavior. As observed by SEM and optical microscopy, the Waterberg chars often cenospheric are more visibly porous which results in a higher accessible active surface area which could result in a higher reaction rate.

As seen in Table 3-1 the demineralized samples of both chars reach higher maximum combustion rates and burn out faster than the raw chars. The hindrance of ash is therefore most likely the governing effect where it acted as a barrier for the reactants to reach the char. By removing the high concentration of ash (~17 and 36% dry respectively) from the samples, the access to the char is significantly increased resulting in higher combustion reactivity. The Highveld char has an ash yield almost double the percentage of the ash yield in Waterberg char. Therefore, if the hindrance was the governing impact factor, the removal of the larger amount of ash in the Highveld char should result in a larger reactivity change. Furthermore, the removal of mineral matter resulted in a decreased particle size which has the same effect. These phenomena most likely overshadowed

<table>
<thead>
<tr>
<th></th>
<th>Max rate (g/g.min)</th>
<th>Burnout Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterberg (W4)</td>
<td>4.1 ± 0.1</td>
<td>650 ± 5</td>
</tr>
<tr>
<td>Highveld (H4)</td>
<td>3.5</td>
<td>680</td>
</tr>
<tr>
<td>W4 Deminerlized</td>
<td>4.9</td>
<td>620</td>
</tr>
<tr>
<td>H4 Deminerlized</td>
<td>7.4</td>
<td>600</td>
</tr>
</tbody>
</table>
the possible reactivity decrease associated with removal of catalytic minerals. This observation agrees with that by Hippo and Walker\textsuperscript{55} where an increased reactivity in was observed for two demineralized chars generated from high-rank coals. The increased reactivity was attributed to generation of additional (feeder) porosity.\textsuperscript{55}

3.4.3 Char Reactivity through Temperature Programmed Oxidation

Figure 3-6 shows the temperature-programmed oxidation (TPO) profiles obtained for the raw and demineralized Waterberg and Highveld chars. All the curves were normalized with respect to their weight and ash yields (as determined through proximate analyses). The raw vitrinite-rich Waterberg char started combustion at 300°C and had a slightly larger peak than the raw inertinite-rich Highveld char that only started combusting around 420°C. Although the two chars burns out at similar temperatures (~800°C), the Waterberg char profile shows a maximum at a lower temperature than the Highveld char (590°C compared to 650°C).

The lower temperature peak in the TPO profile of the Waterberg char can be attributed to the presence of less ordered carbon species compared to the Highveld char profile.\textsuperscript{62} Due to a slight negative skewness in the distributions, it is possible that the profiles consist of two peaks. Two peaks are often observed in TPO of carbonaceous material, where they correspond to the combustion of less and more ordered carbon respectively. To investigate this, the TPO heating rate was decreased but no significant change in the profile shape was observed. Curve fitting was then applied to each profile, and the best fit was achieved with two Gaussian peaks, where the first smaller peak indicates the presence of less ordered carbon material. See Appendix A for curve fitting results. Eser et al.\textsuperscript{62} used temperature staging and quenching combined with SEM to examine morphology changes that occurred during conversion of carbon deposits, and the oxidation reactivity associated with the different forms of carbonaceous deposits.
These results confirmed that the high-temperature peaks in the original TPO profiles can be attributed to the presence of highly ordered carbon species in the original deposit and that it was not the result of chemical alterations of the original deposit during TPO.\textsuperscript{62}

Figure 3-6 also shows TPO profiles for the demineralized char samples. For both chars, the intensity of the peaks increased and the width (or variance) decreased. Mineral matter can act as a barrier, preventing access to surface area. By removing the mineral matter, the accessible surface area increases, which could result in faster combustion. In general the trends correspond well to those observed by non-isothermal TGA combustion of the same chars.
3.4.4 Calculation of Intrinsic Rate Parameters

Intrinsic activation energy is important since it indicates the reaction rate’s sensitivity to temperature. Several methods have been proposed throughout literature for determining activation energy and pre-exponential factors, achieving values for that vary with up to 30%. The main objective here was not to evaluate the different calculation approaches but rather obtain values from a single method to compare the two coal chars. The isothermal reactivity measurements were used for determining kinetic parameters. These reactivity profiles were obtained at sufficiently low temperatures to assume negligible diffusional effects with the chemical reaction being the rate limiting step. Figure 3-7 shows the Arrhenius plots for both chars indicating the dependence of the rate constant \(k\) on temperature (see Appendix A for calculation of \(k\)-values at different temperatures).

![Arrhenius plots of Waterberg (W4) and Highveld (H4) chars](image)

The reaction rate constant is strongly dependent on temperature but independent of the concentration of the reacting species. It is only constant at a single temperature. The slope and intercept of each Arrhenius plot was used to determine the activation energy
and pre-exponential factor respectively (Table 3-2). These activation energies represent averages for the reactions occurring during char combustion.

**Table 3-2: Intrinsic reactivity parameters**

<table>
<thead>
<tr>
<th></th>
<th>Ea (kJ/mol)</th>
<th>A (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterberg char (W4)</td>
<td>100.1</td>
<td>3.6 x 10³</td>
</tr>
<tr>
<td>Highveld char (H4)</td>
<td>153.8</td>
<td>1.5 x 10⁷</td>
</tr>
</tbody>
</table>

The lower activation energy of the Waterberg char is associated with a lower energy barrier for combustion reactions to initiate. The Highveld’s higher activation energy can be due to more energy needed to distort or stretch bonds in order for them to break, or higher steric and electron repulsion forces to be overcome as the reacting molecules come together.⁵⁹ To provide some perspective Table 3-3 presents activation energies for the combustion of two char samples and multiple organic compounds found in literature.

**Table 3-3: For comparison - Activation energies of single compounds and other coal chars**

<table>
<thead>
<tr>
<th>Component</th>
<th>Activation Energy (kJ/mol)</th>
<th>Notes</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pittsburgh no.8 coal char</td>
<td>108</td>
<td></td>
<td>⁹²</td>
</tr>
<tr>
<td>High-volatile bituminous coal char</td>
<td>132</td>
<td>DTR generated char</td>
<td>⁵⁰</td>
</tr>
<tr>
<td>Illinois no.6 coal char</td>
<td>142</td>
<td></td>
<td>⁹³</td>
</tr>
<tr>
<td>Benzene</td>
<td>58</td>
<td>V₂O₅–WO₃/TiO₂ catalyst</td>
<td>⁹⁴</td>
</tr>
<tr>
<td>Benzene</td>
<td>62</td>
<td>Pt/Al₂O₃ catalyst</td>
<td>⁹⁵</td>
</tr>
<tr>
<td>n-Butane</td>
<td>71</td>
<td>Platinum catalyst</td>
<td>⁹⁶</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>94</td>
<td>Pt/Al₂O₃ catalyst</td>
<td>⁹⁷</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>62</td>
<td>V₂O₅–WO₃/TiO₂ catalyst</td>
<td>⁹⁴</td>
</tr>
<tr>
<td>Toluene</td>
<td>73</td>
<td>Pt/Al₂O₃ catalyst</td>
<td>⁹⁷</td>
</tr>
<tr>
<td>Toluene</td>
<td>64</td>
<td>V₂O₅–WO₃/TiO₂ catalyst</td>
<td>⁹⁴</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>90</td>
<td>Pt/γ-Al₂O₃ catalyst</td>
<td>⁹⁸</td>
</tr>
</tbody>
</table>
The South African coals are high volatile bituminous coals and fall in the same rank range as Illinois no.6 coal.\textsuperscript{1} Although there is no information given regarding the generation of the Illinois no.6 coal char, the activation energy falls within the same range as the South African coal chars. The method used for char generation and reaction rate parameter calculation is not necessarily comparable.

### 3.4.5 Calculation of Effectiveness Factor – Extent of Diffusion Control

The extent of diffusion control in the measured combustion rates can be quantified by using an effectiveness factor, $\eta$.\textsuperscript{58} The effectiveness factor is defined as the ratio of the measured reaction rate to that which would occur if the reacting gas concentration was uniform throughout the sample.\textsuperscript{99, 100} Table 3-4 shows the maximum of the experimental reaction rates and the estimated reaction rates assuming there was no diffusion limitations. The effectiveness factor is then calculated based on the ratio of these two rates.

**Table 3-4: Calculated effectiveness factor**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Experimental max rate (g/g.min)</th>
<th>Estimated max rate (g/g.min)</th>
<th>Effectiveness factor((\eta))</th>
<th>(\eta_{\text{Highveld}}/\eta_{\text{Waterberg}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(HV)</td>
<td>(WB)</td>
<td>(HV)</td>
<td>(WB)</td>
</tr>
<tr>
<td>1000</td>
<td>0.32</td>
<td>0.39</td>
<td>5.20</td>
<td>19.61</td>
</tr>
<tr>
<td>950</td>
<td>0.31</td>
<td>0.35</td>
<td>3.82</td>
<td>13.68</td>
</tr>
<tr>
<td>850</td>
<td>0.29</td>
<td>0.31</td>
<td>1.90</td>
<td>6.05</td>
</tr>
</tbody>
</table>

Using an effectiveness-factor-based approach, the effects of pore-diffusion and intrinsic reactivity are separated, allowing determination of the high temperature ‘intrinsic’ reaction rate. As the value (\(\eta\)) approaches zero, the diffusional limitations increase and
therefore the influence of chemical reactivity on the overall conversion rate decreases. At the temperatures shown, the effectiveness factors are all small suggesting diffusional limitations. At all three combustion temperatures, the Waterberg char has a factor that is around 3 times smaller than that of the Highveld char. This indicates that the diffusion limitations for the Waterberg char is larger than those present in the Highveld char.

3.4.6 Mathematical Modeling

**Shrinking Core Model**

The shrinking core model, with different controlling phenomena, was evaluated against experimental results obtained isothermally at different temperatures. The shrinking core model (SCM) has the ability to indicate which phenomenon is rate controlling based on the best fit of either gas film diffusion, ash film diffusion, or chemical reaction. The SCM for all three cases were fitted to the isothermal reactivity data determined at six different temperatures. Due to similarity between the fits at lower temperatures (450, 500, and 550°C) and higher temperatures (850, 950, and 1000°C) respectively, only predictions for one lower (500°C) and one higher temperature (850°C) are shown here. See Appendix A for plots at other temperatures. Figure 3-8 shows plots of Highveld and Waterberg chars with the experimental reactivity data determined at 500°C (red), and the three different SCM predictions for the rate controlling phenomena.
The experimental data for combustion of Highveld char at 500°C agrees well with the SCM prediction where the combustion reaction is the rate controlling step, with a $R^2$-value of 0.954. This is an expected result because at the lower temperatures reactions occur at a low enough rate that diffusion limitations are negligible in comparison (notice the substantial deviation from gas film diffusion predictions to the measured data). For the Waterberg char, a reasonably good fit is also obtained assuming chemical reaction is the rate controlling mechanism with the $R^2$-value of 0.837. Notably the $R^2$-value for the Highveld char with chemical reaction as the rate controlling step is much closer to unity than its Waterberg counterpart, implying that the Highveld char resembles the inherent assumptions of the SCM much closer. One can thus conclude that the Highveld char is denser and that the combustion reactions take place mostly on the surface. This will be evaluated through structural characterization of the chars in Chapter 4.

From Figure 3-8 it can also be argued that ash layer diffusion is a plausible explanation for the rate controlling mechanism as its $R^2$-values for both chars are reasonably close to the values for chemical reaction control. This result is also not surprising as both these chars have a substantial ash yield which may influence the ease at which reacting gases
diffuse through the ash layer to the core. Very similar observations were made for combustion at 450 and 550°C and can be found in Appendix A.

At the higher combustion temperatures, the crescent shape of the conversion-time data found at lower temperatures (shown in Figure 3-8) approaches more linear behavior, as predicted by gas film diffusion. Figure 3-9 compares the experimental reactivity of Highveld and Waterberg chars at 850°C (red circles), again compared with the three different SCM predictions.

![Graph showing conversion-time data and R² values](image)

**Figure 3-9: Shrinking core model for combustion of Highveld and Waterberg chars at 850°C**

It is evident that gas film diffusion is the rate controlling mechanism at this higher temperature as its $R^2$-values approach unity. Clearly, neither chemical reaction nor ash layer diffusion are capable of explaining the observed behaviour satisfactorily. With an even further increase in combustion temperature, gas film diffusion still dominates the combustion reactions as shown in Appendix A.
Random Pore Model

Figure 3-10 compares experimental combustion data at 500°C against theoretical predictions made by the RPM. The RPM predictions agrees well with the experimental data with $R^2$-values of 0.987 and 0.985 for the Highveld and Waterberg chars, respectively.

As outlined in section 3.2.3, the RPM model contains a structural parameter ($\Psi$), unique to a specific char and only dependent on the initial properties of the char like pore length, porosity, and surface area (see Equation 3-8), and not on the actual combustion process (like combustion temperature, pressure, etc). Furthermore, the RPM is not suited to accounting for diffusion effects, and therefore only has physical relevance at lower combustion temperatures where pore diffusion is negligible. For the Highveld char, the structural parameter was determined to be 0.13±0.01 for the crescent shaped curves at lower temperatures. In comparison, the Waterberg char had a calculated value of 0.09±0.01 for the Waterberg char. It is evident that the estimate for $\Psi$ is reliable for both chars since the standard deviation from the mean value is small and the average $R^2$-value at each temperature for both chars is greater than 0.98, as shown in . Thus, the RPM model is adequate for predicting the combustion behaviour of these chars. The Highveld...
char has a higher Ψ value, indicating lower porosity and surface area. To verify the denser char structure of the Highveld char, structural characterization should be done.

3.5 Conclusion

It is important that reactivity parameters like the activation energy and rate constants are accurately estimated, and subsequently interpreted. The familiar Arrhenius equation was used to determine these parameters for DTR chars generated from inertinite- and vitrinite-rich South African coals, which showed higher activation energy for the inertinite-rich char.\textsuperscript{30, 53, 82} The reactivity of these chars were compared by utilizing TGA isothermal and non-isothermal combustion, and TPO. The isothermal burnout profiles of the vitrinite-char displayed a higher maximum reaction rate at all combustion temperatures, with the largest difference during combustion at 500, 550 and 1000°C. Non-isothermal burnout profiles obtained at a heating rate of 5°C/min in air showed the maximum rate of weight loss was at 480°C for the vitrinite-rich char and at 530°C for the inertinite-rich char indicating significant reactivity differences. Similar trends were observed in TPO where the maximum of the vitrinite-char was higher and obtained at a lower temperature. Since the South African coals have a high ash yield, it was important to quantify the effect the ash has on combustion behavior. After demineralization of the chars, faster burnout was achieved during non-isothermal TGA runs. While the maximum reaction rate of the vitrinite-char increased from 4.1 to 4.9g/g.min after demineralization, the inertinite-char showed a more significant increase in rate from 3.5 to 7.4g/g.min. The increase in combustion reactivity was attributed to the removal of the hindrance/barrier of the ash layer, blocking the access to the active surface area. Since the inertinite-char has a much larger ash yield (36% compared to 16%), the larger change in combustion reactivity with its removal could be expected. Furthermore, the applicability of the shrinking core and random pore models were evaluated. These models were able to only predict behavior at low combustion temperatures. The structural parameter, estimated by
fitting the random pore model, was 0.13 and 0.09 for the Highveld and Waterberg chars, where a larger value indicates a less porous structure.
Chapter 4

Characterization of Structural Transformations Associated with Devolatilization of an Inertinite-Rich and Vitrinite-Rich South African Coal in a Drop-Tube Reactor

4.1 Abstract

The structural transformations of coal and the resultant char morphologies are strongly dependent on the initial structure and degree of thermoplasticity achieved during coal-to-char transition these are a function of petrographic composition, rank, particle size, and heating rate. Two South African coals (Waterberg with 91.8% vitrinite content and Highveld with 87.7% dmmf inertinite) were selected for analysis since they capture the petrographic compositional differences but have similar carbon content, vitrinite reflectance, and organic precursors. Therefore they provide the opportunity to examine maceral influences on the chars that are expected to have different morphologies, structure, ash contributions, and hence different reactivity. This chapter compares the coal to char transformations during rapid-heating pyrolysis of narrow size cuts of these two coals. Char samples representing different stages of mass loss were generated in a drop-tube reactor under rapid-heating. The morphologies of the chars were characterized with SEM and optical microscopy, while quantitative information on the ordered nature of chars was obtained through XRD on demineralized chars. The vitrinite-rich coal reached a high degree of fluidity, producing mostly extensively swollen crassisphere, tenuisphere, and network-type chars. The inertinite-rich coal had limited fluidity which resulted only in rounding of particle edges and a large fraction of mixed-dense type chars. The final inertinite-rich char had a higher crystallite height (12.6Å) than the final vitrinite-rich char (11.7Å). The vitrinite-rich sample has a higher crystallite width (26.8Å) than the inertinite-rich sample (24.5Å). Although these stacking parameters were
similar, the inertinite-rich parent coal was significantly more ordered than the vitrinite-rich coal prior to heat treatment (11.8Å compared to 4.3Å), indicating a more extensive transformation for the vitrinite-rich coal.

4.2 Background

The chemical and physical structure of char directly influences combustion behavior as it affects the intrinsic char reactivity and transport of reacting gases and products at conditions relevant to industrial combustion for electricity generation (pulverized coal). The chemical and physical structure of char depends on the transformations occurring during devolatization. Chemical characteristics of the char such as aromaticity and crystallite size play an important role in reactivity since it influence the active sites available for reactions. The physical structure (morphology and pore size distribution) of char determines the ease at which gases are transported to and from the reactive sites. As a result, combustion kinetics is influenced by char structure, affecting burnout and heat release. It is therefore valuable to explore the thermoplastic behavior during devolatilization which affects the chemical and physical structural differences of a reactive vitrinite-rich coal and a less reactive mineral-matter rich and inertinite-rich (semifusinte) South African coals that are otherwise of the same/similar maturation (vitrinite reflectance). In South Africa, the less reactive inertinite-rich bituminous coals are used domestically while the export market is dominated by vitrinite-rich bituminous coals. It total 285 million tons of coal are mined annually, where 171 million tons are consumed domestically and the remainder exported.
4.2.1 Chemical Structure of Coal and its Transformations During Rapid Devolatization

Coal has a complex molecular structure that consists out of hydroaromatic clusters connected by various cross-links for much of the rank range. As the rank increases, the macromolecular structure is expected to change from being lignin-like for lignites to graphitic-like structure for anthracites. Low-rank coals generally have a relative open structure with abundant oxygen-containing groups, extensive cross-linking, and smaller aromatic ring systems (in the order of one to two ring structures). With maturation to the bituminous range, the structure will have larger aromatic units and reduced cross-linking. Even within a certain rank of coal, the structure will vary depending on the plant materials and the depositional environment in which the coal was formed, i.e. the maceral contribution and maceral diversity.

The chemical composition of coal has traditionally been characterized by ultimate analysis. Even though this technique does not provide direct evidence of coal structure, it provides insight to the basic structural features. The low H/C ratio of coal obtained through ultimate analyses, for instance, supports a highly aromatic structure. Molecular representations of coal are often based on data obtained from these basic analyses combined with data obtained from more advance methods like X-ray diffraction (XRD), infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. While XRD provides information on the aromatic structure, NMR provides information on aromatic structure and functional groups, and Fourier transform infrared (FTIR) supplies functional group data.

XRD is a well-established technique that measures the intensities scattered from the sample to provide quantitative information on coals ordered nature. A crystalline substance like graphite provides a very characteristic sharp x-ray diffraction pattern. Although many low-rank coals are highly amorphous, high-rank coals contains
small graphite-like stacked aromatic layers which form crystallites. While coal usually does not generate the same sharply-defined x-ray patterns as graphite, it is possible to detect graphite-like signals from coals in the bituminous rank. X-ray refractrograms for coal typically show (002) and (10) peaks, where their width and intensity are used to calculate structural parameters. The (002) peak is associated with the average domain height along the c-axis, which is a measure of the number of aromatic layers in a stack. The (10) peak corresponds to the crystallite length commonly termed the “diameter” which is expected to remain mostly constant and then increase with rank above medium-volatile bituminous as aromatic units become larger. Crystallite size can also be used to estimate the number of carbons per structural unit. Since carbon atoms at the edges of aromatic clusters are active while the non-flawed basal carbon atoms are considered inactive under normal combustion conditions, the crystallite size and height play an important role in oxidative reactivity. Another structural property obtained by XRD is interlayer spacing calculated with Bragg’s law using the position of the (002) peak. As coal becomes more ordered, interlayer spacing decreases and approaches 3.354Å, the interlayer spacing of graphite. The carbon content and crystalline order increases in macerals typically in the order: exinite, vitrinite, inertinite. Both FTIR and NMR spectroscopy provide important chemical structural features of coal. FTIR provides quantitative concentrations of hydroxyl, aliphatic and hydroaromatic hydrogen, aromatic hydrogen, aliphatic carbon, and aromatic carbon. Solid-state C NMR can quantify the average carbon skeletal structure through 12 structural parameters. These structural parameters, combined with an empirical relationship between bridgehead carbons and aromatic carbons per cluster, provide information on the aromatic and aliphatic arrangement in coal. Structural parameters include the mean number of attachments per cluster (coordination number), the average aromatic cluster molecular weight, the number of bridges and loops, the ratio of bridges to total attachments, and the average side chain molecular weight. Fletcher et al. used NMR to study chemical structures of chars from five coals of different ranks, and its
implications on char reactivity. Large differences were observed in the char combustion reactivity over the different ranks but all the chars had very similar NMR parameters. It was therefore concluded that reactivity differences were most likely due to mineral matter influences and physical structural differences, rather than chemical structure.\textsuperscript{121} Therefore, NMR might not be one of the most effective techniques to capture structural differences relating to reactivity differences.

Even though these techniques are powerful, especially when combined, they typically only provide average parameters of the structure. Direct evidence concerning the arrangement of the aromatic layers can be obtained through high resolution transmission microscopy (HRTEM).\textsuperscript{122} Different approaches using various software tools have been demonstrated for HRTEM image processing and fringe recognition.\textsuperscript{123-126} Processing algorithms often include filtering in the frequency domain (by means of Fourier transform), which is an important step in noise reduction to accurately achieve quantitative stacking parameters for coal char,\textsuperscript{123, 127} soot, and carbon black.\textsuperscript{125} While Palotas et al.,\textsuperscript{125} and Shim et al.\textsuperscript{124} utilize a band-pass frequency filter, Sharma et al.\textsuperscript{123} uses a step filter which extracts more fringes by allowing more noise.

Temperature-programmed oxidation (TPO) is a technique that provides information on structure (degree of crystallinity) as well as reactivity of carbonaceous material. Characterization is based on the oxidation of different carbon domains as the structural order directly relates to reactivity.\textsuperscript{53} The combination of TPO results with structural data from other techniques, such as XRD and Raman, provides a more comprehensive view of the chemical structure of carbonaceous materials.\textsuperscript{44, 63} There is generally good agreement between TPO data compared to other techniques.\textsuperscript{65, 128} For example Aso et al.\textsuperscript{129} determined H/C ratios by analyzing the H\textsubscript{2}O that evolved during TPO using GC-MS. The results were then utilized to elucidate average crystallite properties of three Chinese anthracites.\textsuperscript{44} Although the TPO estimated values were in the same order, the values were larger than those determined by through XRD and HRTEM.
Char structure is associated with the thermoplastic behavior of coal upon heating. The degree of thermoplasticity determines to what extent structural changes can occur. Lynch et al. describes the transient nature of bituminous coal’s thermoplasticity as three overlapping processes; a physical mobilization of the aromatic-rich structure, thermochemical decomposition of the macromolecular structure and rapid condensation to form a rigid structure. A higher degree of thermoplasticity will allow the growth of small bubbles resulting in a more porous char. The thermoplasticity is very dependent on pyrolysis conditions such as the thermal history and pressure as well as the petrographic composition and rank of the coal, among other factors.

The influence of coal’s petrographic composition on fluidity have been investigated at a molecular level. Compared to inertinite- rich coals, vitrinite- rich coals usually have more cross-linking between aromatic clusters which increase the ease of hydrogen transfer and consequently the thermoplasticity. The low fluidity of inertinite-rich coals could therefore be attributed to the large aromatic structures present as determined by $^{13}$C NMR.

The molecular structure does not only become more ordered along the coalification pathway but also typically upon heat treatment. The mobilization occurring during the plastic stage of pyrolysis for some coals allow for the possibility of transformation to a more ordered structure. XRD can be utilized to study the increasing degree of order as pyrolysis progresses. In-plane crystallite growth or coalescence of aromatic crystallites along the a-axis is responsible for an increase in $L_a$, and coalescence of crystallites along the c-axis are responsible for an increase in $L_c$ value. According to Radovic, an enhancement of the (10) peak could indicate a decrease in the concentration of carbon active sites leading to deactivation. An increase in crystallite size, combined with an increase in crystallite height causes a decrease in the ratio of active (edge) carbon atoms to inactive (basal) carbon atoms.
4.2.2 Physical of Coal and its Structural Transformations During Rapid Devolatization

Physical properties of coal and char are not only important for predicting behavior but also in determining the approaches used in handling and utilization. Important physical parameters of coal include porosity (pore size distribution), particle size and shape, density, and surface area.\textsuperscript{135} Porosity is defined as the fraction of volume that is occupied by pores.\textsuperscript{135} It is not only the total porosity but also the pore frequency, distribution and interconnectivity that are important since it affect coal’s total surface area and behavior,\textsuperscript{107, 136} i.e. pyrolysis, swelling, and moisture capacity. The porous structure of coal can be complex and the dimensions and distribution of the pores are mostly random with overlap and linkages between them.\textsuperscript{46} Porosity can be measured or estimated from other properties like, equilibrium moisture or specific gravity.\textsuperscript{135} Techniques to directly determine porosity include gas sorption (nitrogen or carbon dioxide), liquid displacement (mercury intrusion porosimetry), small angle X-ray scattering (SAXS), 129-Xe NMR, SEM and optical microscopy.\textsuperscript{39, 137, 138} Pores can be classified through different classification systems\textsuperscript{46, 137, 139} according to size by using the pore width. According to the IUPAC classification system a pore is a micropore if the pore width is smaller than 20 Å.\textsuperscript{137} If the width is larger than this but smaller than 500 Å it is a mesopore and a pore with a width larger than 500 Å is a macropore. Determining pore size distribution is imperative to study behavior since larger pores might increase the rate of mass transfer in the particles. Since porosity is also related to accessible surface area, larger pores can result in lower specific surface areas.\textsuperscript{39}

Large N\textsubscript{2} specific surface areas are often associated with low-rank coals. Apparent surface area is measured through adsorption of N\textsubscript{2} or CO\textsubscript{2} in conjunction with sorption theories like BET (Brunauer Emmett Teller)\textsuperscript{10, 46, 58}. Surface areas measured by CO\textsubscript{2} (~100-200m\textsuperscript{2}/g) at 298K are usually larger than those measured by N\textsubscript{2} adsorption (<20m\textsuperscript{2}/g) at 77K which is attributed to the diffusion of gases through pores being
activated (temperature-dependent) \(^{39,137}\). The higher temperature can result in more rapid diffusion and the ability of the gas to overcome the activation barrier and enter pores with restricted openings, resulting in higher measured surface area \(^{39}\). Consequently there is no uniquely defined surface area of coal \(^{39}\). The pore size distribution of porous solids is also evaluated from the adsorption isotherms. At 77K, the diffusional limitations of nitrogen influence adsorption in micropores, and therefore results produced by traditional theories, such as BET might not include the The density function theory (DFT) based method for calculation of pore size distribution of porous carbons from N\(_2\) adsorption isotherms has been widely used in characterization.\(^{140-142}\)

Radovic et al. \(^{53}\) demonstrated that it is not simply the total accessible surface area (measured using the techniques as discussed) that is of importance but rather the total active surface area. The importance of active surface area lies in the fact that it provides an indication of the concentration of carbon active sites on the surface \(^{10,43}\). Since deactivation of these sites can occur at the conversion conditions it is an important parameter to take into consideration when studying reactivity \(^{10}\). The active surface area of char can be measured with oxygen chemisorption and the results obtained in previous work indicated that it provides a good index of reactivity.\(^{53}\)

Scanning electron microscopy (SEM) and reflective light microscopy are other techniques to examine the porosity and surface area of coal.\(^{9,22,23,32}\) While SEM has the ability to provide accurate information on external surface of even a single particle, reflective light microscopy can provide insight on the interior nature of particles. Optical microscopy provides the capability to directly observe pore macropores. Even though microscopy can be used to analyze the particle size distribution, laser light diffraction is a simpler method of obtaining quantitative results.

When coal particles are rapidly heated, they can undergo radical changes in their physical structure. The extent of the structural changes is closely related to the thermoplastic behavior.\(^{51}\) Different mechanisms for the mass transfer of released volatile matter have
been proposed for various char forms.\textsuperscript{143, 144} Mass transfer can occur through a bubble mechanism which is a combination of diffusion and evaporation. Bubbles form when the volatiles released during the plastic stage are trapped inside the coal particle.\textsuperscript{144} At the onset of the plastic stage there are usually a large number of bubbles of the same size and uniform distribution.\textsuperscript{144} As volatile matter diffuses into the bubbles, the bubbles grow which result in swelling of the coal particle. The bubbles can burst when they reach the surface of the particle. However, the behavior of these bubbles during devolatilization depends on the heating conditions and resulting thermoplasticity.

Gray\textsuperscript{130} suggests that pyrolysis could occur by the explosive ejection of gases and liquids from the coal particle with rapid heating. This sudden release results from mechanical failure of the outer shell of the particle caused by internal pressure. The pressure builds up as vapor evolution occurs at higher temperatures with insufficient means of escape. Larger particles develop even stronger outer shells which cause a more violent burst resulting in thick walled spherical char particles.\textsuperscript{130} Consequently the open structure of these particles will result in improved evaporation and diffusion.

Surface area and porosity, two important parameters in diffusion behavior, both undergo changes during devolatization which makes prediction of mass transfer and subsequent combustion reactivity difficult.\textsuperscript{51} Even though both these properties often increase as pyrolysis progress,\textsuperscript{70} no general trend exists since they strongly depend on the thermoplastic behavior of the specific coal.\textsuperscript{145} Microscopic examination can be used since it provides information on pore size distribution, dimensions and shape of the particle, degree of anisotropy and wall thickness.\textsuperscript{2, 146} Optical microscopy can quantify these parameters by examining sectioned particles,\textsuperscript{9, 22, 23} while scanning electron microscopy can examine the external surfaces of the particles.\textsuperscript{147} The information obtained through microscopy can then be used to classify char.

Char classification systems are important since they provide a meaningful way of describing the complex structure chars.\textsuperscript{2} Numerous char classification systems have been
proposed throughout the literature, all of which incorporate the morphological parameters.\textsuperscript{9, 10, 24, 32} A classification system that has recently been proposed in a review by the International Committee for Coal and Organic Petrology was used throughout this study.\textsuperscript{2} The system includes nine char types that are summarized in the Figure 4-1.\textsuperscript{2, 88}
Table 4-1: Char classification as proposed by the ICCP \(^2\)

<table>
<thead>
<tr>
<th>CHAR TYPE</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenuisphere</td>
<td>Spherical to angular, porosity &gt;80%, &gt;50% of wall area &lt;3μm. &gt;75% fused material</td>
</tr>
<tr>
<td>Crassisphere</td>
<td>Spherical to angular, porosity &gt;60%, &gt;50% of wall area &gt;3μm. &gt;75% fused material</td>
</tr>
<tr>
<td>Tenuinetwork</td>
<td>Internal network structure, porosity &gt;70%, &gt;50% of wall area &lt;3μm. &gt;75% Fused</td>
</tr>
<tr>
<td>Crassinetwork</td>
<td>Internal network structure, porosity 40-70%, &gt;50% of wall area &gt;3μm. &gt;75% Fused</td>
</tr>
<tr>
<td>Mixed porous</td>
<td>Char with 25-75 % unfused material. Porosity &gt;60%</td>
</tr>
<tr>
<td>Mixed dense</td>
<td>Char with 25-75 % unfused material. Porosity 40-60%</td>
</tr>
<tr>
<td>Inertoid</td>
<td>Dense, porosity 5-40%, &gt;50% of wall area &gt;3μm. Fused or unfused</td>
</tr>
<tr>
<td>Fusinoid/Solid</td>
<td>Inherited cellular fusinite structure or solid particle with &lt;5% porosity. &gt;75% unfused</td>
</tr>
<tr>
<td>Mineroid</td>
<td>Particle with &gt;50% inorganic matter.</td>
</tr>
</tbody>
</table>
Studies show that char morphology is strongly dependent on the rank, heating rate, as well as the petrographic composition of coal.\textsuperscript{9, 132, 148} Low-rank coals, such as lignites tend to generate network-type to solid char structures but as the rank increases up to low-volatile bituminous, the portions of network char decrease and “spherical” chars increase. This can be attributed to the increase in coal’s aromaticity and fusibility.\textsuperscript{9}

Char morphology is also dependent on the petrographic composition of the coal since it influences the degree of thermoplasticity. Since vitrinite usually has more cross-linking between aromatic clusters it consequently reaches a higher degree of thermoplasticity.\textsuperscript{22, 131} Vitrinite-rich particles from bituminous coals therefore tend to form spherical chars while the inertinite produces a higher fraction of unfused chars.\textsuperscript{149} Jones et al.\textsuperscript{22} compared inertinite- with vitrinite-derived bituminous coal-chars by using reflective light microscopy and found that inertinite-derived chars had a lower porosity and smaller pore size compared to vitrinite-derived chars.

Bend et al.\textsuperscript{24} however suggested that relationships like these appear equivocal, and that the affect of petrographic composition on char structure should not be isolated. They found that the rank of vitrinite-rich coals strongly influence char morphology. Network-type chars with a high CO$_2$ surface area (\textasciitilde 200m$^2$/g) tend to form from low-rank vitrinite-rich coals (subbituminous to high-volatile C bituminous). With increasing rank, up to medium volatile bituminous, the network chars are replaced by cenospheric-type chars with lower surface area (\textasciitilde 20m$^2$/g) and porosity. Similar trends were found by Benfell et al.,\textsuperscript{149} where the influence of increasing the coal rank were investigated for both inertinite- and vitrinite-rich coals. The porous structure of inertinite-derived chars remained relatively unchanged with increasing rank, while vitrinite-derived chars was found to decrease in porosity.\textsuperscript{149} Consequently the structure of vitrinite and inertinite chars converges (above semi-anthracite where maceral differences are muted).\textsuperscript{22, 132}

Heating rate influence the physical properties of char.\textsuperscript{150} Le Manquais et al.\textsuperscript{18} compared chars produced in a drop-tube furnace (heating rate of \textasciitilde 10$^4$C/s) with those produced in a
TGA (with a heating rate of 500°C/s). While the TGA generated chars displayed undeveloped pore structures; the drop-tube chars were highly porous, swollen and possessed much larger internal surface areas. The undeveloped pore network of the TGA chars is attributed to a liquid film forming on the outside of the char particle, preventing volatiles from escaping. During rapid-heating, the volatiles are released faster and the liquid film layer becomes thinner allowing the formation of more and larger pores. This will however not occur for all coals; the structure of some inertinite-rich coals will remained unaltered regardless of the heating rate. Everson et al. conducted a detailed characterization of char derived from South African inertinite-rich coal and found that these chars have a low porosity (<5%), as expected from a coal with low thermoplasticity. The chars were however generated in equipment that does not provide a fast heating rate, which has been proven to limit the evolution of the pore structure.

The amount and dispersion of mineral matter has an influence on char structure. The porous structure of the char has an impact on the formation of the ash where porous particles are expected to fragment easier than denser particles during oxidation. Kantrorovich et al. studied this finding the extent of fragmentation during conversion was mainly related to the porous structure. They found that an increase in microporosity will result a drastic increase in fragmentation. Another study showed the existence of a strong relationship between the structure of the char and its fragmentation which influences the ash formation.
The proposed fragmentation mechanism (Figure 4-1) shows how char particles of different structural types (as earlier defined) exhibit different fragmentation behavior, burnout history, and ash formation mechanisms. The authors$^{16}$ suggest that highly porous type I char particles fragment extensively and burnt out faster, while char particles with a low porosity (the group III type) exhibit less fragmentation and burn out during later stages of combustion. Consequently the char structure affects the particle size distribution of the ash which affects the design of the equipment.$^{11}$

4.3 Experimental

4.3.1 Scanning Electron microscopy

A FEI Quanta 200 environmental scanning electron microscopy was used to observe particle morphology and surface features. Careful sampling was done to ensure the observed samples were representative. The sample was mounted on a stub by well dispersing it over carbon tape.
4.3.2 X-ray diffraction

X-ray diffraction (XRD) patterns were obtained for demineralized char samples to determine the change in size of the carbon crystallites during heat-treatment. XRD patterns of were collected using a PANalytical X’Pert Pro MPD goniometer with Cu-Kα radiation, and fixed slit incidence (0.5 deg. divergence, 1.0 deg. anti-scatter, specimen length 10 mm) and diffracted (0.5 deg anti-scatter, 0.02 mm nickel filter) optics. Samples were prepared by the back-loading method in which a powder sample is pressed into the cavity of a quartz low-background support. Data was collected at 45 kV and 40 mA from 5-110 deg 2θ using a PIXcel detector in scanning mode. Resulting patterns were corrected for both 2θ position and instrumental peak broadening using NIST 640c silicon and analyzed with Jade+9 software. The full width half maximum (FWHM), d-spacing (d_{002}), diffraction angle, and crystallite size (L_c) were calculated from the broadening of the Gaussian profiles for the (002) peak using the Bragg equation and the Scherrer equation. The crystallite size (L_c) and the average crystallite length (L_a) were calculated using the Scherrer equation:

$$L_a/c = Kλ/β\cos θ$$

where θ is the peak position, λ is the wavelength of the x-rays which is 1.5409 Å for copper Kα radiation and K is a constant depending on the reflection plane. For the (002) band, K is 0.89 and for the (100) band K is 1.84. The interlayer distance between aromatic sheets (d_{002}) was calculated from the position of the (002) band using the Bragg equation.

$$d_{002} = λ/(2\sin θ)$$
4.3.3 Optical Microscopy

Petrographic analyses were performed with a reflecting light microscope to examine polished cross-sections of coal and char particles. Samples were embedded in an epoxy resin, left overnight, cut, and polished for the microscopic examination under oil immersion. To examine the optical texture, samples were observed under cross-polarized light. Char particle morphologies were identified on a point-counting basis (with 800 points), and classified according to the system proposed by the International Committee for Coal and Organic Petrology.²

4.3.4 Surface Area measurements

Surface area and porosity analysis were carried out using Micromeritics ASAP 2020. The samples were degassed for at least 24 hours in vacuum prior to measurement. Nitrogen gas was used for analysis, at the analysis temperature of 78 K and a maximum manifold pressure of 925 mm Hg. The adsorption measurements were translated to surface area based on the BET equation.¹⁵⁶ The porosity distribution was calculated using the original Density Functional Theory (DFT) considering slit pores.

4.3.5 HRTEM

To investigate the char morphology and nanostructure, a 200-kV field-emission TEM (JEOL EM-2010F) was used by Dr. Randy vander Wal to take high-resolution images.
4.4 Results

4.4.1 Coal and Char Morphologies

Figure 4-2 is an SEM micrograph showing the initial shape and narrow size distribution of the Waterberg coal. Both coals consisted of sharp-edged particles within a narrow size cut (200 x 400 mesh) as expected for a wet-sieved coal.

![Figure 4-2: Waterberg coal SEM micrograph](image)

Figure 4-3 shows images of drop-tube generated chars, sampled at four different residence times. The left column is the Highveld chars generated at 100, 200, 300, and 400ms and the right column is the Waterberg chars at 120, 160, 200, and 240ms. The SEM micrographs revealed differences in char morphologies, relating to differences in thermoplasticity of the two coals.
Figure 4-3: Micrographs of Highveld chars generated in DTR at 1a) 100 ms, 1b) 200 ms, 1c) 300 ms and 1d) 400 ms and Waterberg chars generated at 2a) 120 ms, 2b) 160 ms, 2c) 200 ms and 2d) 240 ms
After 100ms (Figure 4-3a) the Highveld coal still had mostly sharp edged particles. After 200ms (Figure 4-3b) the sharp edged particles transformed to slightly swollen particles with rounded edges. After 300ms (Figure 4-3c) there were a small number of visible pores as well as spherical particles with rough surfaces. Even though larger particles with visible pores and cracks were present after 400 ms (Figure 4-3d), the majority were irregularly-shaped “dense” chars lacking significant expansion due to a low degree of thermoplasticity of inertinite.\textsuperscript{46, 132}

Even at early stages of devolatization (Figure 4-3a), sharp edged Waterberg coal particles transformed to swollen spherical particles. At 120ms, some spherical chars have smooth surfaces, while others have large bubble-derived pores (Figure 4-3a). In Figure 4-3b, after 160ms, larger particle size and larger surface pores were observed. According to Huang et al.,\textsuperscript{157} the presence of visible open surface “holes” (as seen in Figure 4-3b) could be due to the expansion of existing bubbles or the localized acceleration of devolatization due to catalytic effect of dispersed minerals. At 200 ms (Figure 4-3c), bubbles-derived pores beneath the particle surface are clearly visible, which implies a thin wall. Some smaller char fragments can be observed caused probably by fragmentation of friable cenospheric char particles.\textsuperscript{158} Here particles appear to reach a maximum size, after which they slightly decrease in diameter to form the wrinkled fabric particles shown in Figure 4-3d. The decrease in diameter is likely due to the rapid release of volatiles within “balloon”-like gaseous spheres. Some particles have one “blow-hole” (as shown in Figure 4-3c) which was likely caused by the explosive ejection of built up gases as explained by Gray.\textsuperscript{130} The open structure of these char particles will result in improved evaporation and diffusion. Higher magnification of chars at this residence time showed regions of smooth surface typologies.

Figure 4-4a shows one of many agglomerations of multiple particles of Waterberg chars at 240 ms. The adhesion of particles was probably caused by released tar which overwhelmed the available oxygen present in the system. Tetrahydrofuran (THF) can be used to extract the molecular weight fraction that includes tar.\textsuperscript{41} None of these
agglomerations were found at higher residence times and THF extraction results indicated there was no tar present at higher residence times (no solvent discoloration). According to Gray\textsuperscript{130} the open structure of cenospheres after explosive ejection of the volatile matter, would allow the heavy tar molecules to be ejected. Figure 4-4b is an example of a particle that experienced a high degree of thermoplasticity allowing extensive particle swelling (coal sample was -70μm while the char particle has an approximate diameter of 120μm). The wrinkles or folds visible on the surface of the particle could be due to contraction (decrease in particle size) after explosive ejection of volatile matter.\textsuperscript{130}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4-4.png}
\caption{SEM micrographs of Waterberg chars (at estimated residence time of 240ms)}
\end{figure}

These observations agree with previous studies that found inertinite-rich coals produce mainly dense and unfused chars (e.g. fusinoid, inertoid),\textsuperscript{22, 24} while vitrinite reaches a higher fluidity, allowing transformation to more porous and swollen char structures.\textsuperscript{153} Although the external char morphology is useful, the cross section of the particles was necessary to classify char morphology.

Figure 4-5 shows optical micrographs of polished char samples. After 100ms (Figure 4-5, 1a) only small pores and cracks started to form in the Highveld sample and after 200ms (Figure 4-5, 1b) rounding of sharp edges start to occur. At initial residence times the particles appear relatively dull, with greater reflectance after 200ms. This is consistent
with the loss of aliphatics and the resulting increase in aromaticity and size/stacking of polycondensed aromatic units. After 400ms (Figure 4-5, 1c), the optical texture under cross-polarization was characterized by long parallel domains (not shown). According to Jones et al. the limited fluidity of inertinite prevent structural breakdown of the coal but is sufficient to allow refinement of the natural anisotropy of the bedding plane to form the
Figure 4-5: Optical micrographs of Highveld chars generated in DTR at 1a) 100 ms, 1b) 200 ms, 1c) 300 ms and 1d) 400 ms and Waterberg chars generated at 2a) 120 ms, 2b) 160 ms, 2c) 200 ms and 2d) 240 ms
long parallel domains. Even though some limited visible porosity was evident, the original generic angular particle shape was retained for most Highveld char particles.

For the Waterberg coal, char spheres started developing at early stages of devolatilization (Figure 4-5, 2a). Structural changes occur far more rapidly and multiple spherical pores (bubbles) are present after 100ms. The spheres are mostly smaller thick-walled cenospheres (crassinpheres). A large amount of crassinetworks (Table 4-2), along with some mixed porous and unchanged coal particles were observed. From point counting ~40% of the particles have a lower reflectance than the rest, which signifies a higher aliphatic content and a less condensed aromatic structure. A lower reflectance is due to a lower degree of order, therefore the reflectance is expected to increase as crystalline order increases. With increasing residence time, the amount of low-reflecting particles decrease and less than 1% (vol) is observed after 240ms (Figure 4-5, 2d). After 160ms (Figure 4-5, 2b) only a few unchanged particles were observed, and by 200ms (Figure 4-5, 2c) all the particles have experienced some structural transformation. The particle size increases with residence time and reaches a maximum after 200ms (Figure 4-5, 2c), where a large amount of extensively swollen spherical and network chars were observed. Sample W4 consist mostly of thick-walled rounded cenospheric particles exhibiting isotropic texture and abundant secondary porosity within the walls. The presence of small bubbles in the wall indicate pyrolysis within the particle wall after the swelling of the particles has been restricted. Tsai et al. suggest that the outer surface of the particle could have resolidified, restricting growth, while the inner wall was still plastic. The formation of thick-walled cenospheres could be due to inertinite contributions, which would restrict fluidity needed to form thin-walled cenospheres, although mineral matter and other entities can negatively impact fluidity also.

Samples W2 and W3 exhibited a pinpoint (mosaic) anisotropy distributed throughout the char particles. As seen if Figure 4-6, this morphology also forms part of large particle agglomerations. Since the char had a strong “tar” odor, it was likely tar-adhesion causing particle agglomeration and pinpoint anisotropy that was evident. Solvent (THF)
extraction indicated that tar was present in these chars (solvent discoloration). The tar also likely reduced the volatile matter yield reduction seen in Table 2-3.

Figure 4-6: Waterberg char at 160ms

The internal char morphology was quantified through reflected light microscopy (Table 4-2). The classification system proposed by Lester et al.² (shown in Table 4-1), was utilized with point counting (~800 points) for the two final chars for each coal. During point counting the amount of likely inertinite-derived and vitrinite-derived particles were also quantified.

Table 4-2: Char Morphology determined by point counting (Vol %)

<table>
<thead>
<tr>
<th></th>
<th>Waterberg Char (W4)</th>
<th>Highveld Char (H4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent vitrinite-derived</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>Apparent inertinite-derived</td>
<td>9</td>
<td>63</td>
</tr>
<tr>
<td>Other (incl. tar and ash)</td>
<td>11</td>
<td>30</td>
</tr>
<tr>
<td>Crassisphere</td>
<td>43</td>
<td>7</td>
</tr>
<tr>
<td>Tenuisphere</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Crassinetwork</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Tenuinetwork</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Mixed Porous</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Mixed Dense</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Dense (incl. Solid/Inertoid/Fusinoid)</td>
<td>5</td>
<td>28</td>
</tr>
<tr>
<td>Other (incl. Mineroid/Fragment)</td>
<td>9</td>
<td>20</td>
</tr>
</tbody>
</table>
The amount of inertinite-derived and vitrinite-derived char particles were comparable to the composition of the parent coal (Highveld coal included 87.7% (organic basis) inertinite and Waterberg coal included 91.8% (organic basis) vitrinite). The Waterberg char samples were characterized by 43% crassispheres, with a smaller fraction of crassinet networks and tenuispheres (21% and 14% respectively). Ash was present in mineroids but also incorporated within char particles that may aid catalytic combustion. Alternatively, the ash may act as physical barrier for structural development and subsequent reactions. The particles had less than 10 vol.% unfused material, and displayed various types of optical textures under polarized light. Both isotropic and anisotropic regions were detected, where the anisotropic units were mostly small (<1µm). The assessment of anisotropic types are subjective in nature, and the limitations in the resolution of the optical microscopy (with wavelength of visible light between 0.39 and 0.75µm) makes the identification of smaller flow domains problematic. Transmission electron microscopy is a technique that has been used to study smaller (nano-scale) anisotropic units and flow domains. Marsh and Walker describes the texture of semi-cokes derived from high-volatile coal (which is comparable to the properties of raw Waterberg coal) as mostly isotropic with a few small-sized anisotropic units. Alonso et al, compared the optical texture of chars generated from two vitrinite-rich coals of different ranks (high volatile and low volatile bituminous coals). The low volatile coal produced a char with slightly lower reflectance and less anisotropic textures. However, it is not possible to relate the fluidity and resulting flow domains and anisotropic units in heat-treated carbon to a single property, such as rank. The anisotropic structure is a balance of reaction temperature, chemical composition, and the extent of the re-polymerization occurring during heating.

The Highveld sample included mainly “denser” particles such as solids, inertoids, fusinoids, and mixed-dense particles. A significant amount of crassinet networks and mineroids were also observed (Table 4-2 and Figure 4-5). The sample contained fewer char fragments than the Waterberg sample and the 20 vol. % mostly represent the large
amount of mineroids. The mixed dense and solid particles included a large amount of isotropic unfused material, with little sign of plasticization or swelling. The crassinetworks and some inertoids displayed lenticular anisotropic domains of various sizes. The cenospheres were amorphous and appeared to be mainly produced from the vitrinite.

4.4.2 Char Structure – Degree of Stacking

XRD is a well-established technique that measures the intensities scattered from the sample to provide information the ordered nature of coal.\textsuperscript{1,108,109} Figure 4-7 shows XRD patterns of the demineralized Highveld and Waterberg chars.

The (002) and (10) peaks at \( \approx 23 \) and 43°, respectively, were characteristic of highly unorganized carbon. Compared to vitrinite-rich Waterberg coal, the inertinite-rich Highveld coal has a higher degree of structural order prior to heat treatment.\textsuperscript{1} This was evident from more prominent (002) and (10) peaks in XRD patterns for Highveld coal (obtained by van Niekerk et al.\textsuperscript{1}) and reflected in the calculated structural parameters.
Figure 4-7: XRD micrographs for (a) Highveld and (b) Waterberg chars

After 100ms the Highveld char still shows a sharper (002) peak compared to the Waterberg char at 120ms. A slight enhancement of the (002) and (10) peaks with increasing residence time for both coals signified an increase in structural order. There is also a shift of the (002) peak to a lower 2θ value. The (11) reflection, which is also typically observed in graphite, was not present for either of the parent coals. It is evident
that this (11) peak, at about 79°, starts to become visible in chars. Table 4-3 shows the quantitative XRD structural parameters of the drop-tube char samples and the parent coals, as acquired from other work.1

Table 4-3: XRD parameters for char samples

<table>
<thead>
<tr>
<th></th>
<th>Volatile Matter (% daf)</th>
<th>Interlayer spacing (d_{002}) (Å)</th>
<th>Crystallite height (L_c) (Å)</th>
<th>Crystallite diameter (L_a) (Å)</th>
<th>Stacking Number (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highveld coal 1</td>
<td>24</td>
<td>3.42</td>
<td>11.80</td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td>Highveld char (H1)</td>
<td>22</td>
<td>3.46</td>
<td>15.85</td>
<td>13.79</td>
<td>4.57</td>
</tr>
<tr>
<td>Highveld char (H2)</td>
<td>12</td>
<td>3.50</td>
<td>14.11</td>
<td>15.75</td>
<td>4.03</td>
</tr>
<tr>
<td>Highveld char (H3)</td>
<td>4</td>
<td>3.58</td>
<td>12.47</td>
<td>19.53</td>
<td>3.48</td>
</tr>
<tr>
<td>Highveld char (H4)</td>
<td>3</td>
<td>3.59</td>
<td>12.61</td>
<td>24.51</td>
<td>3.52</td>
</tr>
<tr>
<td>Waterberg coal 1</td>
<td>35</td>
<td>3.97</td>
<td>4.27</td>
<td>-</td>
<td>1.08</td>
</tr>
<tr>
<td>Waterberg char (W1)</td>
<td>21</td>
<td>3.58</td>
<td>13.32</td>
<td>17.87</td>
<td>3.72</td>
</tr>
<tr>
<td>Waterberg char (W2)</td>
<td>24</td>
<td>3.55</td>
<td>13.88</td>
<td>18.50</td>
<td>3.91</td>
</tr>
<tr>
<td>Waterberg char (W3)</td>
<td>10</td>
<td>3.60</td>
<td>12.86</td>
<td>21.10</td>
<td>3.57</td>
</tr>
<tr>
<td>Waterberg char (W4)</td>
<td>5</td>
<td>3.60</td>
<td>11.74</td>
<td>26.76</td>
<td>3.26</td>
</tr>
</tbody>
</table>

The average interlayer spacing \(d_{002}\) of the Highveld coal (3.42Å) falls in the range for graphite structures (between 3.36 and 3.44Å).166 Upon heat treatment, there is a slight increase in the \(d_{002}\) value which is associated with a slight shift of the (002) peak to a lower 2θ value. A similar trend for this coal was observed by Malumbazo et al. with much larger particles within a pipe-reactor combustion unit.167 The \(d_{002}\) for Waterberg coal was initially higher (3.97Å) than the Highveld coal but the value decreases with heat treatment and the final char has a \(d_{002}\) similar to that of the Highveld coal.
There is a significant increase in crystallite diameter ($L_a$) during devolatization for both coals, with the Waterberg chars having slightly larger values than Highveld chars. The crystallite size of Highveld char changes from 13.8 Å to 24.5 Å, while Waterberg changed from 17.8 Å to 26.8 Å. These values were not calculated for the raw coals since the intensity of the (10) peak, at 43°, were to weak. With increasing residence time (time-temperature history) growth of crystallites in chars occurs, increasing the crystallite size. This is consistent with an increased reflectance observed with optical microscopy. In-plane crystallite growth or coalescence of crystallites along the a-axis is responsible for an increase in $L_a$, and coalescence of crystallites along the c-axis were responsible for an increase in $L_{oc}$ value. Although there is an initial increase in crystallite height ($L_c$) as both coals start to devolatilize, it is followed by a slight decrease in $L_c$ as devolatization progresses. The decrease in $L_c$ could be due to re-arrangement of aromatic crystallites. The change in crystallite height during devolatization for the Waterberg coal (from 4.27 to 11.74 Å) is higher than the change for the Highveld coal (from 11.8 to 12.6 Å). This can be attributed to the Waterberg coal reaching a higher degree of thermoplasticity which permits larger mobility and enhanced stacking of aromatic layers. According to Radovic, an enhancement of the (10) peak could indicate a decrease in the concentration of carbon active sites leading to deactivation. The significant increase in crystallite size, combined with the overall increase in crystallite height causes a decrease in the ratio of active (edge) carbon atoms to inactive (basal) carbon atoms.

Even though a demineralization procedure was carried out prior to x-ray analysis to reduce the high percentage of ash (~36% for Highveld and 15% for Waterberg), the final chars still contained residual mineral matter (~4% and 2% respectively). Although was only a small amount in comparison to the initial ash yield, it could have influenced the accuracy of the calculated parameters. The ash in South African coal consist mainly of silica (44%), aluminium oxide (34%), and calcium oxide (8%). Therefore, crystalline inorganic materials that could be present in the micrographs in addition to the carbon band include; quartz at 26.7°, kaolinite at 29.4° and dolomite at 31°, and lime at 37.3°.
among others.\textsuperscript{170} By closely studying the XRD micrographs, the lime band is visible in the H1 char sample (at 100ms) but not at higher residence times or in the Waterberg chars. The quartz, kaolinite, and dolomite peaks falls within the range of the (002) peak and therefore it could have interfered with the calculations of interlayer spacing and crystallite height. Sillimanite (Al\textsubscript{2}SiO\textsubscript{5}) is a mineral that is often observed in the spectrum as a peak at 41\%, when quartz and lime are heat-treated. This band, if present, could influence the calculation of crystallite diameter.

### 4.4.3 Char Surface Area and Density

Table 4-4 contains helium density data for the coal, char and demineralized char. Surface areas from N\textsubscript{2} adsorption were calculated through the BET and Langmuir isotherms. The adsorption of N\textsubscript{2} at 77K is restricted due to the limitations in activated diffusion into pores at such low temperatures. Therefore N\textsubscript{2} adsorption are expected to only give data on the easily accessible, larger pores (macropore area).\textsuperscript{171} The Highveld char had larger BET surface areas than the Waterberg char (3.9 compared to 2.7m\textsuperscript{2}/g), as shown in Table 4-4. This could be an indication of that the Highveld char has a larger degree of macroporosity. Demineralization of the chars increased the BET surface area; the demineralized Highveld char has a surface area almost 8 times as large as the raw char. Studies have used density functional theory (DFT) to study microporosity through N\textsubscript{2} adsorption.\textsuperscript{140-142} Table 4-4 includes estimated values for the volume of the micropores, as calculated by DFT. These values indicate that the Waterberg char has a open volume of 0.00054cm\textsuperscript{3}/g attributed to the presence of pores smaller than 25.14Å, while the Highveld char has no pores smaller than 25.14Å (determined by DFT). Once again, demineralization increased the porosity of the Highveld char.
Table 4-4: Surface area and Porosity measurements through Nitrogen adsorption

<table>
<thead>
<tr>
<th></th>
<th>Highveld (inertinite)</th>
<th></th>
<th>Waterberg (vitrinite)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Char</td>
<td>Demin. Char</td>
<td>Coal</td>
</tr>
<tr>
<td><strong>He Density g/cm³</strong></td>
<td>1.6</td>
<td>2.0</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Surface Area m²/g</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single point surface area at P/Po</td>
<td>3.9</td>
<td>28.9</td>
<td>2.4</td>
<td>5.0</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>3.9</td>
<td>29.9</td>
<td>2.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Langmuir Surface Area</td>
<td>5.6</td>
<td>39.9</td>
<td>3.6</td>
<td>8.8</td>
</tr>
<tr>
<td><strong>Pore Volume cm³/g</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJH Adsorption cumulative pore volume (17.Å - 3000Å)</td>
<td>0.0076</td>
<td>0.0496</td>
<td>0.0038</td>
<td>0.0118</td>
</tr>
<tr>
<td>BJH Desorption cumulative pore volume (17.Å - 3000Å)</td>
<td>0.0079</td>
<td>0.0439</td>
<td>0.0045</td>
<td>0.0126</td>
</tr>
<tr>
<td><strong>Pore Size Å</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJH Adsorption average pore width (4V/A)</td>
<td>286</td>
<td>138</td>
<td>88</td>
<td>90</td>
</tr>
<tr>
<td>BJH Desorption average pore width (4V/A)</td>
<td>157</td>
<td>169</td>
<td>67</td>
<td>86</td>
</tr>
<tr>
<td><strong>DFT Pore Size</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume in Pores &lt; 25.14 Å (cm³/g)</td>
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<td>0.00054</td>
<td>0.00047</td>
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<td>Total Volume in Pores &lt;= 443.19 Å</td>
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<td>0.00267</td>
<td>0.00979</td>
</tr>
<tr>
<td>Area in Pores &gt; 443.19 Å</td>
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</tr>
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<td>2.946</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
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<td>2008</td>
<td>23711</td>
<td>10903</td>
</tr>
</tbody>
</table>
4.4.4 Char Pore Size Distribution

The pore size distributions were determined through small angle x-ray scattering (SAXS). These results indicated that both char samples are mostly mesoporous. The pore distribution (by volume) of the Highveld char, as shown in Figure 4-8, shows a large number of pores around 30Å. The Highveld char also has a significant amount of larger pores (macropore size range).

![Figure 4-8: Pore size distribution as obtained from SAXS of inertinite-rich Highveld char](image)

The pore distribution (by volume) of the Waterberg char, as shown in Figure 4-9, shows the largest number of pores around 25Å. The frequency of pores in this size range, is larger than the frequency for the corresponding size range in the Highveld char; 40 x 10\(^{-6}\) for Waterberg compared to 25 x 10\(^{-6}\) for the Highveld char. This suggests that the Waterberg char has a larger amount of slightly smaller pores in comparison with the Highveld char.
The general trend observed in SAXS agrees with the nitrogen adsorption, where the Waterberg char has a slightly larger porosity attributed to the presence of more pores smaller than 25 Å. The Highveld char however, has a larger amount of porosity available due to the presence of macropores.

4.5 Conclusion

Coal to char transformations during rapid-heating pyrolysis of narrow size cuts of two South African bituminous coals were compared. These coals had different petrographic compositions but similar carbon content, vitrinite reflectance (mean-max), and organic precursors. Char were generated in a drop-tube reactor under rapid-heating conditions. The vitrinite-rich Waterberg coal transformed to swollen spherical particles with visible round bubble-derived pores, while the inertinite-rich Highveld coal produced denser...
chars with less pores (SEM and optical microscopy). The differences could be attributed to the thermoplastic behavior upon heating, where the Waterberg coal reaches a higher degree of fluidity allowing greater structural transformations. The vitrinite-rich coal produced mostly extensively swollen crassispheres and tenuispheres (43 and 14 vol% respectively) while the inertinite-rich coal produced mainly denser chars (28 vol%) and network chars (23 vol%). The network and spherical chars can provide larger surface areas for reactions compared to dense chars, which would result in reactivity differences. XRD analyses quantified structural ordering with progressing devolatization. Compared to the Waterberg coal, the Highveld coal had a significantly higher degree of order (with a crystallite width of 11.80Å compared to 4.27Å). Upon heat treatment the Waterberg coal experienced significantly larger development in crystallite order, to produce a final char with a stacking number of 3.26 and crystallite height of 26.76Å, which in the same order than the Highveld char’s stacking number of 3.52 and crystallite height of 24.51Å. The more significant crystallite growth and stacking of the Waterberg sample were attributed to its high degree of fluidity.
Chapter 5

Quantification of Structural Parameters of South African CoalChars through HRTEM Image Analysis

5.1 Abstract

In this study, HRTEM was used to further characterize the carbonaceous structures of an inertinite-rich and a vitrinite-rich South African coal char. Here, a semi-automated image analysis approach was developed on Photoshop to extract the carbon layers of chars as observed through HRTEM producing a lattice fringe image. Furthermore, a user-friendly graphical user interface (GUI) was developed in a mathematical programming language, Matlab, to perform statistical analyses on the extracted lattice fringes to quantify the distributions of structural parameters: interlayer spacing, aromatic fringe length, and orientation angle. The GUI also enables the identification of crystallite stacks based on user defined criteria, and quantitative fringe length variability, angle, spacing, and fringes in a stack. This semi-automated approach allows for a rapid analysis of char structure, and is rigorous; eliminating researcher bias when assessing the structure manually. Analysis of the processed images indicated that the inertinite-rich char have a slightly larger average fringe lengths that are less preferentially aligned, compared to the vitrinite-rich char.

5.2 Background

It is well-known that the microstructure of carbon-rich material such as soot, and char can vary from amorphous to well-ordered crystalline regions. The degree of order is of interest since it relates to the oxidative reactivity of the material, where non-catalyzed
less ordered carbons are generally more reactive. The structural degree of order depends on the properties of the precursor as well as the thermal time-temperature histories. Structures information is important to rationalize the transformations occurring during thermal treatment, and the various subsequent/concurrent processes such as combustion, gasification, graphitization etc. Carbon materials are characterized by crystalline structural parameters such as interlayer spacing ($d_{002}$), crystalline “diameter” ($L_a$), and stacking height ($L_c$) that can be determined by X-ray diffraction patterns (XRD). Although XRD has been proven to be of value in deriving crystalline parameters of bulk samples, it lacks the ability to examine localized crystallite structures within a sample. Alternatively, high resolution transmission electron microscopy (HRTEM) has the unique ability to directly observe the structure at a molecular level which limits the averaging effects occurring with other bulk average diffraction techniques.

**5.2.1 Microcrystalline Structure of char**

Different analytical techniques can be used to infer structural alignment in carbonaceous material such as char.\(^{135}\) Popular techniques include: XRD which gives quantitative but average data on the structural order, optical anisotropy can be used to identify regions of alignment (typically above 1 µm resolution), solid-state NMR can provide quantitative structural information on the carbon types, and Raman spectroscopy can provide a measure of disorder relative to carbon content. None of these techniques are however able to adequately capture the microstructural diversity of char. Advances in HRTEM have made it possible to capture this structural diversity with advances in image processing allowing the direct quantification of the *distribution* of structural features like length of fringes (size of aromatic molecules), interlayer spacing, stacking number (aromatic molecules per stacks) and degree of orientation.\(^{17,123,125}\) These depend on the structure of the parent coal as well as the time-temperature histories occurring during devolatilization. Quantifying these structural features and their transformations
contributes to the ability to rationalize behavior and appropriately predicting the subsequent reactivity.

Early attempts to capture structural features of raw coal were not very successful and the intense radiation caused damage to the structure.\textsuperscript{172, 173} Significant improvements have since been made to the technique which provides the ability to successfully evaluate coal structure.\textsuperscript{123, 174} A HRTEM lattice micrograph consists of fringes representing the edges of aromatic ring structures. These fringes can be extracted from the micrographs and analyzed to provide fringe parameters such as fringe orientation, stacking, interlayer spacing, and length distribution.\textsuperscript{1, 175} Multiple attempts have been made to quantitatively investigate the turbostratic structure of soot,\textsuperscript{126, 176} graphite,\textsuperscript{177} and char.\textsuperscript{123, 127} Sharma et al.\textsuperscript{173} showed good agreement between structural parameters obtained from XRD and HRTEM for heat treated coal. The advantage of HRTEM over XRD however, is that it provides distributions of stacking height and fringe lengths. Mathews et al.\textsuperscript{175} used HRTEM images to constrain the molecular weight distribution of Pocahontas coal, comparable to the distribution measured with laser desorption ionization mass spectra. This was achieved by assuming a shape of the aromatic coal molecules relative to the fringe length.\textsuperscript{175} Recently a tool was developed (Fringe3D)\textsuperscript{122} that enables the rapid generation of atomistic representations by means of directly capturing the aromatic structural features obtained through HRTEM lattice fringe images. This approach can potentially simplify the model construction process and better enable large scale models to be generated with the capability to capture the structural features of stacking and alignment.\textsuperscript{122, 178}

HRTEM is a well established technique that has been widely used, in combination with other techniques, to study the graphene structure of carbonaceous material.\textsuperscript{127, 176, 177, 179} Early work includes the utilization of HRTEM to explore the mechanism of carbonization and graphitization, and studying the microtexture of activated carbons and graphite.\textsuperscript{177, 180} According to Bandosz et al.\textsuperscript{181} HRTEM images also provide sufficient contrast between pores and the surrounding carbon matrix that detailed information regarding pore size
distribution and shapes should be obtainable. Most of the analysis work has been qualitative or semi-quantitative, with a few exceptions where quantitative information was extracted from the images. Image analysis is complex due to amorphous interference, contrast variation, overlapping of the aromatic layers, and curvature present in micrographs. Additionally, the correct operation of the equipment is as important as the subsequent image analysis to obtain accurate analytical results. In HRTEM, electron beams are emitted from the electron gun and transmitted through a thin specimen, interacting with the specimen. The intensity behind the specimen depends on the interaction of the transmitted electrons with the specimen, and forms an image. The image, where the crystallite layers are visible, is recorded digitally and can be qualitatively interpreted without any computer-aided processing. Quantification can then be performed through advance image processing algorithms where lattice fringes from the HRTEM micrographs are extracted and analyzed.

5.2.2 Image Processing of HRTEM micrographs

Different approaches using various software tools have been demonstrated for HRTEM image processing and fringe recognition. Only a few of these algorithms are well described, and in addition they only apply to one or two types of carbon structures. The absence of details in many of the published works also limits comparison of specific steps followed in different techniques. Processing involves various steps often including digitization, Fourier transform filtering, binarization, skeletonization, post-processing, and quantitative analysis. Although the individual steps of each processing algorithm varies, they generally include filtering in the frequency domain, which is an important step in noise reduction to obtain quantitative stacking parameters for coal char, soot, and carbon black. Another important step in image processing is thresholding, which is necessary for extracting lattice fringes. Based on the thresholding value, each pixel is converted to white (if the intensity of the pixel is larger than the threshold value) or black (if the intensity is less than the threshold value). The threshold value can be
manually defined based on the specific image and requirements, or it can be automatically selected through selection methods such as Otsu’s.\textsuperscript{188} While an automated selection method can reduce user bias, it is not as accurate when the intensity of the pixels is unbalanced (non-unimodal distributions).

Oberlin et al.\textsuperscript{177} applied optical diffraction techniques to TEM micrographs of amorphous carbon, where the pattern gives information on interlayer spacing. Based on the optical diffraction pattern, Oberlin et al.\textsuperscript{177} deduced that there is a strong parallel orientation to the fringes. The quantitative analysis in this work is very limited. Palotas et al.\textsuperscript{125} applied frequency band filtering in the Fourier space, and obtained fringe parameters such as length and orientation for carbon black and soot particles. A similar strategy for image processing was followed in the semi-quantitative procedure suggested by Shim et al.\textsuperscript{124} which provided average values of fringe length, tortuosity, and orientational order for different carbonaceous material, including char. More quantitative results are achieved in the work done by Sharma et al.\textsuperscript{123} and more recently by Yehliu et al.\textsuperscript{126} Yehliu et al.\textsuperscript{126} characterize diesel soot structure by selecting the region of interest and then processing it with an algorithm which includes a Gaussian low pass filter and a top-hat transformation. The low-pass filter attenuates noise, while the top-hat transformation improves the uneven illumination of the original image by subtracting the morphological opened image from the original. Morphological opening suppresses the fringes, leaving only the background, which after subtraction leaves an image with a smoother background. Sharma et al.\textsuperscript{123} utilized a step filter, instead of a band-pass filter, to extract more lattice fringes but also include more noise. An algorithm was also developed for obtaining the distribution of layer size, layer spacing etc. and for the identification of stacks.

The most prominent difference between the different processing algorithms is the filtering in frequency domain. Palotas et al.\textsuperscript{125} and Shim et al.\textsuperscript{124} utilize a band-pass filter to eliminate frequencies in the frequency domain image which fall outside a certain range, while Sharma et al.\textsuperscript{123} use a step filter which only has a lower limit, thereby allowing more noise and extracting a larger number of fringes. Using a filter like this
with a sharp cut-off in the frequency domain can however result in ringing artifacts near edges.ⁱ⁸⁴ To avoid ringing effects, Yehliu et al. uses a Gaussian low-pass filter in the frequency domain to reduce the high-frequency noise. Using a Gaussian function reduces ringing since the Gaussian function has a smoother roll-off compared to a regular step function where overshoot occurs.

5.3 Methodology

5.3.1 Image Analysis of HRTEM

The HRTEM micrographs were taken by Dr. Randy vander Wal. HRTEM examined the edges of char particles but without any particular orientation and therefore, as suggested by Mathews and Sharma¹⁰⁵, the dominant angle is calculated and a virtual rotation is performed (via an Excel manipulation of the alignment data). Each of the micrographs was orientated such that the dominant orientation is vertical. This aids viewing and comparing different micrographs, as well as allowing addition of data from different micrographs. After the extent of the rotation was determined mathematically the micrograph was rotated and analyzed.

Image Processing Toolkit coupled with Adobe Photoshop software was used to perform quantitative image analysis of 002 lattice fringe images of the coal chars. The technique presented here is derived from many different techniques that have been proposed to recognize and extract quantitative information from digital lattice fringe images.¹²³, ¹²⁴, ¹⁸⁴ Photoshop allowed a considerable improvement since it made automation of the analysis possible which increases the speed and further decreased investigator bias. Figure 5-1 gives a graphic illustration of the semi-automated procedure. It includes steps of digitization, contrast enhancement, histogram equalization, Fourier transform filtering, binary image conversion, skeletonization, fringe separation, and quantitative analysis.
The images were digitized and stored as 512 x 512 pixel 8-bit grayscale images. To apply a fast Fourier transform, the image requires dimensions equal to an exact power of two (e.g. 256, 512 etc.). For all operations, calibration was determined from the scale bar. The contrast of the image is then enhanced by means of clipping pixels at the low and high ends of the histogram to make effective use of the dynamic range of the display system (Figure 5-1a). This was followed by histogram equalization to increase the appearance of light-dark transitions (Figure 5-1b). Histogram equalization transforms the image intensity histogram into a uniform probability density function that spans over the full intensity range, thereby enhancing the visibility of gradients. Essentially this step spreads out the peaks to increase the intensity difference between a fringe and a background pixel.
Although the previous step improved the contrast, it also elevated the contrast of background noise. Therefore, a Gaussian blur was applied to smooth the image (Figure 5-1c). The Gaussian blur is a low-pass filter attenuating high frequency noise. The digitized images were then converted to frequency domain by a fast Fourier transform (Figure 5-1d) and filtered through a band-pass filter (Figure 5-1e). The filter selects a annular region in frequency space corresponding to the typical spatial frequency for graphitic carbons. This removes high-frequency artifacts to accentuate the features by sharpening the edges, and smoothes the low-frequency noise. Smoothing the edges of the aperture is important to reduce ringing which occurs with sharp frequency cut-offs. This was achieved by generating the annular filter using a built-in function allowing the amplitude of the frequency filter to be set (the value varies between white and black), thereby generating a filter with a gradual transition between the stop and pass band. In Figure 5-2 the effect of filter smoothing is demonstrated by looking at the scale bar. With the regular, sharp annular filter, on the left, ringing (white ringing) is observed around the scale bar, while the use of a smoothed filter drastically reduces the ringing effect.

![Figure 5-2: Effect of filter smoothing on ringing](image)
The filtered image (Figure 5-1f) is then inverse Fourier transformed and converted to a binary image by adjusting the threshold value (Figure 5-1h). The threshold value is adjusted to select the maximum fringe number and length without causing the fringes to overlap and merge. The binary images were skeletonized which essentially erode the fringe widths (Figure 5-1i). The images were further processed by removing small features and trimming off branches smaller than 3Å. Exceptionally small fringes can be the result of noise and can be removed without significant loss of data. This was followed by a series of actions to separate the combined structure and reconnect disconnected segments of structures. These structures were identified based on number of branch points and nearest neighboring distance and angle. Branch points were identified and deleted by inspecting fringes until a pixel with three neighbors was found. Based on orientation, two of the fragments were reconnected to form a single fringe and the third now formed a new fringe. This fringe would be deleted if it was too short (less than a certain number of pixels). Another parameter that was evaluated was the aspect ratio, which is defined as the ratio of the major axis to the minor axis if an ellipse would be fitted to each fringe. This parameter defines a limit for curvilinearity in the fringes for calculation purposes. Fringes with an aspect ratio less than 2 was deleted since the curvature was unrealistic.

5.3.2 Stack Identification Algorithm

Conventionally, quantitative information on carbon-rich structure, such as coal and char, was obtained through XRD providing average values for interlayer spacing, crystallite sizes, and stacking numbers. Direct evidence addressing the arrangement of the aromatic layers can be obtained through HRTEM providing not only average structural parameters but distributions. Through a processing algorithm in Photoshop (section 5.3.1) lattice fringes were extracted from HRTEM micrograph. Image analysis of these results provided a quantitative means to compare structural order, e.g. stacking number,
interlayer spacing, and orientation, of aromatic entities. While quantification can be performed manually it is time consuming, challenging, and subject to investigator bias.

Here, a computer algorithm was developed to quantitatively obtain structural parameters and distributions. Sharma et al.\textsuperscript{1} used a similar algorithm for extracting quantitative structural parameters, but unfortunately this is no longer available and the absence of detail prevents its direct reconstruction. Therefore a new algorithm was developed in MATLAB (The Math Works, Inc.) for statistical analysis of the extracted fringes. A graphical user interface (GUI) was developed in Matlab, and has consequently been compiled as an executable such that it can run on any computer (even those without Matlab installed). A user needs to install the accompanying Matlab Compiler Runtime before running the executable for the first time.

The image analysis procedure (section 5.3.1) provides the coordinates for the centroid of each fringe, its orientation, and length. The analysis is performed on the image analysis data of the lattice fringes. Currently, curvature information is not captured and fringes are therefore approximated and analyzed as straight lines. To classify when a fringe forms part of a stack is challenging. There is limited consensus on stack definition for statistical comparison.\textsuperscript{1,2,3} This is further complicated by the different stacking arrangements; face-to-face, staircase stacking, herringbone, and T-stacking.\textsuperscript{105} Here, only face-to-face and staircase stacking will be considered as there was limited evidence of the other forms. The following three conditions were used to compare each fringe to all other fringes to identify stacks:

1. Difference in angle

The difference in fringe orientation is calculated for all fringes. In order for layers to form a stack, they should have similar orientation. Mathematically this is implemented as the difference between two fringe angles should be less than the specified critical difference ($\theta_{\text{diff}}$).
2. Distance between midpoints

The direct (Euclidean) distance between the midpoints of all fringes are calculated. Between two fringes this parameter checks if the midpoints lay within a reasonable distance, for example, the ends of two long fringes can lay within the specified perpendicular distance from each other but the midpoints of these fringes could still be too far apart to be considered a stack. Additionally this relatively simple test criterion eliminates some of the data points for the next, comparatively complex calculations associated with the perpendicular distance criteria, thereby decreasing computational time. Figure 5-3 demonstrates the difference between the midpoint distance ($r_m$) and the perpendicular distances ($r_{perp}$) between fringes. These will strongly depend on the angles and relative lengths of the fringes.

3. Perpendicular distance

The perpendicular distance is calculated from the midpoint of the reference fringe to the next fringe as demonstrated in Figure 5-3. The slope of the perpendicular line is used to determine the coordinates of point (PP2) where it intersects the second fringe. The coordinates of this point is then used to calculate the distance between the midpoint of the fringe and PP2. This allows the identification of fringes whose perpendicular distance (or interlayer spacing) falls within a specified distance ($r_{perp}$). Fringes are usually identified as a stack when the interlayer spacing falls between 3.3Å and 3.8Å$^{123}$. For each pair of fringes there will be two parameters where the average will be used for identification.
Figure 5-3: Illustrating the distance between fringe midpoints and perpendicular distances between two fringes

The user is able to choose the critical angle difference ($\theta_{\text{diff}}$), spacing ($r_{\text{perp}}$) and midpoint distances ($r_m$) in the user-friendly GUI. The flow diagram of the stack identification algorithm is shown in Figure 5-4.
The fringe data which includes coordinates, orientations angle, and lengths was imported into Matlab. Matlab (“matrix laboratory”) was chosen since it converts the data to a matrix which makes data comparison relatively simple. The information of each fringe
was compared to all others, and if all three conditions were met, the data was stored in a new matrix which contains only fringes that form part of a multiple fringe stack. The data was manipulated to eliminate duplicates and organize the fringes into two, three, four or five layered stacks. The final check ensures that all stacks are unique so no single fringe forms part of more than one recognized stack.

The GUI, as shown in Figure 5-5, allows the user to define the critical values for three parameters defining a stack; midpoint distance, perpendicular distance, and orientation difference.

The GUI provides the option to generate an Excel spreadsheet containing fringe information of each stack, Excel spreadsheet with statistical values for stacking parameters, and a figure illustrating different stack sizes by color. The fringe information can then be used, along with Fringe3D to generate 3D representation of the stacks. Statistical averages and standard deviations of the interlayer spacing, fringe length, and orientation are also available in the generated spreadsheet. The GUI also provides the option of producing histograms presenting the distributions of the aforementioned
stacking parameters. The user can also define the number of bins in the histogram which will automatically define the bin size.

The ability to determine d-spacings is heavily influenced by the resolution of the micrograph. Resolution improvements in lattice fringe micrographs will increase confidence. In the current work a typical d-spacing is ~ 5 pixels (one pixel per 0.7 Å), thus limiting the confidence in the current determinations. The advantage of this stack identifying algorithm is that it removes human subjectivity and significantly decreases the analysis time. It is also user friendly and the user does not need experience with the software to run the analysis. The automation approaches created here are essential for improved approaches in the sampling process for HRTEM micrographs for char. Following heat treatment it is common that the distribution of features becomes significantly more varied than the parent coal.

5.4 Results and Discussion

Using the procedure outlined above, the HRTEM micrographs of the prepared char samples were processed. The stacking parameters and structural features of the two chars were quantified and compared. All the results and analyses presented in this chapter were performed on the Highveld char sampled at 400ms and the Waterberg char sampled at 240ms (selected due to the low volatiles values that were assumed to be at the end of their respective devolatilization).

5.4.1 Experimental Observations of Char’s Microstructure

Figure 5-6 contains six original, eight-bit, grayscale, bright-field HRTEM images of the Waterberg char as well as their corresponding skeletonized images. The skeletonized
images are only of the regions of interest which excludes any areas where overlap of layers occurred or which appeared to be out of focus.
In the HRTEM images carbon layers appear as dark lines in the bright-field image as the fringes block or scatter the incident electron beam. Since the incident electron beam is blocked by the carbon layers (fringes), dark segments are picked up at the detector. The bright areas are formed as the incident electron beam passes between the graphene layers. Visual assessment of the vitrinite-rich char micrographs showed that the carbon layers show development of anisotropic units with preferential alignment. Sharma et al.\textsuperscript{174} found that the size of anisotropic units are strongly influenced by plasticity. The vitrinite-rich char experienced thermoplastic transformations during heating (devolatilization) which allowed the growth and re-alignment of the carbon crystallites to form these regions with preferential orientation.\textsuperscript{174} In all the lattice fringe images, the fringe lengths appear to be in the same order. It is likely that the curvature observed in the individual carbon layers is due to the presence of internal unmatched non-hexagonal rings.\textsuperscript{191} The skeletonized images were generated through image processing of the region of interest with the
Photoshop and Image Processing Toolkit. To further illustrate the degree of ordering, false coloring by momentum angle was performed on the lattice fringes.

Figure 5-7 shows image W4i that have been rotated 145° clockwise, such that the largest percentage of fringes (by percentage of total fringe length) was vertically orientated. By rotating all the micrographs, makes comparison easier. Figure 5-7 shows a rotated false colored image of W4i and the distribution of fringe orientation based on the % of the total fringe length. In the false colored image, fringes with the same orientation have the same color, clearly indicating regions with similar orientation. The histogram shows that when the image is rotated, 26% of the total fringe length is vertically aligned (at 90°) and the most of the other fringes have an angle within 45°, clearly indicating preferential alignment.

![False colored image (W4i) by orientation obtained from HRTEM and the distribution of fringe orientation within 15° bins](image)

Other micrographs, such as W4 shown in Figure 5-8, showed a less sharp probability distribution with a larger tail (a fat-tailed distribution).
When rotating the W4 skeletonized image with a 90° angle (clockwise), the mode of the distribution is at 90° but includes only 16% of the total fringes. However, the false colored image clearly indicates distinct regions of preferential alignment. If the micrograph is divided into multiple regions, the distributions should be sharper. Figure 5-9 shows distributions obtained if W4 is divided in two regions (as indicated by the black dashed line).
The shape of the individual probability distributions now approaches that of a normal distribution, where 24% of the total fringe length falls at the mode of the distribution. Regions of alignment (or turbostratic order) are present in all the observed Waterberg char micrographs.

Figure 5-10 contains five original, eight-bit, grayscale, bright-field HRTEM images of the Highveld char as well as their corresponding skeletonized images of the region of interest (in-focus region).
Figure 5-10: Raw and processed HRTEM images of inertinite-rich Highveld char
Upon visual inspection, some Highveld char micrographs (H4, H4i, and H4iii) show turbostratic regions where multiple layered stacks with preferential alignment are visible. These turbostratic regions are visible in micrographs H4, H4i, and H4iii. Even though the Highveld char displays these regions of highly ordered alignment, it also contains a large fraction of less ordered carbon with no preferential alignment which was not observed in the Waterberg images. Micrograph H4ii is an example of an isotropic structure where there is no clear, favored orientation of the fringes. Through observation, the fringe lengths in the skeletonized images H4 – H4iii appear to be in the same size range as the Waterberg fringe lengths. Exceptions are shown in micrographs H4iv and H4v where distinct fringes are not as evident (lack of contrast) and the observable lattice fringes are mostly very short. This could be due to amorphous regions in the char but could also indicate experimental error caused by imaging a sample that was not thin enough, resulting in overlap of multiple layers.

5.4.2 Quantification of Char’s Microstructure

Identification of Stacks:

The Matlab GUI, as shown in Figure 5-5, allows user defined critical parameters (maximum angle difference, midpoint distance, and perpendicular distance) to characterize stacks. Figure 5-11 shows the stacks identified in the H4ii skeletonized image for two different sets of parameters. Stacks identified with two layers are colored red, three layers are colored blue, four layers are colored pink, and five and more layers are colored teal.
A trial and error approach was used to adjust the stacking conditions until the optimum number of true stacks were achieved (albeit a personal preference). Figure 5-10(a) shows stacks identified with a maximum distance of 4 Å and angle of 20°. Figure 5-10(b) shows stacks identified when the maximum distance was increased to 4.5 Å and the angle to 22°. As the black arrows point out on Figure 5-10(b), if the stacking limits are too high, multiple stacks will be grouped and mathematically identified as a single stack (colored teal). The grey arrow points out a stack, which if it had been evaluated by eye, would not have been identified as a stack due to its large interlayer spacing. Figure 5-11 is an example of stack identification for the skeletonized W4iv image.
Figure 5-12: W4iv- Stacks identified with (a) the correct parameters and (b) parameters too small

Figure 5-11 (a) shows the stacks identified with the same parameters used in Figure 5-5 (a). These optimum stacking parameters were developed through multiple runs on all the skeletonized images. Figure 5-11(b) is presented to show a case where the stacking limits were chosen too low. They were just slightly decreased from the values used in Fig 5-12 (a) but it is evident that many layers that should be, were not identified as part of a stack. Once these parameters are decided, running the GUI takes only a few seconds. The GUI does not only produce these images but also creates graphical representations of probability distributions for all the calculated stacking parameters (see Appendix B). A worksheet is also created with all the quantitative results if needed for further processing.

**Distribution of Stacking Parameters**

The stacking distributions, such as the number of layers per stack, layer orientation, and lengths, were determined for each micrograph. These distributions were combined to produce average stacking distributions for both char samples. Figure 5-13 shows the stacking size distributions calculated from the four and five micrographs of the Highveld and Waterberg chars respectively.
Figure 5-13: Distribution of stacks according to the number of layers in a stack

Figure 5-13 shows that a large fraction of the aromatic layers do not form part of a stack (with the specified stacking requirements) but are present as individual layers. A similar trend of stacking sizes was observed in the HRTEM analysis on char presented by Sharma et al.\textsuperscript{174}. The fraction of single layers observed in the Highveld char (0.61) is significantly larger than the fraction for the Waterberg char (0.44). In order for aromatic layers to reorganize and stack during devolatilization, the sample has to go through a plastic stage where the mobility of molecules increases. The higher degree of stacking observed in the Waterberg char can corroborate evidence of the thermoplastic state observed in optical microscopy (section 4.3.3).

Figure 5-14 shows the distribution of layer lengths as determined through analysis of the lattice fringe images. The size ranges are represented as a fraction of the total layers in each size of stack. Error bars are shown that have been calculated from standard deviations from the different micrographs.
Figure 5-14: Normalized distribution of layer lengths for stacks of different sizes

For both char samples, if fringes larger than 5Å are included, the largest fraction of layers is smaller than 10Å. This is true for stacks of all sizes, and there is no notable trend as the layers per stack increase. Error bars indicate the standard deviation. As Figure 5-14 indicated the number of single layers is more than the multiple layered stacks which means the sample size for single layers is larger, decreasing the uncertainty, and therefore the error bars.

To fully capture stacking parameters it is important to note that within each stack, the layers commonly have variable, yet often similar lengths. To quantify this, a ratio was calculated between the layer lengths in each stack. The length of the shortest layer in each stack is divided by the length of the longest layer in each stack. Therefore, a ratio of 1 is approached when the layers in a stack are similar lengths. Figure 5-15 shows the percentage of the total stacks (consisting of at least two layers) with a ratio larger and smaller than 0.5.
Figure 5-15: Distribution of layers according to the average ratio between fringe lengths in the same stack.

Figure 5-15 shows that 59% of stacks identified in the Highveld char have a ratio higher than 0.5. This signifies that in 59% of the stacks, one of the layers is never less than half the length of another. Also, 41% of the stacks consist of layers that vary more significantly in length. This ratio could be used as another condition for identifying stacks if stacks that vary too much in layer length should be excluded. Some 80% of the Waterberg fringes in a stack have length ratios higher than 0.5, indicating a larger amount of stacks have similar layer lengths compared to Highveld char. Similar to previous observations, this could also be due to the higher thermoplasticity during heat treatment.

Section 5.4.1 demonstrated how the micrographs were rotated in order to move the mode of the distribution to 90°. Figure 5-16Figure 5-17 presents these distributions for all the analyzed Highveld char micrographs. The distribution of the layer orientation is based on the percentage of the total layer length falling in that range. Of the Highveld histograms, H4i is the only sample which has clear preferential alignment with a significant fraction of the fringes (30%) at the histogram mode of 90°. Less than 15% of the total fringes in
H4, H4ii and H4iii are oriented at 90° and a large fraction of the fringes in these images are oriented almost perpendicular to the mode (i.e at 0 and 180°). The average of all the micrographs was calculated and it still shows a definite peak at 90°, although the error bars are large due to the reduced sampling frequency (occurrence). Figure 5-17 shows the angle distribution obtained through analyzing the Waterberg char’s HRTEM micrographs.

Figure 5-16: Distribution of layer orientation for Highveld chars as determined from processing of HRTEM micrographs
In all the Waterberg distributions, at least 17% of the total fringe length is oriented at 90°. However, the average of the Waterberg samples oriented at 90° was only slightly larger than the Highveld average (18% compared to 21%). The average distribution of the Waterberg samples is smoother with less standard deviation. Overall, the distributions indicate that the micrographs of the Waterberg char show slightly more preferential alignment than those of the Highveld char. If each micrograph is divided in two domains (as demonstrated in Figure 5-8), the Waterberg distributions would show much greater preferential alignment compared to the micrographs of the Highveld chars. The presence of a thermoplastic stage during heat treatment would allow the aromatic layers to reorganize and form preferentially aligned domains. With the preferential alignment observed here, regions of anisotropy would be expected under cross-polarized light during optical microscopy. Although regions of optical anisotropy were observed during optical microscopy in Chapter 4, there were also multiple isotropic domains. This could be due to the anisotropic domains being smaller than the optical microscope was able to detect.
**Compare HRTEM to average XRD parameters**

The main advantage of HRTEM over XRD is that distributions can be obtained rather than a single average value which does not capture the structural complexity of carbonaceous material. However, comparison of the averages obtained through these two techniques has been made. Before direct comparison, it is important to note the differences in what they measure. While HRTEM provides the capability to examine all aromatic layers in focus, XRD only measures crystallites (stacks). Therefore, for comparison, stack distribution should not take into account the fraction of single layers that was obtained from TEM analysis. Yehliu et al. suggest that in order to effectively compare the interlayer spacing with XRD results, the fringes has to be screened for curvature and only linear portions of the lattice fringes should be considered. This suggestion is based on XRD only representing the layer diameter of the linear portions. Even though the image analyses proposed in this work used the aspect ratio to eliminate fringes with unrealistic curvature, the curvature was not considered in the algorithm for stack identification.

Furthermore, Yehliu et al. only included layers whose perpendicular distance falls within a certain range (3.3 – 3.8\(\text{Å}\)). Sharma et al. only included stacks in the average parameter calculation if the layers had less than 10\(^\circ\) difference. Since XRD only measures crystallites consisting of nearly parallel layers, this strict criterion is reasonable for comparison purposes. However, the goal of this work was not to compare XRD parameters or evaluate the accuracy of HRTEM image analyses, since that has already been done. The motivation here was to capture and quantify the diversity in the microstructure of char, which includes ‘non-perfect’ stacks, which would then be utilized to accurately reproduce the complex and diverse molecular structure of char in three-dimensional space. Therefore, the above mentioned criterion should be taken into consideration to obtain structural parameters similar to that of XRD. It is however still important to acknowledge the shortcomings of HRTEM. Table 5-1 summarizes the
average stacking parameters obtained through both techniques. For the HRTEM analysis layers larger than 5Å were considered.91

Table 5-1: Comparison of stacking parameters calculated with XRD to those estimated from HRTEM analyses

<table>
<thead>
<tr>
<th></th>
<th>Average layer length Å</th>
<th>Interlayer spacing Å</th>
<th>Number of layers per stack</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD</td>
<td>HRTEM</td>
<td>XRD</td>
</tr>
<tr>
<td>Highveld</td>
<td>24.5</td>
<td>11.5</td>
<td>3.59</td>
</tr>
<tr>
<td>Waterberg</td>
<td>26.8</td>
<td>10.8</td>
<td>3.60</td>
</tr>
</tbody>
</table>

Table 5-1 shows that there is reasonable agreement between the average interlayer spacing calculated through the two different techniques. There is a significant difference between the techniques for average layer length and number of stacks. Although the average HRTEM layer length presented here includes single layers, the averages were also calculated with only multiple layered stacks and the values were still in the same range. An important factor is the minimum size of fringes taken into account. Here, only fringes smaller than 5Å were rejected, which is still reasonably small considering a molecule such as coronene is ~10Å. Hurt173 obtained similar results, where the XRD parameters indicated larger crystallite sizes compared to HRTEM parameter. Here the HRTEM fringes were calibrated according to the XRD results to obtain comparable average HRTEM values. Hurt only rejected fringe lengths smaller than 15Å, and therefore calculated a much higher average (in better agreement with XRD values). Davis et al.127 found the mean crystallite diameter of heat treated carbon coals measured by HRTEM to differ by a factor of 3.7 from values determined with XRD. Sharma et al.173 found comparable values for the average layers per stack calculated with the two techniques. When looking at the fringe length distributions in this work, they only consider fringes larger than 8Å. If only lengths larger than 8Å are considered for this work, the Highveld char has an average layer length of 15Å and the Waterberg has an
average of 14Å. Hence, comparing averages are highly dependent on what is considered to be a part of the range.

The above results show that although some of the HRTEM values agree with XRD data, there are also mayor inconsistencies. HRTEM provides supplementary structural information to XRD but it is important to note the limitations of this technique. A severe drawback of HRTEM is that the studied sample is very small, and it considers only of a limited number of regions within single particles. Although time consuming, this problem can be overcome by taking more micrographs and thereby increasing the sample size. The development of semi-automated approaches for image analyses and stack identification, as presented here, significantly reduces the time associated with processing multiple images. In the past, the lack of contrast or overlap of particles was another factor complicating the analysis of micrographs. But with recent advancement in instrumentation, and the correct operation thereof studies have shown that reliable images representing true carbon structure can be obtained through HRTEM.

5.5 Conclusion

The development of a semi-automated approach for HRTEM image analysis, in combination with a new technique for quantifying distributions, enabled further characterization of the crystalline structure of the inertinite-rich and vitrinite-rich South African coal chars. Quantification is based on image filtering and geometrical parameters, such as the minimum layer length and stacking criteria. Along with choosing these parameters, accurate structural quantification depends on consistent and accurate microscopic techniques. Here, the parameters were chosen based on literature and trial-and-error approaches to obtain realistic parameters. Image analysis indicated that the Waterberg char showed a larger degree of preferential alignment, compared to the Highveld char. Waterberg also demonstrated a larger degree of stacking, where only 44% of the total stacks are single layers (not part of a stack), while 66% of the total layers
identified in the Highveld micrographs do not form part of a stack. The Highveld char had a slightly larger average layer length; 11.5Å compared to 10.8Å for Waterberg char, when considering all fringes larger than 5Å. Although these values do not compare well to average XRD layer lengths, the two techniques do not measure the exact same parameter and furthermore the HRTEM image analysis averages are highly depended on the range of fringes included. The image processing algorithm made the HRTEM analysis and quantification procedure less time consuming, which would enable the analysis of significantly more micrographs in future work. Furthermore, the semi-automated approach also removes human subjectivity involved in computational analysis. The proposed technique can be utilized to quantitative analyze the structure of any carbonaceous materials from their HRTEM images.
Chapter 6

Construction of Large Atomistic Char Representations Capturing Structural Differences

6.1 Abstract

Molecular models of coal have populated the literature in the quest to describe coal structure at a molecular level and their utility has been demonstrated. However, coal char models are fewer, remain small in scale, and are more limited in their utility despite there being a considerable interest in relating char structure to reactivity. Recently the ability to increase the scale of molecular representations has significantly been improved which, together with further advances in analytical techniques, potentially enables the incorporation of distribution of structural features such as stack size, orientation, porosity, density, and pore size distribution.

Here the ability is increased to inexpensively create improved char structural models by adding an additional capability: the construction of large-scale models by first producing the desired distribution of crystallites (with control over the distribution of width, height and orientation). Earlier work generated carbon-rich structures through Fringe3D, a Perl script that is able to directly reproduce aromatic structures by utilizing HRTEM image analysis. This allowed the direct determination of structural diversity of the aromatic structure. Although good agreement was achieved between the model and the pair distribution function of the structure, this approach limits the depth of the molecular representations which restricts further use. To improve the ability to generate large-scale representations, an additional step is proposed here. Fringe3D is used to produce the desired distributions of aromatic stacks (as determined from HRTEM image analysis) with control over the stacking diameter, orientation and height. This approach offers the
unique capability to incorporate distributions of poly-aromatic hydrocarbons within the diversity of stack sizes. An additional Perl script, Vol3D was developed to populate a specified cuboid volume with the distribution of crystallite stacks in a more realistic representation with control over the height, width, and depth of the rectangular cuboid volume. Similarly, the mesopore size distribution can be controlled. Two large molecular representations of char were rapidly generated with this new approach. A vitrinite-rich char (42703 atoms) and inertinite-rich char (32206 atoms), incorporated structural diversity that other approaches could not capture. The large representations can be utilized to explore reactivity differences which occur as a result of structural differences.

Here, a rule-based approach was developed to evaluate combustion behavior for these large char molecular representations with control over structural features. Reactivity was explored by following the oxygen accessibility into the structure assuming that reactive carbons are “lost” when an oxygen atom comes within a close proximity of an edge carbon or hydrogen atom. In this manner a more rapid exploration of reactivity can be explored and related to structural features. This approach significantly reduces the computational intensity and mainly focuses on the effect of oxygen diffusion through the char structure simulating combustion at high temperatures where diffusion controls the overall reaction rate. Diffusion and atom deletion steps were repeated until 80% of the original structure was “combusted”. As combustion progressed, the oxygen obtained access to internal pores which increased the combustion rate. The combustion rate for both char structures increased with conversion to reach a maximum at 40% and 65% conversion for the inertinite- and vitrinite-rich structures respectively. After the maximum, the reactivity decreased which is in agreement with reactivity profiles found in literature. Comparison of mass loss showed that the vitrinite char structure reacted in fewer steps than the inertinite-derived char structure. One of the factors contributing to the higher combustion rate was the presence of internal pores, which resulted in larger accessible reactive surface. The two models were explored without considering ash contributions. Future work can increase automation which will further limit user bias. Accuracy can be improved by incorporating functional groups, considering diffusion of
products out of the structure and incorporation ash into the model, which will act as a barrier to the oxygen

6.2 Background

Devolatilization is an important initial step in many coal conversion processes including combustion, gasification, and liquefaction. During devolatilization thermal decomposition of the coal structure takes place to produce light gases, condensable fragments such as tar, and char. Although chars are typically highly aromatic, they can still exhibit different degrees of structural order even within a single sample. The structure of char depends on time-temperature history, the precursor properties, and operating pressure, which is important since it affects the overall char reactivity. The structure influences the ease at which oxygen can diffuse to the reaction sites, as well as the ease at which the reaction products can diffuse out of the particle.

During combustion the char structure may go through further transformations (often termed annealing), changing the porous structure and therefore the accessibility of reacting gases to the reactive sites. Despite extensive research on char structure, structural representations of char are still limited in size and have not been able to even partially capture the structural diversity. Char molecular modeling is challenging and time-consuming. Generating a char model of a large enough scale to capture the diversity requires extensive char structural information beyond average values and it is not currently possible to create a char structure that captures an appropriate reactivity. The development of realistic molecular representations of char can contribute to a better understanding of the structure-behavior relationship during combustion and can improve design strategies for the effective utilization of coal in gasification and combustion systems. It is therefore desirable to develop new tools for the construction of large-scale char representations capturing the distribution of structural diversity. Simplifying the construction of large-scale models will enable capturing various aspects influencing
reactivity that cannot be evaluated by traditional experimental approaches. Specifically a highly automated construction approach that can control structural orientation, stack size diversity and orientation(s), pore size distribution, ash particlesize and its distribution, and char morphology will allow these contributions to reactivity to be evaluated independently. To achieve this goal with char structures at scale (100,000 atoms) also requires a new construction approach and a means to evaluate reactivity via atomistic simulation and calculation.

6.2.1 Development in Carbon Modeling

While coal char modeling is limited there is a wealth of work related to carbon modeling. Bandosz et al.\textsuperscript{181} divides structural models of porous carbons in two broad categories; geometric models such as the single pore – and slit models which assume uniform pore geometry, and more complex models which incorporate more features such as pore connectivity and more realistic carbon sheets. The slit pore model was one of the earliest and most commonly used models to characterize the micro- and mesoporosity in porous carbons.\textsuperscript{195, 196} This model assumes that carbon has slit-like pore geometry, as originally proposed by Everett and Powl,\textsuperscript{197} and illustrated in Figure 6-1. Each individual pore is represented as the space between two parallel, perfectly aligned, graphitic-like crystallites separated by a width, H.\textsuperscript{198}

![Figure 6-1: Slit-pore model\textsuperscript{197}](image-url)
Although this simplistic model is easy to apply and has been successful in developing a theoretical basis for adsorption in carbons,\textsuperscript{199} it is based purely on geometry and does not account for any specific carbon structural features or the interconnectivity of pores.\textsuperscript{200} Results show that the ideal slit-like carbon pores is far from reality since porous carbons are disordered with heterogenous pore structures,\textsuperscript{201} and therefore the model fails to accurately predict adsorption capacities.\textsuperscript{202} Despite the model’s simplicity, it is still utilized. Computer-based molecular modeling provides the potential to go beyond the simplistic slit pore model approach, and incorporate geometry, topology, and chemical heterogeneity of different carbons.\textsuperscript{195}

Existing char structural representations range from small simplistic representations that are easily constructed to more complex representations generated through high-powered computational approaches. Several smaller char models have been generated by modifying existing coal structures to reproduce the char properties.\textsuperscript{34, 203} A more recent “smaller scale” char model was developed by Domazetis et al.\textsuperscript{204, 205} which transformed an existing low-rank coal model into char according to pyrolysis chemistry. This model examined the inorganic interactions with coal through higher modeling approaches but the model was less than 300 ion-exchangeable atoms, which prevents the incorporation of any diversity.\textsuperscript{195}

Reverse Monte Carlo (RMC) is a reconstruction technique, where the molecular model is rearranged to best match experimental structure data obtained from NMR or XRD.\textsuperscript{206} This technique enables the construction of more complex representations and has been used to model various porous carbons.\textsuperscript{199, 201} Figure 6-2 shows the model developed by Segarra and Glandt\textsuperscript{207} where the structure was modeled as an isotropic collection of cylindrical disks representing graphitic sheets of specific thickness (corresponding to two graphene sheets) and uniform density. The model has pores (blue spheres) of uniform size distributed throughout the structure.
The carbon model was generated by randomly orienting the disks into a periodic simulation cell. Monte Carlo experiments were then performed to attain thermodynamic equilibrium. In contrast to the simple geometry discussed earlier, this model introduced different pore shapes and connected pore topology, but the geometrical disorder of the carbon sheets in the model does not reproduce experimental observations. Furthermore the platelets are all the same size and thickness which doesn’t represent realistic chemical features. The RMC approach has been used to modify the chemical features to correspond better to experimental data. A large porous carbon structure was generated through RMC by Thomson and Gubbins\textsuperscript{199} from a cubic, periodic simulation cell containing rigid, parallel graphene layers. The layers were moved and removed to match the experimental pair distribution function from SAXS (small-angle X-ray scattering) for an activated carbon. The model provided a simplified representation for a highly ordered, graphitizable carbon given the starting structure. This approach will not permit the incorporation stacking diversity found in a more disordered char structure. Furthermore the model was unable to capture any ring defects, flow domains or mesoporosity.\textsuperscript{199} Since RMC is a fitting method, the resulting model can contain some unrealistic or unphysical small features that have significant bond angle dependence, e.g. three membered rings.

Figure 6-2: Graphitic platelet model generated by Segarra and Glandt.\textsuperscript{207} Reprinted with permission from Elsevier whose permission is required for further use.
Jain et al.\textsuperscript{206} found that models generated through a RMC approach can be unstable and significant changes in the structure occur upon relaxation.

The Hybrid Reverse Monte Carlo (HRMC) is an improved approach, where the radial distribution function and the potential energy are simultaneously minimized.\textsuperscript{201, 208} The inclusion of the energy term in the routine decreases the probability of having unphysical bonding environments\textsuperscript{208} but this also increases the computational expense. HRMC has been used to model different forms of carbon, including the microstructure of an industrial char shown in Figure 6-3.

![Figure 6-3: Side view of an atomic configuration for char generated through HRMC. From Petersen et al.\textsuperscript{209}, reprinted with permission from Elsevier whose permission is required for further use.](image)

The char structure was regenerated from dense graphite with nearly equal dimensions of 20Å. The atoms were selected and then randomly moved around until the error between the simulation and the experimental pair correlation function data was minimized. The structure consists of only carbon atoms (~1300 atoms), where dark atoms identify two-fold coordinated atoms, white atoms identify three-fold coordinated atoms, whilst light
grey atoms correspond to four-fold coordinated (diamond-like) atoms. Model construction via RMC requires considerable computing power, which limits the scale of the model. Therefore, this modeling technique is largely applicable to crystalline (highly ordered) carbons, and not structurally diverse samples. Both the RMC and idealized slit models have drawbacks that reduce their usefulness.

An alternative approach to char modeling is to generate representations based on structural features directly captured from HRTEM lattice fringe images. HRTEM has been one of the indispensable tools for characterization of diverse structure of porous carbons such as activated carbon and char. Analysis of these images provides information on the degree and distribution of turbostratic (crystalline) order. The image analysis data in combination with a generation tool such as Fringe3D enables more rapid model generation of carbon materials with the inclusion of nanostructural features.

Fringe3D is a Perl script that was developed and utilized by Fernandez-Alos et al. to generate slice models of char and soot directly from lattice fringe images. Fringe3D, along with additional Perl scripts, were also utilized by Castro-Marcano et al. to generate atomistic representations of Illinois no.6 coal and char. The lattice fringe images of the Illinois no. 6 coal and char (obtained through image processing of HRTEM micrographs) were taken obtained in literature. This approach enabled the models to capture crystallite parameters such as stacking height, layer size and interlayer spacing. The coal and char models are composed of 50789 and 7458 atoms respectively which offer a significant scale improvement over most other similar type models. Thus, HRTEM based char modeling has the advantage of capturing large scale, structurally diverse chars with a practical computing effort. Even though the above mentioned char model captures the distribution of aromatic layers, it uses an approach (Theodorou and Suter) which randomly distributes the constructed layers into a periodic simulation cell. Therefore, there is no control over the alignment of the layers since the structure is generated by placing layer by layer based on the minimum energy, taking the interactions
of atoms into account. This prevents the ability to generate the regionally orientated and the flow domains seen in HRTEM micrographs, as well as incorporation of specific pore sizes to agree with the exact pore size distribution.

6.2.2 Modeling Coal Devolutilization and Char Combustion

Molecular modeling can serve as a predictive tool for coal devolatilization which allows progress in the understanding of the behavior and products, such as char. The first molecular model of coal by Fusch and Sandoff\textsuperscript{216} also included a pyrolysis pathway. The pyrolysis pathway attempted to visualize the structural transformations occurring during thermal decomposition which involves carbon-oxygen bond breaking to yield low molecular weight fragments. Mathematical modeling of coal devolatization chemistry includes predictive simulations by Solomon et al.\textsuperscript{134, 217} and Niksa and Kerstein.\textsuperscript{218} These models provide quantitative relationships between the molecular structure of coal and the physical and chemical properties of the devolatilization products.

Visual representations of devolatilization include those by Mathews et al.\textsuperscript{219} and Jones et al.\textsuperscript{203} which intended to capture the coal to char transitions. This was achieved by utilizing different analytical characterization techniques to capture the structural information of the chars generated in drop-tube and wire-mesh reactors, respectively. The original, small coal structures were then manipulated manually with the goal to produce model with the structural properties (H/C, aromaticity etc.) of the resultant char. This manipulation approach is impractical for larger structures due to the complexity and was also highly simplistic. The structures were not able to capture the stacking of the aromatic layers, as indicated by X-ray diffraction, or orientated micro-domains observed in HRTEM images. As capturing the time-temperature histories and the dependent thermoplastic transformations are extremely challenging an alternative approach to directly generate a char structure from analytic data is likely to result in a more appropriate structural representation.
As discussed in Chapter 3, several mathematical models have been proposed for prediction of reaction rates in chars and other carbons. One of the most simplistic models is the shrinking core\textsuperscript{220} model which assumes that all reactions occur on the external surface. Internal reactions are thereby ignored, which limits its prediction ability since the internal reactions strongly influence the overall reaction rates. Petersen\textsuperscript{221} proposed a model that takes the evolving surface area into account by assuming uniform cylindrical pores. According to Kyotani\textsuperscript{222} this model contains too many adjustable parameters. Other models taking the volume and internal reactions into account include those proposed by Hashimoto and Silveston\textsuperscript{223}, and Gavalas\textsuperscript{50}. These models have the drawback of not taking any structural changes into account that occur during conversion, and thereby they are unable to predict the rate maximum often observed in reactivity profiles. The random pore model\textsuperscript{48, 224} considers competing mechanisms of pore growth and overlap, and can therefore predict the maximum rate observed in reactivity profiles. These mechanisms are incorporated in the model through a structural parameter which is obtained from experimental reactivity data. While useful in data fitting and in qualitative predictions, the structural parameter have been found to be inconsistent with values from structural characterization.\textsuperscript{225, 226} Although these models offer a broad prediction of reactivity, the they do not offer any explanation of structural influences, catalytic effects of ash, ash layer influence, etc. Mathematical models provide a basis for connecting a simplistic average structure to reactivity behavior, but it is necessary to incorporate a distribution of chemical and physical parameters to provide an accurate predictive tool for process analysis purposes.

A major deficiency of existing reactivity models are that they do not account for the nature and distribution of the stacking of planar aromatic layers (i.e. turbostratic structure), and can therefore not incorporate the associated anisotropy that influences reactivity. These models essentially assume that all the surface carbon atoms are accessible to and equally reactive towards oxygen. It is well known that the alignment and size of carbon crystallites affect the amount of edge sites, which is more reactive than
internal sites.\textsuperscript{227} The accessibility to these sites is also important and is affected by the physical structure of the char. Figure 6-4 shows 3 different types of graphitic carbon edge sites.

![Figure 6-4: Demonstrating the different carbon active sites (modified from Kyotani et al.\textsuperscript{222}s)](image)

Kyotani et al.\textsuperscript{222} provided useful insights into the reaction behavior and mechanism of a single carbon layer. The reactive surface area was found to be independent of crystallite shape (related to the type of sites) but highly depend on crystallite size and the presence of the active sites. Therefore it is necessary to consider the distribution of crystallite sizes in reactivity predictions. Bhatia\textsuperscript{225} suggests the need for a new reactivity model based on this concept of char being composed of aromatic layers of different size forming stacks.

Here it is proposed that a modeling approach that uses the distribution of crystallite stacks and the structural diversity within stacks, obtained from HRTEM image analysis, as building blocks for a large scale char structure with control over the orientation, stacking, and lengths of aromatic layers, the pore size distribution, and ash composition and dispersion. The goal of providing a highly automated approach to construct char structures that offer approaches that are cognitive of inherent reactivity differences or permit the influence of those parameters on char reactivity to be explored independently. Due to the lack of control over coal char structural transformations this offers a route for scientific exploration of char reactivity that cannot be explored experimentally. The generation of large-scale and accurate char models would provide the opportunity to
explore char conversion chemistry. Insight to the dissociation and formation of chemical bonds at an atomic level could be achieved through reactive molecular dynamics.

Numerous chemical and physical phenomena that influence combustion reactivity have been extensively studied. These include evolution of surface area, effective oxygen diffusion through the changing porous char, developing regions of anisotropy, maceral reactivity differences, mineral matter influences (includes increased reactivity due to catalysis as well as decrease due to obstruction of reactive sites and energy loss due to phase change), changes in functional groups (e.g. hydrogen loss), and alterations to the aromatic layers (due to rearrangement and oxygen reactions). Including the detailed quantitative contributions of all those phenomena is currently not realistic, due to time and computational constraints. In the present work we have focused on incorporating some major structural parameters but also the development of the tools providing the capability to improve the inclusion of structural influences.

Reactivity molecular dynamics has shown to be effective in the exploration of char oxidation reactions. The ReaxFF force field for hydrocarbon combustion has been used to perform simulations to examine the structural transformations and chemical processes associated with char combustion at high temperatures (3000 – 4000 K). Unfortunately, the high computational cost and the use of very high temperatures to reduce simulation times will dismiss structural details in char structures and prevent exploration of structure-reactivity relationships due to the extensive processing required for large scale structure (up to a months for a single structure). Thus, a simplified approach is created here utilizing regular molecular dynamics at reasonable temperature with carbons being removed when oxygen is within the required range of reactive carbons. Using an iterative approach the reactivity of an inertinite-rich char and a vitrinite-rich char is evaluated in this work.
6.3 Methodology

Model construction
Since char is highly aromatic, the stacking structure of its aromatic carbon layers provides a good basis for generating a char representation. The approach suggested here uses distributions of aromatic stacks as ‘building blocks’ for large structures. For different carbonaceous materials, representations of the aromatic structure have been based on average parameters obtained through NMR and XRD.\textsuperscript{199, 201} Figure 6-5 demonstrates the average structures of the Highveld and Waterberg chars based on XRD data. Although there are small differences in crystallite height and length, the ‘average’ structures are very similar and one would not expect to see any behavioral differences in a structure based on these average parameters.

![Figure 6-5: Average structures of Highveld and Waterberg chars based on XRD parameters](image)

As discussed in Chapter 5, in addition to XRD, HRTEM was utilized for characterization of the aromatic structure of char. This was supplemented by image processing and statistical analyses of the micrographs, which provided distributions of fringe length, their orientation, and their stacking parameters. Stacking parameters include the number of layers per stack, the ratio between their lengths, and the variation
in angles of the layers in each stack. With normal computational power, these distributions were used to generate individual files (.pdb) containing stacks ranging from single aromatic layers to larger, multi-layered stacks. This was accomplished by making small changes to the existing Fringe3D script, in order to produce multiple files where each file contains a single stack centered around the origin (0,0,0 location), as shown in Figure 6-6. The length of each fringe was used to calculate the average number of carbon atoms corresponding to that length, assuming the fringe is as long as it is wide.\textsuperscript{212} This was included in the input to Fringe3D which populated the appropriate aromatic structure at the (0,0,0) coordinates with the assumption that the molecules are all in the same \( z \)-plane.\textsuperscript{211, 214} A circular catenation file was used for construction of polyaromatic layers, which allows the addition of 6-member rings around a central ring until the desired layer size is achieved. Graphene sheet growth via carbon atom additions in a circular catenation approach creates zigzag and armchair sites, enhancing the structural diversity. Fringe curvature was not considered, no ring defects, and all fringes were duplicated as flat molecules.
A new Perl script was developed to populate a 3D volume according to a specified distribution (obtained from HRTEM analysis) of input stacks. The first step was calculating the volume of each individual stack (the volume was calculated as a cube around the stack as demonstrated in Figure 6-6). Based on the total desired volume, the volume of individual stacks, and the distribution, the script calculates the total number of stacks that can be placed in the 3D space within minuets. The user defines the maximum number of iterations that should be repeated to move around the stacks to obtain an arrangement that would yield the minimum unoccupied volume. Along with the output, the unoccupied volume is given and if this is too large, the number of iterations can be increased. The output file (pdb) contains a large structure based on the input files, distributions and desired size.

To avoid packing related catenations, artifacts or bonding between aromatic units, it is necessary to start with a low initial density. The script allows the user to specify the size of a buffer which will be added between input stacks to avoid unwanted bond formation due to close contact. A series of structure optimizations and dynamic simulations can then be followed to geometrically minimize the structure to obtain the desired density. Forcite, an advance molecular mechanics tool in Material Studio, was used for the energy calculation and geometry optimizations. The structure has to be slowly compressed as large time steps during dynamic simulations, causes the unrealistic movement of molecules over large distances. This is especially important since the orientation of the molecules want to be preserved. The density equilibration was based on the scheme proposed by Hofmann et al. where dynamics stages, consists of NVT and NPT simulations, which corresponds to compression, decompression, annealing, and cooling cycles under various conditions of temperature and pressure. This method was also utilized by Castro-Marcano et al. for rearrangement of an atomic representation of Illinois no.6 coal to obtain the most stable configuration.

The chemical nature of the atoms in char model is characterized by their force field parametization. Prior to energy calculations, each atom is assigned a force field type.
relating to their chemical functionality. The force field accounts for the bonded and non-bonded interactions between the atoms in the systems.\textsuperscript{232} In molecular mechanics, a force field refers to the functional form and parameter sets used to describe the potential energy of a system of particles (atoms, molecules, etc). The all-atom consistent valence force field (cvff) was selected here.\textsuperscript{233}

**Molecular dynamics combustion simulation**

A simplified method was used for evaluating and comparing the combustion reactivity for the char structures. For the combustion simulations, cubic models of approximately 75Å in length were generated with Vol3D containing the char structure composed of 32206 atoms and 42703 atoms for Highveld and Waterberg char, respectively. The simulation started with the oxygen around the walls of the cube. After energy minimization the temperature was slowly ramped up to 1000ºC, which allowed oxygen to diffuse towards the constrained carbon structure. After 10ps of diffusion, the position of all the atoms were exported and analysed. A Matlab code was developed to identify edge carbon atoms that were within a certain distance of the oxygen atoms. If the atoms were within the critical distance of each other, the edge site was deleted but the oxygen atoms were retained. The carbon structure and the oxygen were imported back into Material Studio, and the oxygen was again diffused for ~10ps. The sequential steps were repeated until the carbon structure decreased to approximately 10% of the initial structure.

The combustion of the char was simplified by assuming the following:

- All hydrogen atoms and edge carbons within the critical distance of oxygen ‘reacted’.
- Reactions were simplified by simply deleting the carbon atoms.
- The critical reaction distance was assumed to be 3Å.
- No structural re-arrangement was allowed.
6.4 Results and Discussion

6.4.1 Model construction

Molecular representations of the aromatic structure of inertinite-rich Highveld and vitrinite-rich Waterberg chars were generated consisting of 556 and 650 polyaromatic sheets, respectively. Models consisting of more atoms can be constructed but the subsequent energy minimizations are then extremely time-consuming. Views of two different sides, the top and from a diagonal of the Highveld (inertinite-rich) and Waterberg (vitrinite-rich) are shown in Figure 6-8 and Figure 6-9, respectively. The Highveld char representation contains 32206 atoms and has dimensions of 73 x 61 x 69 Å, and the Waterberg char contains 42703 atoms and has dimensions of 86 x 66 x 83 Å.
Figure 6-8 shows the model for Highveld char, and Figure 6-9 shows the model for Waterberg char. The largest noticeable difference between the two models is the alignment differences. Similar as observed in HRTEM, the aromatic layers in Waterberg char shows more of a preferential alignment, while the alignment in the Highveld char is more scattered. At this stage, the atomistic representation only contains aromatic carbon atoms.

![Figure 6-8: Different views of Highveld char model](image-url)
This new script allows the generation of large-scale structures consisting of various domains with different preferential alignment. Figure 6-10 shows a model based on the structural parameter distribution of Waterberg char but unlike the model in Figure 6-9, this representation was constructed to include two domains with different preferential alignment.
The top part of the model has a mean angle of 0°, while the domain in the bottom (highlighted with yellow) has a mean orientation of 135° (Figure 6-10). Although the mean angle of orientation is different, both the domains are still constructed based on the Waterberg angle distribution data determined through image processing. Therefore, if the two domains would be separated and rotated, they would have the exact same distribution.

This new construction approach also allows the incorporation of pore size distribution by using pores of specific sizes as input files. Structures simulating different pore sizes were built with elements, like phosphor, that would otherwise not be included in the model and could be easily identified and removed. Figure 6-11 shows a molecular representation of the Highveld char “doped” with pores. The cubic simulation cell has dimensions: 75.4 x 72.4 x 75.9Å, and the model has a final density of 1.5g/cm³ close to expected helium density for this char. After the model was minimized and relaxed, all of the phosphor atoms in the structures were deleted, which now form pores (empty spaces) of specific sizes (and shapes if desired) that are distributed randomly throughout the model. The
scale of the model limits the size of pores that can be included. Since both char samples displayed mostly mesopores, the models were constructed at a scale that could incorporate at least small mesopores (~30 Å). The nitrogen adsorption and SAXS data were used to determine the amount and distribution of pores in the molecular char representations. The pore volume occupied by pores smaller than 30 Å (as determined by NLDTF of N₂ adsorption data) was used to calculate the total volume of pores in the model, while the SAXS data was used to obtain the distribution of pore sizes as previously discussed.

Figure 6-11: (a) Molecular model for Highveld char including pores, and (b) cross-section of the same model where ‘pores’ (yellow atoms) are visible.

The phosphor atoms are selected and deleted, which leaves pores of different sizes distributed throughout the structure. Figure 6-12 shows the porosity generated in the structure when the atoms, in Figure 6-11, are removed. To evaluate the effect of pore size distributions differences between the Waterberg and Highveld chars, gas can be diffused through the structure (continuing work), and diffusivity parameters can be calculated.
By using a similar approach ash can also be distributed throughout the structure. Input files can be generated to the size and compositional distribution. Both South African coals contain large amounts of silica and alumina oxides, and therefore the ash for both Waterberg and Highveld consist mainly (~80%) of alumina silicates. A study by Weeber et al. used XRD to determine that Kaolinite composed 62.7% of ash for a similar South African coal. Figure 6-13 shows a structure of Highveld coal with Kaolinite distributed throughout the structure. Size distributions of mineral inclusions are usually larger (µm range) than indicated in the Highveld representation. Due to the size of the model, smaller crystallites was incorporated since even the smaller mineral inclusions would obstruct the access of reacting gases to the reactive surfaces. Inclusion of ash is especially important for the high-ash yield South African coals since they have a large influence on the overall behavior as observed with reactivity and demineralized samples.
Figure 6-13: (a) Molecular model for Highveld char including kaolinite, and (b) cross-section of the same model where clusters of minerals are visible.

Although data regarding the type and distribution of heteroatoms for the chars were not available, an atomistic representation of the Highveld char was constructed to demonstrate the ability to include heteroatoms. The elemental analysis data for Highveld char (as determined in Chapter 2), along with literature on the functional groups usually found in bituminous coal chars was used to construct the model. The oxygen functionalities were primarily to carbonyl and ether structures, and nitrogen and sulfur atoms were included as pyrrolic and quaternary, and thiophenic type structures. Scripts created for other large-scale coal molecular model generation were utilized to populate the heteroatoms throughout the char model.
Figure 6-14: Atomistic representation of Highveld char with heteroatoms

6.4.2 Model evaluation

Evaluation of char models included calculation of the helium density, pore size distribution, interlayer spacing, number of layers per stack, pair distribution functions, and x-ray scattering. The helium density of the model was determined by using the molar mass and the total volume of the model following the approach suggested by Gelb and Gubbins,\textsuperscript{237} where grid points are placed throughout the model and each is defined as occupied or void. This is done by placing a probe molecule at every grid point to determine if overlap between the molecule and the char structure occurs. To evaluate helium density, the probe molecule is set to have the same radius ($r$) as helium. The total volume of the char is the sum of the occupied grid points, while the total pore volume is
the sum of the unoccupied grid points. The pore size distribution was obtained by plotting the change in volume with probe radius \((-dV(r)/dr)\) versus the radius. Since the pore size distribution of the model is directly based on the experimental pore size distribution (SAXS), the trends are not shown here since they are very similar.

Even though the models were constructed based on the stacking parameters, the interlayer spacing and stacking numbers of the final chars were still manually evaluated through counting. The stacking number of the models was slightly higher than the experimental values, which is most likely due to stacking of layers during the minimization/relaxation of the structure. Although experimental values for the pair correlation function, \(g(r)\), was not determined, the model was compared to characteristic peaks associated with char structure. The \(g(r)\) function provides the probability of finding an atom at a specific distance, \(r\) from another atom. Values can be obtained for distances between atoms in the same molecule (intra particle) as well as atoms between neighboring atoms (inter particle). The latter provides information that can be related to the interlayer spacing. Figure 6-15 shows the correlation function for the Highveld char model. A peak was observed in the distributions for both char models at 1.4Å, which is related to the presence of aromatic carbons. The next two observed peaks, at 2.4 and 2.8 are also observed in graphite and in the Illinois no.6 char model by Castro-Marcano et al.\(^{213}\) Peaks at further distances (\(r>3\)Å) correspond to intramolecular contributions which relates to interlayer spacing. The general trend of the correlation function is therefore in fairly good agreement with that of organized carbonaceous structure. The correlation function for the Waterberg char model was similar, also showing the peaks characteristic of ordered carbon material.
The characteristic (002) and (10) peaks at 23 and 43°, respectively, that were observed in the XRD micrographs for both chars were also observed in the x-ray scattering plots of the model. The two scattering intensity plots are very similar, with the Waterberg char showing a slightly sharper (002) peak, suggesting a more ordered structure. This agrees well with the experimental XRD data which indicated that Waterberg char has a slightly more ordered structure with a larger crystallite height and diameter, compare to that of Highveld. Since the models were generated based on HRTEM distribution data, which was also very similar for the two chars, similar peaks would be expected.
A simplified method was used for approximately evaluating and comparing the combustion reactivity for the two char structures. The method involved repetitive steps that diffused oxygen through the char structure, and then allowing them to react according to certain pre-defined reaction rules. Each diffusion step was 10ps and edge carbons within 3Å of oxygen were deleted, while oxygen atoms were retained. Figure 6-17 and Figure 6-18 shows the simulated combustion steps for the Highveld and Waterberg char, respectively. The inertinite-rich Highveld char required additional simulation time (steps) to reach 80% burnoff. The Waterberg char on the other hand, obtained 80% conversion in 15 steps compared to 18 steps for the Highveld char. The structural factor that most likely has the largest influence contributing to the faster consumption of the Waterberg char is the presence of larger pore(s). In Figure 6-18X shows the oxygen obtaining access to an internal pore which was not accessible until the
outer surface was consumed. The oxygen diffused into the pore and resulted in an increased reactive surface area (or accessible edge carbon sites).

Figure 6-17: Simplified simulated combustion of inertinite-rich coal (Highveld) char
The number of atoms deleted in each step was recorded and converted to mass loss during the combustion process. The percentage residual atoms (initial atoms in model minus total atoms deleted) are represented as a function of simulation time in Figure 6-19. For the vitrinite-rich char, 80% of the initial atoms ‘combusted’ in less simulation time than the same percentage of atoms for the inertinite-rich char. The inertinite-rich char took more iteration steps to reduce the atoms in the char structure to 20% of the original size.

Figure 6-18: Simplified simulation of combustion of vitrinite-rich coal (Waterberg) char
The number of atoms reacted in each step was noted and converted to a relative reaction rate. Figure 6-20 shows a plot of these relative simulated reaction rates against the conversion of the total model. The combustion simulation for the vitrinite-rich char obtained a slightly higher reaction rate at a higher conversion. The higher reaction rate is in correlation with the experimental results thus capturing a reactivity component to char structural modeling. As expected, the reaction rate increases as the pores grow and coalesce, and access to the active sites increase. During the combustion simulation, oxygen ‘reacted’ with the char structure, allowing access to pores within the structure that was earlier not accessible. The vitrinite-rich structure contained more internal pores, resulting in this phenomenon to play a stronger role to obtain a higher maximum reaction rate. The profile goes through a maximum as seen in experimental reactivity profiles, followed by a decrease in reactivity corresponding to collapsing pores that result in decreased surface area.
Similar to the experimental results shown in Figure 6-21, the combustion simulation predicted a combustion profile where the maximum combustion rate for the vitrinite-rich char was higher than that of the inertinite-rich char. However, the predicted reactivity profile did not exactly mimic the shape of the experimental profile. The predicted combustion profile reached a maximum combustion rate at lower conversion (approx. 20%) compared to the experimental profile. The inconsistency of the model predictions could be attributable to the parameters influencing reactivity not incorporated, such as functional groups (different active sites) and ash. Addition of ash to the model will decrease the reactivity since it will act as a barrier to the oxygen. Incorporating more of the reactivity factors should enhance the predictability of molecular modeling predictions.
This rules-based simulation approach has demonstrated the capability to evaluate the effect of diffusion on combustion behavior. Enhancements to this approach should provide a technique which can be used to provide information regarding reactivity in regime II and III conditions. Future work should improve the automation, demonstrate repeatability, and consider structural factors and their transformation to explore the structure-reactivity relationship.

6.6 Conclusions

A new Perl script, Vol3D was developed which can be used to populate a 3D cubic volume with a specified distribution of polyaromatic stacks. The distribution of stacks was obtained from HRTEM image processing and statistical analysis. Individual files containing stacks were generated using Fringe3D. The script calculates the volume of each stack to determine the maximum number of stacks, in agreement with the indicated distribution, to populate the total desired model volume. As each individual stack is in an individual file (.pdb), the files could also contain distributions of ash or a pore of specific size. This creates the unique ability to incorporate pore size distribution and mineral
matter inclusions based on experimental data obtained through SAXS and XPS respectively. Furthermore this approach limits user bias, and produces realistic aromatic structures that are able to capture the distribution of aromatic structural features. To date, there has been no approach that offers the ability to capture not only the alignment of individual layers within a stack but also the overall alignment (anisotropy) observed with HRTEM.

All the characteristic peaks, associated with char and other carbonaceous material, were observed in the pair correlation function and x-ray scattering analysis of the models. Since the models were constructed based on stacking parameters, layer size (and therefore H/C ratio), and pore size distributions, the values of the model agrees well with experimental data available. Although information on heteroatoms and cross-linking were not available, the tools are now in place to incorporate them in large atomistic structures.

A rules-based approach was developed, using Material Studio and Matlab, to evaluate combustion behavior on larger molecular representations of char with control over structural features. This approach significantly reduces the computational intensity and mainly focuses on the effect of oxygen diffusion through the char structure simulating combustion at high temperatures (~1000°C) where diffusion controls the overall reaction rate. The combustion of the vitrinite-rich char structure reached a higher maximum reaction rate compared to the combustion of the inertinite-rich char. This could be attributed to internal pores becoming accessible as combustion progresses. Although several assumptions had to be made, this technique was able to provide valuable insight on the diffusion behavior during combustion.
Chapter 7

Conclusions

A drop-tube reactor was used to devolatilize an inertinite- and vitrinite-rich South African coal, under conditions comparable to that of pulverized coal combustion (high heating rate, high temperature, and approximate particle size distribution). The devolatilization time of the inertinite-rich coal was significantly longer (approx. 400ms) than that of the vitrinite-rich coal (approx. 240ms). This was expected to contribute to combustion reactivity since the inertinite-rich sample was exposed to the high temperature in the drop-tube for longer, possibly resulting in deactivation. The combustion reactivity of the rapid-heated chars were compared to those heated under slower heating conditions (in TGA), which indicated that the drop-tube conditions increase the difference between the combustion rates of the two coal chars with a factor of four. The reactivity of the drop-tube generated vitrinite-char was higher than the inertinite-chars during isothermal and non-isothermal TGA runs, as well as TPO runs. The vitrinite-char reached a higher maximum reaction rate during isothermal TGA runs at combustion temperatures from 450 to 1000⁰C. The influence of de-ashing on the char combustion reactivity was also investigated, and it was found that the large ash content of these chars restricts the access of reactive gases, resulting in lower combustion reactivity. After the ash barrier was removed (through de-ashing), there was a reduced difference in combustion reactivity of the two chars.

To quantify the competing structural factors influencing the reactivity differences between these two coal chars, structural characterization through various analytical characterization techniques were utilized. To study the structural transformations during devolatilization, chars were sampled at residence times prior to full devolatilization. Structural characterization demonstrated that the structure of the two chars were remarkably similar. Differences included the faster devolatilization of the vitrinite-rich which produced extensively swollen, cenospheric and porous type of chars with larger
pores (visible through optical microscopy). Although the inertinite-char included swollen particles with developed porosity, a large fraction of the particles displayed very little pore development, producing mostly unswollen, dense type chars. The average crystallite parameters (as determined by XRD) of the vitrinite-rich char increased significantly during devolatilization while there was a very small increase in the crystallite size of the inertinite-rich char.

For further quantitative structural characterization of the char, HRTEM was utilized. Upon visual inspection the average fringe lengths of the two chars looked similar, while the vitrinite-rich char revealed more domains of preferential alignment than the inertinite-char. A new semi-automated filtration technique was developed in Photoshop, which in combination with a new Matlab code, were able to obtain distributions on the graphene layer size, the number of layers per stack, interlayer spacing, and layer orientation. This improved approach creates the possibility to analyze many images from more sample locations, which would increase the consistency and convenience of quantitative HRTEM structural data distributions.

Molecular modeling is a valuable tool in capturing structural parameters. Coal char models remain small in scale, and are more limited in their utility despite the considerable interest in relating char structure to reactivity. Current approaches do not allow the incorporation of all the competing structural factors influencing reactivity. Modifications to Fringe3D, an existing Perl script, allowed the construction of aromatic stacks in molecular modeling space based on the distributions obtained through HRTEM analysis. A new Perl script, Vol3D was developed to enable the construction of large models (to the order of 100Å in diameter) based on a distribution of aromatic layers and stacks, pores, and mineral matter. The aromatic layer distribution generated through Fringe3D is used as input to Vol3D, which then populates a specified volume based on the distribution. In the same manner mineral clusters or ‘space keepers’ can be used as input which then allows the incorporation of mineral matter and pores, respectively. The unique ability to incorporate mineral matter inclusions and pores in the original structure
offers an advantage over the computationally intensive approach where the structure would be manipulated to incorporate such features. This approach allows control over layer orientation in order to construct preferentially aligned domains. To demonstrate the capability of this tool, structural representations of inertinite-rich and vitrinite-rich coal chars were constructed. This construction approach was able to capture structures consistent with experimental data. As experimental data indicated, the two chars has remarkably similar structural properties. The inertinite-rich char model had a higher density, while the Waterberg char demonstrated more preferential layer alignment and larger pores (mesopore).

Further work explored the behavioral differences between these chars through a unique, rules-based approach (developed in Material Studio and Matlab). The main objective to this method was to determine the accessibility of oxygen to edge carbon sites (considered to be reactive). Oxygen was diffused through the char models at temperatures up to, and the carbon edge sites were identified as ‘active sites’. Diffusion and atom deletion steps were repeated until 80% of the original structure was “combusted”. As combustion progressed, the oxygen obtained access to internal pores which increased the combustion rate. The results from this novel, reasonably rapid approach were consistent with experimental data, where the vitrinite-rich char is slightly more reactive than the inertinite-rich char. The inertinite-rich char structure took more iteration steps (18 simulation steps) to reach the same conversion level, compared to the vitrinite-rich char (15 simulation steps). The combustion of the vitrinite-rich char also reached a higher relative reaction rate compared to the inertinite-rich char. The development of this methodology provides a good basis, which can be extended to more comprehensive calculations on diffusion and reactivity behaviour of char combustion.
Chapter 8

Recommendations and Future Work

- Experimental char combustion data from drop-tube and TGA, where the factors influencing reactivity are even further isolated would be helpful to pinpoint the impact of individual structural characteristics on behavior.

- In this thesis, the goal was to evaluate devolatilization behavior closely representing the behavior seen in pulverized coal combustion therefore the as-received coal was devolatilized. To eliminate the effect of mineral matter on the structural evolution during heat treatment of coal, the raw coal could be demineralized prior to devolatilization.

- A more statistical approach to obtain HRTEM images would remove any user bias. These images can then be analyzed through image analyses without the concern that the obtained structural parameters only represent certain regions of the carbonaceous material.

- The type and distribution of heteroatom functionalities in coal and char plays a role in the reactions during combustion. Therefore, characterization of the heteroatoms, especially the oxygen functionality and distribution thereof in the South African coals may lead to better model representations. A technique such as X-ray photoelectron spectroscopy (XPS) can be used to determine and quantify the organic oxygen in the South African coal chars. These functionalities should then be incorporated into the char representations.

- Improved accuracy of the rules-based combustion simulation could be obtained by introducing a probability of certain carbon sites reacting (e.g. chair vs zigzag sites), incorporating ash, dislocations within carbon structure, and other structural defects into the char model. Also consider the diffusion of formed products (carbon dioxide) out of the carbonaceous structure.
• Further enhancements to the combustion simulation could include improvement of automation and speed of the rules-based combustion simulation by using scripts. Engaging supercomputing facilities will allow the evaluation of structure-reactivity relationship of even larger scale molecular models.

• After improvements, the simulation approach can be used to explore combustion in different combustion regimes (zone I and zone II) where inherent reactivity has a larger influence. It can further be used to explore char gasification behavior.
Chapter 9

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Appendix A

Estimate k-value at specific temperature by obtaining the slope of plotting –\(\ln(1-\alpha)\) versus \(t\).

![Graph showing the estimation of k-values for Waterberg char](image)

**Figure A.9-1: Estimating k-values for Waterberg char**
Figure A9-2: Estimating k-values for Highveld char

- \( y = 0.0022x - 0.4729 \)
  - \( R^2 = 0.9925 \)

- \( y = 0.0008x - 0.6519 \)
  - \( R^2 = 0.9971 \)

- \( y = 0.0001x - 0.0157 \)
  - \( R^2 = 0.9992 \)
Appendix B

Temperature programmed oxidation (TPO) curve fitting

Comparing curve fitting with 2 peaks with curve fitting with single peak. Gaussian with 2 peaks showed best fit for all samples (smallest error%)

![Figure B.1: Curve fitting of Highveld char TPO profile ~ double peaks](image)

![Figure B.2: Curve fitting of Highveld char TPO profile ~ single peak](image)
Figure B.3: Curve fitting of Waterberg char TPO profile ~ double peak

Figure B.4: Curve fitting of Waterberg char TPO profile ~ single peak
Appendix C

Matlab code

Function stackcalc2
(rmp_crit, Thetacrit, rperp_crit, xlscreate, figcreate, hist2, hist3, hist4, hist5, histall, b2, b3, b4, b5, ball, stackstats);

% This function calculates 2,3,4 and 5 stack matrices from an input Excel
% file named inputfile.xlsx. The user is required to specify rmp_crit and
% Theta crit, which determines the subsequent stack. Input into Excel
% should be Column 1: X coordinates, Column 2: Y coordinates, Column 3:
% Angle of each fringe, and Column 4: Length of each fringe.

clc
% clear all
warning off
% rmp_crit=5;
% rperp_crit=3.5;
% Thetacrit=10;
tic

% Importing and configuring data
B = xlsread('StackTest.xlsx');  % Read data from Excel file
B = sortrows(B, 1);          % Sorts data so that row 1 goes from small to big
x = B(:, 1); y = B(:, 2); angle = B(:, 3); L = B(:, 4);  % Assign variable names to each
column in Excel
K = ones(1, length(x));   % Create a 1 by length(x) matrix to create a block matrix
nroflines = length(x);

% Make a block matrix for X, Y, Theta and L. Columns repeat with X, Y, Theta and L
vector in each matrix. Each matrix
% size is length(X) by length(X).
Xmat = x * K;    %
Ymat = y * K;
Thetamat = angle * K;  %
Lmat = L * K;

% Calculate the transpose of block matrix (rows and columns just swop)
XmatT = Xmat';
YmatT = Ymat';  % Calculate the transpose of block matrix (rows and columns just
swop)
ThetamatT = Thetamat';  % Calculate the transpose of block matrix (rows and columns
just swop)
LmatT = Lmat';  % Calculate the transpose of block matrix (rows and columns just
swop)

%%% Finding all data that is withing a certain distance r and a within an
%%% angle Theta crit

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\[ r = \sqrt{(X_{\text{mat}} - X_{\text{matT}})^2 + (Y_{\text{mat}} - Y_{\text{matT}})^2}; \] % calculate the distance between ALL coordinates

% Find where \( r < r_{\text{mp\_crit}} \) value
[r\_x] = find(r <= r_{\text{mp\_crit}}); % Identify all the entries for which \( r < r_{\text{mp\_crit}} \)

GoodXs = X_{\text{mat}}(r\_x);
GoodYs = Y_{\text{mat}}(r\_x);
GoodXsT = X_{\text{matT}}(r\_x);
GoodYsT = Y_{\text{matT}}(r\_x);
GoodThetas = \Theta_{\text{mat}}(r\_x);
GoodLengths = L_{\text{mat}}(r\_x);
GoodLengthsT = L_{\text{matT}}(r\_x);

% Simple check to eliminate identical coordinates, i.e. \((X_i, Y_i) = (X_i, Y_i)\)
% causing \( r = 0 \). Arranging subsequent data again.
\[ r_{2} = \sqrt{(\text{GoodXs}_{2} - \text{GoodXs}_{T})^2 + (\text{GoodYs}_{2} - \text{GoodYs}_{T})^2}; \]
[r\_x] = find(r_{2} > 0);

GoodXs2 = GoodXs(r\_x);
GoodYs2 = GoodYs(r\_x);
GoodXsT2 = GoodXsT(r\_x);
GoodYsT2 = GoodYsT(r\_x);
GoodThetas2 = GoodThetas(r\_x);
GoodLengths2 = GoodLengths(r\_x);
GoodLengthsT2 = GoodLengthsT(r\_x);

% Arranging all data that fulfills the \( r_{\text{mp\_crit}} \) requirement

\[ r_{3} = \sqrt{(\text{GoodXs}_{2} - \text{GoodXs}_{T2})^2 + (\text{GoodYs}_{2} - \text{GoodYs}_{T2})^2}; \]

anglediff = abs(GoodThetas2 - GoodThetasT2);
Goodsa = [GoodXs2, GoodYs2, GoodThetas2, GoodLengths2, GoodXsT2, GoodYsT2, GoodThetasT2, GoodLengthsT2, r3, anglediff];

% Finding all remaining data that fulfills the \( \Theta_{\text{crit}} \) requirement, and
% arranging data

Tx = find(anglediff <= \Theta_{\text{crit}});
Goodsb = Goodsa(Tx,:);

m2 = \tan(\text{Goodsb}(:,3));
mT2 = \tan(\text{Goodsb}(:,7));
c2 = Goodsb(:,2) - m2.\*Goodsb(:,1);
cT2 = Goodsb(:,6) - mT2.\*Goodsb(:,5);
mperp2 = -1./m2;
mperpT2 = -1./mT2;
cperp2 = Goodsb(:,2) - mperp2.\*Goodsb(:,1);
cperpT2 = Goodsb(:,6) - mperpT2.\*Goodsb(:,5);
XP1 = (cperpT2 - c2)./(m2 - mperpT2);
YP1 = (m2.*XP1 + c2);
XP2 = (cperp2 - cT2)./(mT2 - mperp2);
YP2 = (mT2.*XP2 + cT2);
rperp1=sqrt((XP1-Goodsb(:,1)).^2+(YP1-Goodsb(:,2)).^2);
rperp2=sqrt((XP2-Goodsb(:,5)).^2+(YP2-Goodsb(:,6)).^2);
Goods=[];rp1=[];rp2=[];
for bg=1:length(rperp1)
    if rperp1(bg)<=rperp_crit||rperp2(bg)<=rperp_crit
        Goods=[Goods; Goodsb(bg,:)];
        rp1=[rp1;rperp1(bg)];
        rp2=[rp2;rperp2(bg)];
    end
end
Goods=[Goods rp1 rp2];
[Txx Tyy]=size(Goods);

%% Sorting data to lie in 5-stack, 4-stack, 3-stack and 2-stack matrices
NR2=[]; NR3=[]; NR4=[]; NR5=[]; NrN=[];l1=[];
Newmat=[];
for i=1:Txx
    Xtest=[Goods(i,5:6)];
    Stack=2;
    Newmat=[Newmat; Goods(i,:) Stack];
    for j=1:Txx;
        if isequal(Goods(j,1:2),Xtest)
            Stack=3;
            Xtest2=[Goods(j,5:6)];
            j1=j;
            Newmat=[Newmat; Goods(j,:) Stack];
            for k=1:Txx;
                if isequal(Xtest2,Goods(k,1:2))
                    Stack=4;
                    Xtest3=[Goods(k,5:6)];
                    Newmat=[Newmat; Goods(k,:) Stack];
                    k1=k;
                    for l=1:Txx;
                        if isequal(Xtest3,Goods(l,1:2))
                            Stack=5;
                            Newmat=[Newmat; Goods(l,:) Stack];
                            l1=[l1;l];
                            end
                        end
                    end
                end
            end
        end
    end
end
else
end
e
end
%  Xtesta=[Goods(i,5:6)];
%  for j=1:Txx;
%    if isequal(Goods(j,1:2),Xtesta)&isequal(Goods(i,1:2),Goods(j,5:6))==0
%      Stack=Stack+1;
%      Xtest2a=[Goods(j,5:6)];
%      Newmat=[Newmat; Goods(j,:) Stack];
%      for k=1:Txx;
%        if isequal(Xtest2a,Goods(k,1:2))&&isequal(Goods(k,5:6),Goods(j,1:2))==0&&isequal(Goods(k,5:6),Goods(i,1:2))==0&&isequal(Goods(k,5:6),Goods(j,5:6))==0;
%          Stack=Stack+1;
%        end
%      end
%      end
%    end
%  if Stack==2;
%    NR2=[NR2;Goods(i,:)];
%  elseif Stack==3;
%    NR3=[NR3;Goods(i,:);Goods(j1,:)];
%  elseif Stack==4;
%    NR4=[NR4;Goods(i,:);Goods(j1,:);Goods(k1,:)];
%  elseif Stack==5;
%    NR5=[NR5;Goods(i,:);Goods(j1,:);Goods(k1,:);Goods(l1(1),:)];
%    l1=[];
%  elseif Stack>5
%    NrN=[Newmat()]
%  end
%  end
%  end
%  Newmat
%  NR3=[];
%  [jk1 jk2]=size(Newmat);
%  find3s=find(Newmat(:,end)==3);
%  find3s(find3s==3);
%  for p=1:length(find3s)
%    NR3=[NR3;Newmat(find3s(p)-1,:);Newmat(find3s(p),:)];

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% end
% NR4=[];
%
% find4s=find(Newmat(:,end)==4);
% for p=1:length(find4s)
%     NR4=[NR4;Newmat(find4s(p)-2,:);Newmat(find4s(p)-1,:);Newmat(find4s(p),:)];
% end
% NR5=[];
%
% find5s=find(Newmat(:,end)==5);
% for p=1:length(find5s)
%     NR5=[NR5;Newmat(find5s(p)-3,:);Newmat(find5s(p)-2,:);Newmat(find5s(p)-1,:);Newmat(find5s(p),:)];
% end
% NR2=[];
% for p=1:jk1-1;
%     if Newmat(p,end)==2&&Newmat(p+1,end)==2
%         NR2=[NR2;Newmat(p,:)];
%     end
% end
% if Newmat(end,end)==2
%     NR2=[NR2;Newmat(end,:)];
% end
%
% NR2
% NR3
% NR4
% NR5
%
%% Check that all entries are unique to a stack number.
% Here we check and eliminate non-unique data. For instance, say (Xi, Yi),(Xj, Yj) and (Xk, Yk) have been identified to lie in the 3-stack matrix. All these points must then be removed from the 2-stack matrix where they also occur because (Xj, Yj) and (Xk, Yk) fulfill rmp_crit and Thetacrit requirements, as well as (Xj, Yj) and (Xi, Yi).

[Stack2 Stack3 Stack4 Stack5]=Uniquecheck(NR2,NR3,NR4,NR5);
%% Remove all duplicate entries
% A simple check to remove duplicate entries. Because we have worked with transposed block matrices, (Xj, Yj) and (Xi, Yi) are identified to lie in a stack, as well as (Xi, Yi) and (Xj, Yj). Clearly this is the same point and one of them needs to be be eliminated.

% [g1 g2]=size(Stack2);
% [g3 g4]=size(Stack3);
% [g5 g6]=size(Stack4);
% [g7 g8]=size(Stack5);
%
[Stack2]=Duplicateremove(Stack2);
[Stack3]=Duplicateremove(Stack3);
[Stack4]=Duplicateremove(Stack4);
[Stack5]=Duplicateremove(Stack5);

[g1 g2]=size(Stack2);
[g3 g4]=size(Stack3);
[g5 g6]=size(Stack4);
[g7 g8]=size(Stack5);
Stack2=[ones(g1,1) Stack2 2*ones(g1,1)];
Stack3=[ones(g3,1) Stack3 3*ones(g3,1)];
Stack4=[ones(g5,1) Stack4 4*ones(g5,1)];
Stack5=[ones(g7,1) Stack5 5*ones(g7,1)];

%% Stack figure
if figcreate==1;
    figure(2)
    hold on
    for i=1:g1;
        plot(Stack2(i,2),Stack2(i,3),'.r','markersize',10);
        plot(Stack2(i,6),Stack2(i,7),'.r','markersize',10);
        m=-tand([Stack2(i,4) Stack2(i,8)]);
        if isinf(m(1))
            m(1)=10^6;
        elseif isinf(m(2))
            m(2)=10^6;
        end
        c=[Stack2(i,3) Stack2(i,7)]-[Stack2(i,2) Stack2(i,6)];
        x1s=roots([1+m(1)^2, 2*m(1)*(c(1)-Stack2(i,3))-2*Stack2(i,2),Stack2(i,2)^2+(c(1)-Stack2(i,3))^2-(Stack2(i,5)/2)^2]);
        y1s=m(1)*x1s+c(1);
        x2s=roots([1+m(2)^2, 2*m(2)*(c(2)-Stack2(i,7))-2*Stack2(i,6),Stack2(i,6)^2+(c(2)-Stack2(i,7))^2-(Stack2(i,9)/2)^2]);
        y2s=m(2)*x2s+c(2);
        plot([x1s],[y1s],'r');
        plot([x2s],[y2s],'r');
        Stack2(i,1)=i;
    end
for i=1:g1;
    plot(Stack2(i,2),Stack2(i,3),'.r','markersize',10);
    plot(Stack2(i,6),Stack2(i,7),'.r','markersize',10);
    m=-tand([Stack2(i,4) Stack2(i,8)]);
    if isinf(m(1))
        m(1)=10^6;
    elseif isinf(m(2))
        m(2)=10^6;
    end
    c=[Stack2(i,3) Stack2(i,7)]-[Stack2(i,2) Stack2(i,6)];
    x1s=roots([1+m(1)^2, 2*m(1)*(c(1)-Stack2(i,3))-2*Stack2(i,2),Stack2(i,2)^2+(c(1)-Stack2(i,3))^2-(Stack2(i,5)/2)^2]);
    y1s=m(1)*x1s+c(1);
    x2s=roots([1+m(2)^2, 2*m(2)*(c(2)-Stack2(i,7))-2*Stack2(i,6),Stack2(i,6)^2+(c(2)-Stack2(i,7))^2-(Stack2(i,9)/2)^2]);
    y2s=m(2)*x2s+c(2);
end
\[ y_{1s} = m(1) \times x_{1s} + c(1); \]
\[ x_{2s} = \text{roots}([(1+m(2)^2), 2\times m(2)\times (c(2) - \text{Stack2}(i,7)) - 2\times \text{Stack2}(i,6), \text{Stack2}(i,6)^2 + (c(2) - \text{Stack2}(i,7))^2 - (\text{Stack2}(i,9)/2)^2]); \]
\[ y_{2s} = m(2) \times x_{2s} + c(2); \]
\[ \text{plot}([x_{1s}], [y_{1s}], 'r'); \]
\[ \text{plot}([x_{2s}], [y_{2s}], 'r'); \]
\[ \text{Stack2}(i,1) = i; \]
\[ \text{end} \]

\[ j = 1; \]
\[ \text{for } i = 1:1:g3; \]
\[ \text{plot}([\text{Stack3}(i,2), \text{Stack3}(i,3), '.b', 'markersize', 10);} \]
\[ \text{plot}([\text{Stack3}(i,6), \text{Stack3}(i,7), '.b', 'markersize', 10);} \]
\[ m = -\text{tand}([\text{Stack3}(i,4) \text{ Stack3}(i,8)]); \]
\[ \text{if } \text{isinf}(m(1)) \]
\[ m(1) = 10^6; \]
\[ \text{elseif } \text{isinf}(m(2)) \]
\[ m(2) = 10^6; \]
\[ \text{end} \]
\[ c = [\text{Stack3}(i,3) \text{ Stack3}(i,7)] - [\text{Stack3}(i,2) \text{ Stack3}(i,6)].*m; \]
\[ x_{1s} = \text{roots}([(1+m(1)^2), 2\times m(1)\times (c(1) - \text{Stack3}(i,3)) - 2\times \text{Stack3}(i,2), \text{Stack3}(i,2)^2 + (c(1) - \text{Stack3}(i,3))^2 - (\text{Stack3}(i,5)/2)^2]); \]
\[ y_{1s} = m(1) \times x_{1s} + c(1); \]
\[ x_{2s} = \text{roots}([(1+m(2)^2), 2\times m(2)\times (c(2) - \text{Stack3}(i,7)) - 2\times \text{Stack3}(i,6), \text{Stack3}(i,6)^2 + (c(2) - \text{Stack3}(i,7))^2 - (\text{Stack3}(i,9)/2)^2]); \]
\[ y_{2s} = m(2) \times x_{2s} + c(2); \]
\[ \text{plot}([x_{1s}], [y_{1s}], 'b'); \]
\[ \text{plot}([x_{2s}], [y_{2s}], 'b'); \]
\[ \text{end} \]

\[ \text{for } i = 1:1:g3; \]
\[ \text{plot}([\text{Stack3}(i,2), \text{Stack3}(i,3), '.b', 'markersize', 10);} \]
\[ \text{plot}([\text{Stack3}(i,6), \text{Stack3}(i,7), '.b', 'markersize', 10);} \]
\[ m = -\text{tand}([\text{Stack3}(i,4) \text{ Stack3}(i,8)]); \]
\[ \text{if } \text{isinf}(m(1)) \]
\[ m(1) = 10^6; \]
\[ \text{elseif } \text{isinf}(m(2)) \]
\[ m(2) = 10^6; \]
\[ \text{end} \]
\[ c = [\text{Stack3}(i,3) \text{ Stack3}(i,7)] - [\text{Stack3}(i,2) \text{ Stack3}(i,6)].*m; \]
\[ x_{1s} = \text{roots}([(1+m(1)^2), 2\times m(1)\times (c(1) - \text{Stack3}(i,3)) - 2\times \text{Stack3}(i,2), \text{Stack3}(i,2)^2 + (c(1) - \text{Stack3}(i,3))^2 - (\text{Stack3}(i,5)/2)^2]); \]
\[ y_{1s} = m(1) \times x_{1s} + c(1); \]
\[ x_{2s} = \text{roots}([(1+m(2)^2), 2\times m(2)\times (c(2) - \text{Stack3}(i,7)) - 2\times \text{Stack3}(i,6), \text{Stack3}(i,6)^2 + (c(2) - \text{Stack3}(i,7))^2 - (\text{Stack3}(i,9)/2)^2]); \]
\[ y_{2s} = m(2) \times x_{2s} + c(2); \]
\[ \text{plot}([x_{1s}], [y_{1s}], 'b'); \]
\[ \text{plot}([x_{2s}], [y_{2s}], 'b'); \]
\[ \text{end} \]
for i=1:1:g5;
    plot(Stack4(i,2),Stack4(i,3),'.m','markersize',10);
    plot(Stack4(i,6),Stack4(i,7),'.m','markersize',10);

    m=-tand([Stack4(i,4) Stack4(i,8)]);
    if isinf(m(1))
        m(1)=10^6;
    elseif isinf(m(2))
        m(2)=10^6;
    end
    c=[Stack4(i,3) Stack4(i,7)]-[Stack4(i,2) Stack4(i,6)].*m;
    x1s=roots([(1+m(1)^2), 2*m(1)*(c(1)-Stack4(i,3))-2*Stack4(i,2),Stack4(i,2)^2+(c(1)-Stack4(i,3))^2-(Stack4(i,5)/2)^2]);
    y1s=m(1)*x1s+c(1);
    x2s=roots([(1+m(2)^2), 2*m(2)*(c(2)-Stack4(i,7))-2*Stack4(i,6),Stack4(i,6)^2+(c(2)-Stack4(i,7))^2-(Stack4(i,9)/2)^2]);
    y2s=m(2)*x2s+c(2);
    plot([x1s],[y1s],'m');
    plot([x2s],[y2s],'m');
end

% size(Stack5)
% Stack5
for i=1:1:g7;
    plot(Stack5(i,2),Stack5(i,3),'.c','markersize',10);
    plot(Stack5(i,6),Stack5(i,7),'.c','markersize',10);

    m=-tand([Stack5(i,4) Stack5(i,8)]);
    if isinf(m(1))
        m(1)=10^6;
    elseif isinf(m(2))
        m(2)=10^6;
    end
    c=[Stack5(i,3) Stack5(i,7)]-[Stack5(i,2) Stack5(i,6)].*m;
    x1s=roots([(1+m(1)^2), 2*m(1)*(c(1)-Stack5(i,3))-2*Stack5(i,2),Stack5(i,2)^2+(c(1)-Stack5(i,3))^2-(Stack5(i,5)/2)^2]);
    y1s=m(1)*x1s+c(1);
    x2s=roots([(1+m(2)^2), 2*m(2)*(c(2)-Stack5(i,7))-2*Stack5(i,6),Stack5(i,6)^2+(c(2)-Stack5(i,7))^2-(Stack5(i,9)/2)^2]);
    y2s=m(2)*x2s+c(2);
    plot([x1s],[y1s],'c');
    plot([x2s],[y2s],'c');
end

%%% Show final stack matrices in a nice form
% Indiviual stack matrices
Stackmatrices=[Stack2; Stack3; Stack4; Stack5];
[g10 g11]=size(Stackmatrices);

if xlscreate==1
    xlswrite('AllFringeData.xls',Stack2(:,1:end-1),'Stack2','A2');
    xlswrite('AllFringeData.xls',{'Stack number', 'Xm1', 'Ym1', 'Theta1', 'L1', 'Xm2', 'Ym2', 'Theta2', 'L2', 'rm', 'DeltaTheta', 'rp1', 'rp2', 'Layer number'},'Stack2','A1');
    xlswrite('AllFringeData.xls',Stack3(:,1:end-1),'Stack3','A2');
    xlswrite('AllFringeData.xls',{'Stack number', 'Xm1', 'Ym1', 'Theta1', 'L1', 'Xm2', 'Ym2', 'Theta2', 'L2', 'rm', 'DeltaTheta', 'rp1', 'rp2', 'Layer number'},'Stack3','A1');
    xlswrite('AllFringeData.xls',Stack4(:,1:end-1),'Stack4','A2');
    xlswrite('AllFringeData.xls',{'Stack number', 'Xm1', 'Ym1', 'Theta1', 'L1', 'Xm2', 'Ym2', 'Theta2', 'L2', 'rm', 'DeltaTheta', 'rp1', 'rp2', 'Layer number'},'Stack4','A1');
    xlswrite('AllFringeData.xls',Stack5(:,1:end-1),'Stack5','A2');
    xlswrite('AllFringeData.xls',{'Stack number', 'Xm1', 'Ym1', 'Theta1', 'L1', 'Xm2', 'Ym2', 'Theta2', 'L2', 'rm', 'DeltaTheta', 'rp1', 'rp2', 'Layer number'},'Stack5','A1');
    xlswrite('AllFringeData.xls',Stackmatrices,'Alldata','A2');
    xlswrite('AllFringeData.xls',{'Stack number', 'Xm1', 'Ym1', 'Theta1', 'L1', 'Xm2', 'Ym2', 'Theta2', 'L2', 'rm', 'DeltaTheta', 'rp1', 'rp2', 'Layer number'},'Alldata','A1');
end

%% Stack stats
rmperpmin2=[];
for k=1:g1
    rmperpmin2(k)=min(Stack2(k,13),Stack2(k,12));
    rmperpmax2(k)=max(Stack2(k,13),Stack2(k,12));
end
rmperpmin3=[];
for k=1:g3
    rmperpmin3(k)=min(Stack3(k,13),Stack3(k,12));
    rmperpmax3(k)=max(Stack3(k,13),Stack3(k,12));
end
rmperpmin4=[];
for k=1:g5
    rmperpmin4(k)=min(Stack4(k,13),Stack4(k,12));
    rmperpmax4(k)=max(Stack4(k,13),Stack4(k,12));
end
rmperpmin5=[];
for k=1:g7
    rmperpmin5(k)=min(Stack5(k,13),Stack5(k,12));
    rmperpmax5(k)=max(Stack5(k,13),Stack5(k,12));
end
for k=1:g11
    rmperpmi

if stackstats==1

xlswrite('StackStats.xls',{"rm', 'DeltaTheta', 'minrp'},'Sheet1','A1');
xlswrite('StackStats.xls',{"rmp_crit Thetacrit rperp_crit"},'Sheet1','A2');
xlswrite('StackStats.xls',{'Number of lines', 'Number of 2 stacks', 'Number of 3 stacks', 'Number of 4 stacks', 'Number of 5+ stacks'},'Sheet1','A3');
xlswrite('StackStats.xls',\[nroflines g1 round(g3/2) round(g5/3)
round(g7/4)],'Sheet1','A4');
xlswrite('StackStats.xls',\{"% no-stacks', '% 2 stacks', '% 3 stacks', '% 4 stacks', '% 5+ stacks"},'Sheet1','A5');
xlswrite('StackStats.xls',100*\[nroflines-g1-g3-g5-g7]/nroflines g1/nroflines g3/nroflines g5/nroflines g7/nroflines\],'Sheet1','A6');
if g11>0
  xlswrite('StackStats.xls',\{"All stacks:','Mean rm', 'Dev rm', 'Mean DeltaTheta', 'Dev DeltaTheta', 'Mean rpmin', 'Dev rpmin"},'Sheet1','A7');
xlswrite('StackStats.xls',\[mean(Stackmatrices(:,10)) std(Stackmatrices(:,10))
mean(Stackmatrices(:,11)) std(Stackmatrices(:,11)) mean(rmperpminall)
std(rmperpminall)],'Sheet1','B8');
end
if g1>0
  xlswrite('StackStats.xls',\{"2 stacks:','Mean rm', 'Dev rm', 'Mean DeltaTheta', 'Dev DeltaTheta', 'Mean rpmin', 'Dev rpmin"},'Sheet1','A9');
xlswrite('StackStats.xls',\[mean(Stack2(:,10)) std(Stack2(:,10)) mean(Stack2(:,11))
std(Stack2(:,11)) mean(rmperpmin2) std(rmperpmin2)],'Sheet1','B10');
end
if g3>0
  xlswrite('StackStats.xls',\{"3 stacks:','Mean rm', 'Dev rm', 'Mean DeltaTheta', 'Dev DeltaTheta', 'Mean rpmin', 'Dev rpmin"},'Sheet1','A11');
xlswrite('StackStats.xls',\[mean(Stack3(:,10)) std(Stack3(:,10)) mean(Stack3(:,11))
std(Stack3(:,11)) mean(rmperpmin3) std(rmperpmin3)],'Sheet1','B12');
end
if g5>0
  xlswrite('StackStats.xls',\{"4 stacks:','Mean rm', 'Dev rm', 'Mean DeltaTheta', 'Dev DeltaTheta', 'Mean rpmin', 'Dev rpmin"},'Sheet1','A13');
xlswrite('StackStats.xls',\[mean(Stack4(:,10)) std(Stack4(:,10)) mean(Stack4(:,11))
std(Stack4(:,11)) mean(rmperpmin4) std(rmperpmin4)],'Sheet1','B14');
end
if g7>0
  xlswrite('StackStats.xls',\{"5+ stacks:','Mean rm', 'Dev rm', 'Mean DeltaTheta', 'Dev DeltaTheta', 'Mean rpmin', 'Dev rpmin"},'Sheet1','A15');
xlswrite('StackStats.xls',\[mean(Stack5(:,10)) std(Stack5(:,10)) mean(Stack5(:,11))
std(Stack5(:,11)) mean(rmperpmin5) std(rmperpmin5)],'Sheet1','B16');
end
end

%% Stack2hist
if hist2==1
if g1>0

figure();hold on
title('Histogram for 2 layered stacks: midpoint distance'); xlabel('Midpoint distance (A)'); ylabel('Frequency')
hist(Stack2(:,10),round(b2))
figure();hold on
title('Histogram for 2 layered stacks: Angle difference'); xlabel(['Angle difference (','^o',')']); ylabel('Frequency')
hist(Stack2(:,11),round(b2))
figure();hold on
title('Histogram for 2 layered stacks: minimum perpindicular distance');
xlabel('Minimum perpindicular distance (A)'); ylabel('Frequency')
hist(rmperpmin2,round(b2))
else
    errordlg('The parameters you have chosen is such that there are no identifiable stacks','Check your input parameters')
end

end

%% Stack3hist
if hist3==1
    if g3>0
        figure();hold on
title('Histogram for 3 layered stacks: midpoint distance'); xlabel('Midpoint distance (A)'); ylabel('Frequency')
hist(Stack3(:,10),round(b3))
figure();hold on
title('Histogram for 3 layered stacks: Angle difference'); xlabel(['Angle difference (','^o',')']); ylabel('Frequency')
hist(Stack3(:,11),round(b3))
figure();hold on
title('Histogram for 3 layered stacks: minimum perpindicular distance');
xlabel('Minimum perpindicular distance (A)'); ylabel('Frequency')
hist(rmperpmin3,round(b3))
else
    errordlg('The parameters you have chosen is such that there are no identifiable 3 layered stacks','Check your input parameters')
end
end

if hist4==1
    if g5>0
        figure();hold on
title('Histogram for 4 layered stacks: midpoint distance'); xlabel('Midpoint distance (A)'); ylabel('Frequency')
hist(Stack4(:,10),round(b4))
figure();hold on
end
end
title('Histogram for 4 layered stacks: Angle difference'); xlabel(['Angle difference ('','^o',')']);ylabel('Frequency') hist(Stack4(:,11),round(b4)) figure();hold on

else
erroldlg('The parameters you have chosen is such that there are no identifiable 4 layered stacks','Check your input parameters')
end

if hist5==1
  if g7>0
    figure();hold on
    title('Histogram for 5 layered stacks: midpoint distance'); xlabel('Midpoint distance (A)');ylabel('Frequency') hist(Stack5(:,10),round(b5))
    figure();hold on
    title('Histogram for 5 layered stacks: Angle difference'); xlabel(['Angle difference ('','^o',')']);ylabel('Frequency') hist(Stack5(:,11),round(b5))
    figure();hold on
    title('Histogram for 5 layered stacks: minimum perpindicular distance'); xlabel('Minimum perpindicular distance (A)');ylabel('Frequency') hist(rmperpmin5,round(b5))
  else
    erroldlg('The parameters you have chosen is such that there are no identifiable 5 layered stacks','Check your input parameters')
  end
end

if histall==1
  if g11>0
    figure();hold on
    title('Histogram for all stacks: midpoint distance'); xlabel('Midpoint distance (A)');ylabel('Frequency') hist(Stackmatrices(:,10),round(ball))
    figure();hold on
    title('Histogram for all stacks: Angle difference'); xlabel(['Angle difference ('','^o',')']);ylabel('Frequency') hist(Stackmatrices(:,11),round(ball))
    figure();hold on
    title('Histogram for all stacks: minimum perpindicular distance'); xlabel('Minimum perpindicular distance (A)');ylabel('Frequency') hist(rmperpminall,round(ball))
  else
    erroldlg('The parameters you have chosen is such that there are no identifiable all stacks','Check your input parameters')
  end
end
errordlg('The parameters you have chosen is such that there are no identifiable
layered stacks','Check your input parameters')
end

toc
clear all

function [Stack2 Stack3 Stack4 Stack5]=Stackidentify(Goods)

Stack2=[];Stack3=[];Stack4=[];Stack5=[]; % Create empty matrices.
[Txx Tyy]=size(Goods);

% First identify 2Stacks
for i=1:Txx-1
    Xtest=[Goods(i,1:2)];
    Xtesta=[Goods(i,5:6)];
    Stack=2;
    for k=1:Txx
        if isequal(Xtest,Goods(k,5:6))
            Stack=3;
            Xtest2=Goods(k,1:2);
            Xtest2a=Goods(k,5:6);
            for j=1:Txx
                if isequal(Xtest2,Goods(j,5:6))
                    Stack=4;
                    Xtest3=Goods(j,1:2);
                    Xtest3a=Goods(j,5:6);
                    for g=1:Txx
                        if isequal(Xtest3,Goods(g,5:6))
                            Stack=5;
                            Xtest4=Goods(g,1:2);
                            Xtest4a=Goods(g,5:6);
                            end
                        if isequal(Xtest3,Goods(g,1:2))&&g~=j
                            Stack=5;
                            Xtest4=Goods(g,1:2);
                            Xtest4a=Goods(g,5:6);
                            end
                        if isequal(Xtest3a,Goods(g,1:2))&&g~=j
                            Stack=5;
                            Xtest4=Goods(g,1:2);
                            Xtest4a=Goods(g,5:6);
                            end
                        if isequal(Xtest3a,Goods(g,5:6))&&g~=k
                            Stack=5;
                            Xtest4=Goods(g,1:2);
                            Xtest4a=Goods(g,5:6);
                            end
                        end
                    end
                end
            end
        end
    end
end

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Stack = 5;
Xtest5 = Goods(g,1:2);
Xtest4a = Goods(g,5:6);
end
end
end
if isequal(Xtest2,Goods(j,1:2)) && j ≠ i
    Stack = 4;
    Xtest3 = Goods(j,1:2);
    Xtest3a = Goods(j,5:6);
for g = 1:Txx
    if isequal(Xtest3,Goods(g,5:6))
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3,Goods(g,1:2)) && j ≠ i && j ≠ k
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3a,Goods(g,1:2))
        Stack = 4;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
for g = 1:Txx
    if isequal(Xtest3,Goods(g,5:6))
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3,Goods(g,1:2)) && g ≠ j
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3a,Goods(g,1:2)) && g ≠ j
        Stack = 5;
        Xtest4 = Goods(j,1:2);
        Xtest4a = Goods(j,5:6);
    end
    if isequal(Xtest3a,Goods(g,5:6)) && g ≠ k
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    end
end
end
if isequal(Xtest3a,Goods(g,5:6)) && j ≠ k
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
end  
end  
if isequal(Xtest2a,Goods(j,1:2))&&j~ =i  
Stack=4;  
Xtest3=Goods(j,1:2);  
Xtest3a=Goods(j,5:6);  
for g=1:Txx  
if isequal(Xtest3,Goods(g,5:6))  
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
if isequal(Xtest3,Goods(g,1:2))&&g~ =j  
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
if isequal(Xtest3a,Goods(g,1:2))&&g~ =j  
Stack=5;  
Xtest4=Goods(j,1:2);  
Xtest4a=Goods(j,5:6);  
end  
if isequal(Xtest3a,Goods(g,5:6))&&j~ =k&&g~ =i  
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
end  
end  
end  
if isequal(Xtest2a,Goods(j,5:6))&&j~ =k  
Stack=4;  
Xtest3=Goods(j,1:2);  
Xtest3a=Goods(j,5:6);  
for g=1:Txx  
if isequal(Xtest3,Goods(g,5:6))  
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
if isequal(Xtest3,Goods(g,1:2))&&g~ =j  
Stack=5;  
Xtest4=Goods(g,1:2);  
Xtest4a=Goods(g,5:6);  
end  
if isequal(Xtest3a,Goods(g,1:2))&&g~ =j  
Stack=5;  

Xtest4=Goods(g,1:2);
Xtest4a=Goods(g,5:6);
end
if isequal(Xtest3a, Goods(g,5:6)) && g~=k
    Stack=5;
    Xtest4=Goods(g,1:2);
    Xtest4a=Goods(g,5:6);
end
end

if isequal(Xtest, Goods(k,1:2)) && k~=i
    Stack=3;
    Xtest2=Goods(k,1:2);
    Xtest2a=Goods(k,5:6);
    for j=1:Txx
        if isequal(Xtest2, Goods(j,5:6))
            Stack=4;
            Xtest3=Goods(j,1:2);
            Xtest3a=Goods(j,5:6);
            for g=1:Txx
                if isequal(Xtest3, Goods(g,5:6))
                    Stack=5;
                    Xtest4=Goods(g,1:2);
                    Xtest4a=Goods(g,5:6);
                    end
                if isequal(Xtest3, Goods(g,1:2)) && g~=j
                    Stack=5;
                    Xtest4=Goods(g,1:2);
                    Xtest4a=Goods(g,5:6);
                    end
                if isequal(Xtest3a, Goods(g,1:2)) && g~=j
                    Stack=5;
                    Xtest4=Goods(g,1:2);
                    Xtest4a=Goods(g,5:6);
                    end
                if isequal(Xtest3a, Goods(g,5:6)) && g~=k
                    Stack=5;
                    Xtest4=Goods(g,1:2);
                    Xtest4a=Goods(g,5:6);
                    end
            end
        end
    end
end

if isequal(Xtest2, Goods(j,1:2)) && j~=i && j~=k
    Stack=4;
    Xtest3=Goods(j,1:2);
    Xtest3a=Goods(j,5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g,5:6))
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
            end
        end
    end
end

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Xtest4 = Goods(g, 1:2);
Xtest4a = Goods(g, 5:6);
end
if isequal(Xtest3, Goods(g, 1:2)) && g ~= i && g ~= j
    Stack = 5;
    Xtest4 = Goods(g, 1:2);
    Xtest4a = Goods(g, 5:6);
end
if isequal(Xtest3a, Goods(g, 1:2))
    Stack = 4;
    Xtest4 = Goods(g, 1:2);
    Xtest4a = Goods(g, 5:6);
end
if isequal(Xtest3a, Goods(g, 5:6)) && g ~= k
    Stack = 5;
    Xtest4 = Goods(g, 1:2);
    Xtest4a = Goods(g, 5:6);
end
end
end
if isequal(Xtest2a, Goods(j, 1:2))
    Stack = 4;
    Xtest3 = Goods(j, 1:2);
    Xtest3a = Goods(j, 5:6);
    for g = 1:Tx
        if isequal(Xtest3, Goods(g, 5:6))
            Stack = 5;
            Xtest4 = Goods(g, 1:2);
            Xtest4a = Goods(g, 5:6);
        end
        if isequal(Xtest3, Goods(g, 1:2)) && g ~= j
            Stack = 5;
            Xtest4 = Goods(g, 1:2);
            Xtest4a = Goods(g, 5:6);
        end
        if isequal(Xtest3a, Goods(g, 1:2)) && g ~= j
            Stack = 5;
            Xtest4 = Goods(j, 1:2);
            Xtest4a = Goods(j, 5:6);
        end
        if isequal(Xtest3a, Goods(g, 5:6)) && g ~= k
            Stack = 5;
            Xtest4 = Goods(g, 1:2);
            Xtest4a = Goods(g, 5:6);
        end
        end
        end
    end
    if isequal(Xtest2a, Goods(j, 5:6)) && j ~= k
        Stack = 4;
        Xtest3 = Goods(j, 1:2);
Xtest3a=Goods(j,5:6);
for g=1:Txx
  if isequal(Xtest3,Goods(g,5:6))
    Stack=5;
    Xtest4=Goods(g,1:2);
    Xtest4a=Goods(g,5:6);
  end
  if isequal(Xtest3,Goods(g,1:2))&&g~=j
    Stack=5;
    Xtest4=Goods(g,1:2);
    Xtest4a=Goods(g,5:6);
  end
  if isequal(Xtest3a,Goods(g,1:2))&&g~=j
    Stack=5;
    Xtest4=Goods(g,1:2);
    Xtest4a=Goods(g,5:6);
  end
  if isequal(Xtest3a,Goods(g,5:6))&&g~=k
    Stack=5;
    Xtest4=Goods(g,1:2);
    Xtest4a=Goods(g,5:6);
  end
end
end
end
if isequal(Xtesta,Goods(k,1:2))
  Stack=3;
  Xtest2=Goods(k,1:2);
  Xtest2a=Goods(k,5:6);
  for j=1:Txx
    if isequal(Xtest2,Goods(j,5:6))&&j~=i
      Stack=4;
      Xtest3=Goods(j,1:2);
      Xtest3a=Goods(j,5:6);
      for g=1:Txx
        if isequal(Xtest3,Goods(g,5:6))
          Stack=5;
          Xtest4=Goods(g,1:2);
          Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3,Goods(g,1:2))&&g~=j
          Stack=5;
          Xtest4=Goods(g,1:2);
          Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a,Goods(g,1:2))&&g~=j
          Stack=5;
          Xtest4=Goods(g,1:2);
          Xtest4a=Goods(g,5:6);
        end
      end
    end
  end
end
if isequal(Xtest2, Goods(j, 1:2)) && j~ = k
    Stack=4;
    Xtest3 = Goods(j, 1:2);
    Xtest3a = Goods(j, 5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g, 1:2))
            Stack=5;
            Xtest4 = Goods(g, 1:2);
            Xtest4a = Goods(g, 5:6);
        end
    end
end
if isequal(Xtest2a, Goods(j, 1:2))
    Stack=4;
    Xtest3 = Goods(j, 1:2);
    Xtest3a = Goods(j, 5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g, 1:2))
            Stack=5;
            Xtest4 = Goods(g, 1:2);
            Xtest4a = Goods(g, 5:6);
        end
    end
end
if isequal(Xtest3a, Goods(g, 1:2))
    Stack=5;
    Xtest4 = Goods(g, 1:2);
    Xtest4a = Goods(g, 5:6);
end
if isequal(Xtest3a,Goods(g,1:2)) && g ~= j
    Stack = 5;
    Xtest4 = Goods(j,1:2);
    Xtest4a = Goods(g,5:6);
end
if isequal(Xtest3a,Goods(g,5:6)) && g ~= k
    Stack = 5;
    Xtest4 = Goods(g,1:2);
    Xtest4a = Goods(g,5:6);
end
end
end
end
if isequal(Xtest2a,Goods(j,5:6)) && j ~= i
    Stack = 4;
    Xtest3 = Goods(j,1:2);
    Xtest3a = Goods(j,5:6);
for g = 1:Txx
    if isequal(Xtest3,Goods(g,5:6))
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3,Goods(g,1:2)) && g ~= j
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3a,Goods(g,1:2)) && g ~= j
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
    if isequal(Xtest3a,Goods(g,5:6)) && g ~= k
        Stack = 5;
        Xtest4 = Goods(g,1:2);
        Xtest4a = Goods(g,5:6);
    end
end
end
end
if isequal(Xtesta,Goods(k,5:6)) && k ~= i
    Stack = 3;
    Xtest2 = Goods(k,1:2);
    Xtest2a = Goods(k,5:6);
for j = 1:Txx
    if isequal(Xtest2,Goods(j,5:6))
        Stack = 4;
        Xtest3 = Goods(j,1:2);
        Xtest3a = Goods(j,5:6);
    end
end
end
end
end
for g=1:Txx
    if isequal(Xtest3, Goods(g,5:6))
        Stack=5;
        Xtest4=Goods(g,1:2);
        Xtest34a=Goods(g,5:6);
    end
    if isequal(Xtest3, Goods(g,1:2))&&g~=j
        Stack=5;
        Xtest4=Goods(g,1:2);
        Xtest4a=Goods(g,5:6);
    end
    if isequal(Xtest3a, Goods(g,1:2))&&g~=j
        Stack=5;
        Xtest4=Goods(g,1:2);
        Xtest4a=Goods(g,5:6);
    end
    if isequal(Xtest3a, Goods(g,5:6))&&j~=k&&g~=i
        Stack=5;
        Xtest4=Goods(g,1:2);
        Xtest4a=Goods(g,5:6);
    end
end
end
if isequal(Xtest2, Goods(j,1:2))&&j~=k
    Stack=4;
    Xtest3=Goods(j,1:2);
    Xtest3a=Goods(j,5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g,5:6))
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3, Goods(g,1:2))&&g~=i&&g~=j
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,1:2))
            Stack=4;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,5:6))&&g~=k
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
    end
end
end
if isequal(Xtest2a, Goods(j,1:2))
    Stack=4;
    Xtest3=Goods(j,1:2);
    Xtest3a=Goods(j,5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g,5:6))
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3, Goods(g,1:2)) && g~=j
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,1:2)) && g~=j
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,5:6)) && g~=k
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
    end
end
end
if isequal(Xtest2a, Goods(j,5:6)) && j~=k && j~=i
    Stack=4;
    Xtest3=Goods(j,1:2);
    Xtest3a=Goods(j,5:6);
    for g=1:Txx
        if isequal(Xtest3, Goods(g,5:6))
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3, Goods(g,1:2)) && g~=j
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,1:2)) && g~=j
            Stack=5;
            Xtest4=Goods(g,1:2);
            Xtest4a=Goods(g,5:6);
        end
        if isequal(Xtest3a, Goods(g,5:6)) && g~=k
            Stack=5;
            Xtest4=Goods(g,1:2);
        end
    end
end
Xtest4a=Goods(g,5:6);
end
end
end
end
end
end
end
if Stack==2;
    Stack2=[Stack2;Goods(i,:)];
elseif Stack==3;
    Stack3=[Stack3;Goods(i,:);Goods(k,:)];
elseif Stack==4;
    Stack4=[Stack4;Goods(i,:);Goods(k,:);Goods(h,:)];
elseif Stack==5;
    Stack5=[Stack5;Goods(i,:);Goods(k,:);Goods(h,:);Goods(v,:)];
end
end
end
VITA for Enette Louw Beneke

EDUCATION

**PhD Energy and Mineral Engineering**
Pennsylvania State University, University Park, PA 2013
Fuel Science Option
GPA: 3.9/4.0

**B.S., Chemical Engineering**
North West University, Potchefstroom, South Africa 2007
Specializing in Mineral Processing

RELEVANT EXPERIENCE

**Candidate Process Engineer**
Sasol Technology, Research and Development, Sasolburg, South Africa
October 2012 – Current

- Determining solutions to deviations, threats and concerns on a daily basis during rotation as Plant support Engineer at Gas Production, Synfuels in Secunda.
- Assisted with root cause analyses by supplying and analyzing relevant process information.
- Responsible for conducting a fundamental study on the flow in ash canals at Gasification for prevention of ash canal blockages resulting in production losses.

**Teaching Assistant/Course Mentor FSC 432**
Pennsylvania State University, University Park, PA
Fall 2009, Fall 2010

- Assisted students with semester project involving simulation of a petroleum processing plant

**Junior Scientist**
Sasol Technology, Research and Development, Sasolburg, South Africa 2008

- Conducted a literature survey on the effect of coal weathering on different properties
- Developed experimental procedure for studying coal weathering and conducted initial experiments

**Summer Intern**
Sasol Technology, Research and Development, Sasolburg, South Africa
December 2006 – January 2007

- Designed experimental setup and performed initial experiments for testing selectivity of a new adsorbent

AWARDS AND MEMBERSHIPS

Sasol scholarship: 2008 – 2011
Member of Golden Key International Honor society 2005 – 2008
Best poster award, Pittsburg Coal Conference: 2011