

The experimental evaluation of nitrogen transformation in South African coal chars and the concomitant release of nitrogenous species

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West University

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*Dedicated to my mother, Mrs Ngonidzashe Phiri, who
could not see the completion of this thesis.*

The only true wisdom is in knowing you know nothing.

–SOCRATES

DECLARATION

I, Zebron Phiri, hereby declare that this thesis entitled: **The experimental evaluation of nitrogen transformation in South African coal chars and the concomitant release of nitrogenous species**, submitted in fulfilment of the requirements for the degree Ph.D. in Chemical Engineering is my own work and has not previously been submitted to any other institution in whole or in part. Written consent from authors has been obtained for publications where co-authors have been involved.

Signed at Potchefstroom on the **29th** day of **May 2018**.



Zebron Phiri

PREFACE

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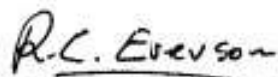
To whom it may concern,

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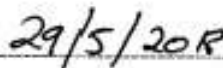
- **Phiri, Z.**, Everson, R. C., Neomagus, H. W. J. P., and Wood, B. J. 2017. The effect of acid demineralising bituminous coals and de-ashing the respective chars on nitrogen functional forms. *Journal of Analytical and Applied Pyrolysis*, **125** 127-135. <https://doi.org/10.1016/j.jaap.2017.04.009>.
- **Phiri, Z.**, Everson, R. C., Neomagus, H. W. J. P., and Wood, B. J. 2018. Transformation of nitrogen functional forms and the accompanying chemical-structural properties emanating from pyrolysis of bituminous coals. *Applied Energy*, **216** 414-427. <https://doi.org/10.1016/j.apenergy.2018.02.107>.
- **Phiri, Z.**, Everson, R. C., Neomagus, H. W. J. P., Engelbrecht, A. D., Wood, B. J., and Nyangwa B. 2018. Release of nitrogenous volatile species from South African bituminous coals during pyrolysis. *Energy & Fuels*, **32** 4606-4616. <https://doi.org/10.1021/acs.energyfuels.7b03356>.

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Signed at Potchefstroom, Pretoria and Johannesburg (South Africa), and Brisbane (Australia).



Raymond C. Everson



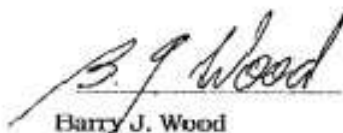
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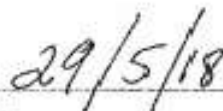
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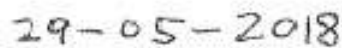
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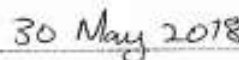
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LIST OF PUBLICATIONS

Journal Articles

- **Phiri, Z.**, Everson, R. C., Neomagus, H. W. J. P., Engelbrecht, A. D., Wood, B. J., and Nyangwa, B. 2018. Release of nitrogenous volatile species from South African bituminous coals during pyrolysis. *Energy & Fuels*, **32** 4606–4616. <https://doi.org/10.1021/acs.energyfuels.7b03356>.
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- **Phiri, Z.**, Everson, R. C., Neomagus, H. W. J. P., and Wood, B. J. 2017. The effect of acid demineralising bituminous coals and de-ashing the respective chars on nitrogen functional forms. *Journal of Analytical and Applied Pyrolysis*, **125** 127–135. <https://doi.org/10.1016/j.jaap.2017.04.009>.

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- **Phiri, Z. (presenter)**, Everson, R. C., and Neomagus, H. W. J. P. Emission of nitrogen volatile species during coal pyrolysis. **Oral presentation** at the Fossil Fuel Foundation (FFF) Sustainable Development of South Africa's Energy Sources. Johannesburg, South Africa, 29–30 November 2017.

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- **Phiri, Z.**, Everson, R. C., and Neomagus, H. W. J. P. (**presenter**). Coal nitrogen transformation and the release of nitrogen species during pyrolysis and combustion in a bench-scale bubbling fluidised bed reactor. **Oral presentation** at the 8th International Freiberg Conference. Cologne, Germany, 12–16 June 2016.
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ABSTRACT

The effect of typical South African (SA) coal properties on nitrogen functional transformation and release were examined in the course of pyrolysis in a fluidised bed (FB) and drop-tube furnace (DTF). Chars were generated at temperatures ranging from 740 °C to 980 °C in the FB, and at 1000 °C up to 1400 °C in the DTF. X-ray photoelectron spectroscopy (XPS) analysis of the parent coals showed that pyrrolic nitrogen (N-5) was the dominant functionality, followed by pyridinic- (N-6), and quaternary nitrogen (N-Q), respectively. On the contrary, analysis of chars revealed that N-Q was the most prevalent N functional form, followed by N-6, N-5, and protonated-/oxidised pyridinic nitrogen (N-X), respectively. Chars generated from DTF, emanating from relatively high total reactive macerals, behaved differently at elevated temperatures.

The nitrogen functionality of all coals and FB chars that underwent HCl/HF/HCl treatment seemed not to experience meaningful alteration. Remnants of acid treated DTF chars that were prepared from inertinite-rich coal, as well as possessing low total reactive macerals, also did not show apparent changes in nitrogen functionalities. Nevertheless, de-ashing of chars emanating from a vitrinite-rich coal, and also from a severely pyrolysed inertinite-rich coal possessing relatively high total reactive macerals, resulted in the emergence of additional moieties of nitrogen in the remnants.

X-ray diffraction (XRD) results illustrated that aromaticity (f_a) and average crystallite diameter (L_a) of chars simultaneously rose as the pyrolysis temperature increased. Nevertheless, increasing temperature resulted in apparent decrease in the fraction of amorphous carbon (X_A) and the associated degree of disorder index (DOI). Examination of XPS and XRD results enabled the correlation of simultaneous transformations of nitrogen functional forms and condensed aromatic crystallites emanat-

ing from pyrolysis. Increase in N-Q exhibited a good relationship with f_a , while the decrease in N-5 displayed a satisfactory correspondence with X_A and DOI .

The fractions of inherent coal nitrogen that were emitted from the volatile stream as NH_3 , HCN and tar-N were also evaluated. Tar-N emitted at 740–900 °C primarily comprised the following functionalities in given order; N-5 > N-6 > N-Q. The N functional form distribution in tars produced at this temperature range was comparable to that of raw coals. Increasing temperature caused a simultaneous increase in N-Q, decrease in N-5, as well as a subtle diminishing of N-6 in tars. XPS analysis of tar-N was limited to tars released from FB. Coals with a substantial composition of vitrinite, total reactive macerals and mineral matter, released a significant fraction of fuel nitrogen as volatile-N during FB and DTF pyrolysis. A greater portion of coal-N was emitted as NH_3 than HCN during FB pyrolysis. However, DTF pyrolysis prompted conversion of an appreciable coal-N fraction into HCN rather than NH_3 . Coals with relatively high total reactive macerals displayed similar behaviour with regard to nitrogen transformations and release patterns. A combination of total mineral matter and maceral composition exhibited greater influence on the nitrogen product distribution.

Keywords: Pyrolysis; Nitrogen forms transformation; XPS; XRD; Coal demineralisation; Char de-ashing; Total reactive macerals; Carbon crystallite; Nitrogen release; South African coal.

EXTENDED ABSTRACT

Pyrolysis of three South African (SA) bituminous coals was performed in a laboratory-scale bubbling FB at temperatures ranging from 740 °C to 980 °C, as well as in a DTF starting at 1000 °C and increasing to 1400 °C. The parent coals along with the generated chars were subjected to a battery of analytical techniques to elucidate their different chemical-structural properties. The conventional proximate and ultimate, maceral, and mineral analyses were performed. Advanced analytical techniques that encompass X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were utilised to determine nitrogen functional forms and carbon structural properties, respectively. Additional coal chemical-structural properties were obtained from solid state ^{13}C nuclear magnetic resonance (ss NMR). A large portion of SA coals are characterised by the richness of the inertinite maceral as well as high mineral content. The influence of typical SA coal traits on evolution of nitrogenous volatile species, that constituted of tar nitrogen, ammonia and hydrogen cyanide was established.

Some of the analytical techniques, like XRD and NMR, require the use of demineralised samples. Therefore it was essential to establish the impact of acid treatment on nitrogen functionalities of coals and the successive chars. XPS was employed to analyse the nitrogen functionalities of coals and generated chars, and their corresponding acid treated counterparts. The nitrogen functionalities of raw coals were consistently analogous to those broadly outlined in literature, whereby N-5 is the dominant nitrogen functionality, followed by N-6 and N-Q, respectively. Whereas the results for pyrolysed chars showed that N-Q was the prevalent functionality followed by N-6, N-5 and protonated-/oxidised pyridinic nitrogen (N-X), respectively. However, XPS N 1s analysis of DTF chars emanating relatively high total reactive

macerals produced spectra with two prominent peaks whose binding energy corresponded to N-Q and N-6. The systematic HCl/HF/HCl chemical treatment procedure appeared to have no significant impact on nitrogen functionalities of the parent coals along with the whole range of chars generated from FB. The systematic de-ashing of DTF chars prepared through pyrolysis of high ash and inertinite-rich coal (low total reactive macerals) displayed no substantial influence on transformation of nitrogen functional forms. Nonetheless, the process of de-ashing chars produced from the drop tube furnace, whose parent coal is characterised by high ash content and rich in vitrinite, and another char from comparatively low ash and relatively high total reactive macerals coal (contributed by high reactive- semifusinite and inertodetrinite), that initially consisted of pyridinic- and quaternary nitrogen, produced two extra nitrogen peaks whose respective binding energies corresponded to N-5 and N-X.

The parallel transformations of nitrogen functional forms and condensed aromatic crystallites in chars as a result of coal pyrolysis was acquired through XPS and XRD analyses. The deviations of XPS N 1s spectra of chars from that of their respective parent coals determined the nitrogen functional form transformations. Information acquired from XPS N 1s spectra showed diminishing N-5 with increasing pyrolysis temperature, whereas N-Q increased substantially. Data obtained through XRD analysis of the entire chars range revealed that aromaticity (f_a) and average crystallite diameter (L_a) concomitantly increased as the intensity of pyrolysis temperature rose. Simultaneously, the fraction of amorphous carbon (X_A), along with the degree of disorder index (DOI), declined meaningfully. The chars that were generated from coals with high total reactive macerals were easily responsive to high temperature exposure with respect to nitrogen functionality and carbon crystallite transformations. Thus implying that the respective high temperature chars only possessed N-6 and N-Q, coupled with considerable growth of crystallite height (L_c) and the average number of aromatic carbons (N_{ave}). XPS and XRD analyses revealed that the structural transformations instituted by pyrolysis displayed a good correlation between N-Q and f_a . In a distinct variation, the decrease in N-5 exhibited an apparent direct correspondence with DOI and X_A . Aromaticity of coals evaluated through XRD as well as ^{13}C ss NMR analyses almost correlated seamlessly.

The effect of typical SA coal traits on evolution of volatile nitrogen components in the course of pyrolysis was also investigated in parallel within the specified temperature ranges. The fractions of coal-N that were converted into ammonia, hydrogen cyanide and tar-nitrogen were evaluated. The nitrogen functionalities of tars that were liberated at 740–900 °C displayed dominance of N-5, with N-6 following, and N-Q being the least. Tars emitted at 740 °C constituted the distributions of nitrogen functionalities that were very similar to that of their respective parent coals. Nonethe-

less, increasing pyrolysis temperature caused a steady heightening of N-Q, along with simultaneous depreciation of N-5, and a subtle diminishing of N-6. XPS analysis of tar-N was limited to tars released from FB. A significant fraction of nitrogen from coals with a comparably large volume of total reactive macerals, coupled with appreciably high mineral matter content, was converted into nitrogenous volatile species within the FB temperature range. In the course of FB pyrolysis, an appreciable quantity of NH_3 was emitted compared to HCN. Nevertheless, a greater portion of HCN was evolved compared to NH_3 in the DTF experimental campaign. Fluidised bed pyrolysis of the two coals with the relatively high total reactive macerals displayed a similar pattern of NH_3 evolution by attaining their respective highest yields at 820 °C. Nevertheless, the emission profile of HCN from the same coals showed a completely different trend with a trough at 820 °C. On the other hand, the coal containing the highest mineral matter as well as the lowest total reactive macerals (rich in inertinite) liberated the most NH_3 at 740 °C and concurrently minimal HCN yields at the same temperature. The fraction of nitrogen contained in coal converted to NH_3 and HCN increased gradually as the DTF pyrolysis temperature intensified. In the course of DTF pyrolysis, the two coals with relatively high total reactive macerals evolved large amounts of nitrogenous volatile components at temperatures ranging from 1000 °C to 1270 °C. The respective yields from the inertinite-rich coal that also constitutes of least total reactive macerals, lagged behind within 1000–1270 °C. Coal characteristics which include absolute mineral matter content and maceral composition significantly influenced the formation of particular nitrogenous volatile products. The effect of total reactive macerals on volatile-N release from the DTF was more pronounced from 1130 °C to 1400 °C. A combination of other factors that influence the output and constitution of nitrogenous components include the reactor type, temperature, particle size, and residence time.

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NOMENCLATURE

		Units
A_{002}	Area under the (002) peak	$\text{\AA}^2$
A_{γ}	Area under the γ band of the (002) peak	$\text{\AA}^2$
A_i	Initial ash content of coal	wt. %
A_d	Demineralised coal or de-ashed char ash content	wt. %
BE	Binding energy	eV
$B.L$	Average number of bridges and loop per cluster (cross-links)	–
C	Average number of aromatic C's per cluster	–
d_{002}	Inter-layer spacing within a cluster of N_{ave} parallel layers	$\text{\AA}$
E_d	Demineralising/de-ashing efficiency	%
DOI	Degree of disorder index	%
f_a	Fraction of aromatic carbons	–
f_a^*	Corrected fraction of aromatics	–
f_{al}	Fraction of aliphatic carbons	–
f_a^{CO}	Fraction of carbonyl/carboxyl and amide carbons	–
f_a^H	Fraction of protonated carbons in aromatic region	–
f_{al}^H	Aliphatic CH+CH ₂	–
f_{al}^O	Fraction of aliphatic carbons bonded to oxygen	–
f_a^N	Fraction of non-protonated carbons in aromatic region	–
f_{al}^{N*}	Fraction non-protonated C's+methyl groups in aliphatic region	–
f_a^P	Fraction of phenolics	–
f_a^S	Fraction of alkylated aromatics	–
h	Planck's constant	J·s
K	Constant dependent on X-ray refraction plane	–

Nomenclature (continued)

KE	Kinetic energy	J
L_a	Average crystallite diameter	Å
L_c	Crystallite height	Å
N-5	Pyrrolic nitrogen	–
N-6	Pyridinic nitrogen	–
M_δ	Average molecular weight of side chain or half of bridge mass	
M_G	Fraction of aromatic ring carbons with a directly attached proton	–
MW	Average molecular weight per cluster	
N_{ave}	Average number of aromatic carbons	–
N-Q	Quaternary nitrogen	–
N-X	Protonated &/or oxidised pyridinic nitrogen	–
P_0	Average number of intact bridges	–
$S.C$	Average number of side chains per cluster	–
T_{CH}	Cross polarisation rate	s^{-1}
$T_{1\rho}^H$	Proton relaxation time	s
wt%	Weight percentage	%
X_A	Fraction of amorphous carbons	–
X_b	Mole fraction of aromatic bridgehead carbons	–

Greek Symbols

ϕ	Work function	J
λ	Wavelength of incident X-ray	Å
β	Full width at half maximum of the respective peak or band	degrees (°)
$\sigma + 1$	Average number of attachments (bridges, loops, side chains) per cluster	–
θ	Peak position / XRD angle of scan	degrees (°)
θ_{002}	Peak position of (002) peak	degrees (°)
θ_{10}	Peak position of (10) peak	degrees (°)
θ_{11}	Peak position of (11) peak	degrees (°)

Acronyms and Abbreviations

ASSAf	Academy of Science of South Africa
ASTM	American Society for Testing and Materials
CAF	Central Analytical Facilities
CasaXPS	Computer aided surface analysis for X-ray photoelectron Spectroscopy

Acronyms and Abbreviations (continued)

CP MAS	Cross polarisation magic angle spinning
CSA	chemical shift anisotropy
daf	dry, ash-free
db	dry basis
DD MAS	dipolar dephasing magic angle spinning
DTF	drop-tube furnace
Eskom	Electricity Supply Commission (South Africa)
FB	fluidised bed
FFF	Fossil Fuel Foundation
FTIR	Fourier Transform Infra Red
FWHM	full width at half-maximum
GWP	global warming potential
HR TEM	high resolution transmission electron microscopy
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
ISO	International Standards Organisation
MAS	magic angle spinning
MW	megawatt
NEXAFS	near edge X-ray absorption fine structure
NIST	National Institute of Standards and Technology
NMR	nuclear magnetic resonance
NO _x	nitric oxide and nitrogen dioxide (NO and NO ₂)
OPEC	Organisation of Petroleum Exporting Countries
ppm	parts per million
SA	South Africa
SO _x	sulphur oxides
SSB1	first spinning sideband
SSB2	second spinning sideband
ss NMR	solid state nuclear magnetic resonance
US EPA	United States Environmental Protection Agency
VM	volatile matter
XANES	X-ray absorption near-edge structure spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XPS	X-ray photoelectron spectroscopy
UCC	ultra clean coal
UNECE	United Nations Economic Commission for Europe

CHAPTER

1

GENERAL INTRODUCTION

The first chapter introduces the importance of coal, and the need to utilise it efficiently and work towards reducing its associated environmental impacts. Coal plays an important role in the global energy mix, particularly in the power generation sector. However, it needs to be utilised efficiently in order to reduce its undesirable environmental footprint. The aim of this chapter is to provide basic coal information in terms of its utilisation and environmental consequences, with the main focus being given to the precursors of nitrogen oxides. A brief background and motivation are furnished in Section 1.1. An overview of South Africa's energy usage and its comparison with global trends is also presented. The coal structure, incorporating coal nitrogen as the source of released oxides of nitrogen, is described in Section 1.2. A concise problem statement is described in Section 1.3, with the subsequent objectives and approach provided in Section 1.4.

1.1 Background and Motivation

1.1.1 Importance of Coal

Energy is the driving force behind any economy in the world. Currently, the world economy is heavily reliant on fossil fuels even though public interest directed towards renewable energy has gathered momentum. Coal is the most abundant fossil fuel, geographically well distributed across the globe. It is safe and reliable, affordable and stable in price (Miller, 2005; Speight, 2015). Coal propels economic growth through

the provision of dependable and inexpensive electrical power needed to satisfy the ever growing electricity demand. Major challenges that the world faces at present include the ever increasing population and the parallel rising energy demands. The utilisation of coal holds a significant function in energy schemes that are earmarked for driving sustainable growth in the world. Coal usage plays an important role in energy systems that are bound to support sustainable development in the foreseeable future. The economic importance of coal, and the scientific challenges involved in comprehending its evolution and composition, as well as optimising its utilisation, and mostly the environmental implications, have drawn interest from many researchers and other stakeholders in the field. The viability of coal utilisation is largely dependent upon successful reduction in the environmental impacts associated with its usage.

Coal is a major viable option for meeting the world's ever growing energy demand. Its uses includes gasification, liquefaction, pyrolysis and in combustion energy systems such as pulverised fired and fluidised bed combustors. The major global utilisation of coal is electricity generation, of which about 40% of the total electricity generated around the world emanates from coal.

1.1.2 Coal in South Africa's Energy Mix

Southern African coals have not been adequately studied despite their importance to the economies in the region. Most of the coals generally possess a large portion of inertinites and high mineral matter, unlike northern hemisphere coals which are predominantly rich in vitrinites and generally have low mineral matter content. Coal is the major energy source in South Africa (SA) and the world at large, and South Africa has the largest coal reserves in Africa ([Energy Information Administration, 2015](#); [World Coal Association, 2015](#)). According to the [BP Statistical Review of World Energy \(2017\)](#), SA's economy ranks second on the continent, and is the top most energy intensive, amounting to approximately 28% of Africa's total primary energy consumption. According to an [Eskom Factsheet \(2017\)](#), South Africa possesses about 53 billion tonnes of coal reserves which are estimated to sustain energy production at current consumption rates for the next 200 years. The enormous dependence of South Africa on coal for primary energy is clearly illustrated in Figure 1.1, compared to the global primary energy consumption by fuel type for 2016. It is apparent that the economy of South Africa is driven by coal; in 2016, the world coal utilisation stood at 28.1% of the energy mix whereas 69.6% of South Africa's energy emanated from coal. The latest data provided by [BP Statistical Review of World Energy \(2017\)](#) shows that the dependence of SA on coal places the country at the top of the continent's list of carbon dioxide emitters, and making it the 14th in the world.

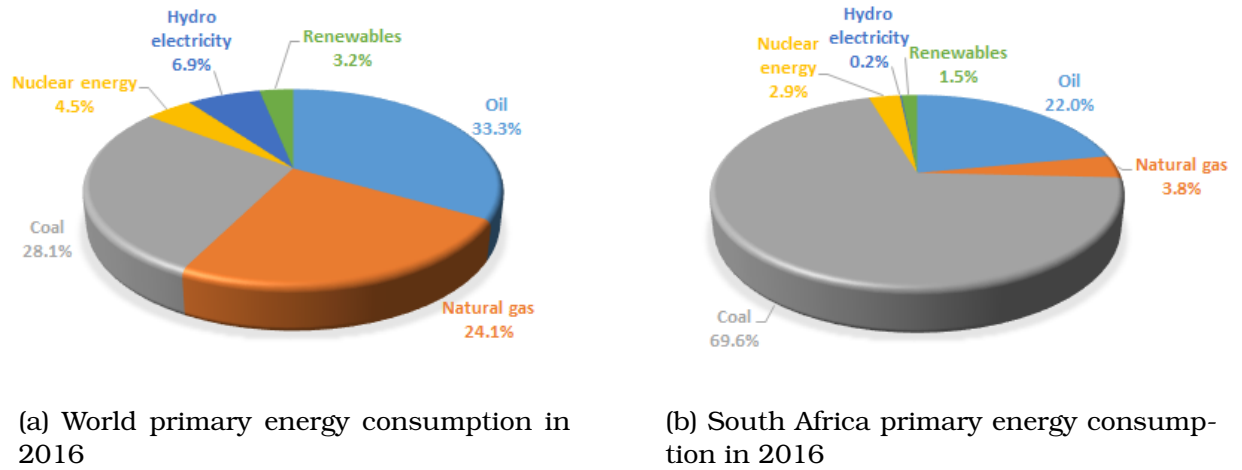


Figure 1.1: World and South Africa primary energy consumption by fuel type in 2016. Source: [BP Statistical Review of World Energy \(2017\)](#)

A greater portion of the oil that is utilised in SA is imported from the Organisation of Petroleum Exporting Countries (OPEC), and then refined locally. Some of the petroleum is also locally produced synthetically through an intricate Fischer-Trosch process in Secunda. A study carried out by the [Energy Information Administration \(2015\)](#) revealed that South Africa possesses shale gas primarily in the Karoo basin, making SA rank number eight on the list of countries with technically recoverable shale gas. Thus shale gas emerges as a dependable option to coal, nevertheless, environmental concerns and uncertainty surrounding legislation have stalled its exploration.

The [World Coal Association \(2015\)](#), stated that 41% of the total world electricity generation in 2012 emanated from coal, while 94% of SA's electricity was derived from coal. This made SA the second highest in reliance to coal for electricity generation in the world, after Mongolia which burnt coal to get 98% of its electricity. In 2008 and 2009, 93% of the electricity generated in SA was produced from coal while 42% of the world's electricity came from coal. It is clear that South Africa's economy is very much reliant on coal, since the country's total primary energy comprises of more than 70% coal consumption. According to [Eskom Factsheet \(2017\)](#), coal used for electricity generation exceeds 50% of SA's total coal utilisation. The process of turning coal into liquid fuels at Sasol accounts for the second highest use of coal. This is followed by coal usage in metallurgical operations, while domestic use accounts for the least portion. In an endeavour to meet the ever growing electricity demand, Eskom (the country's national utility) has expanded its coal-fired electricity generation capacity by adding coal-fired Medupi power station with a generation capacity of 4 764 MW to the grid, and the coal-fired Kusile plant will contribute up to 4 740 MW.

1.2 Coal Characteristics

Coal is a combustible sedimentary rock containing heterogeneous macromolecular structures formed from deposition and compaction of peat emanating from diverse wetland conditions (Miller, 2005; Speight, 2015; Stach et al., 1982; Teichmüller, 1989). Coal is made up of large three-dimensional polymeric structures that are joined by aliphatic bridging groups (Fletcher et al., 1992; Genetti and Fletcher, 1999; Smith et al., 1994). In most instances, coal principally constitutes organic matter with varying amounts of inorganic substances. The organic portion of coal primarily consists of carbon, followed by hydrogen and oxygen, whereas sulphur and nitrogen each constitute up to 2% (Glick and Davis, 1991; Miller, 2005). A wide range of ash forming inorganic substances are also sporadically distributed throughout the coal. The inorganic part of coal mostly consists of different minerals that vary from one coal to another, depending on origin. The inherent minerals have marked effects on the chemical characteristics of coal and the envisaged utilisation. Subjecting coals and the respective chars to an acid or alkali produces carbonaceous remnants with substantially decreased levels of mineral matter or ash content. This procedure is conducted before some coal conversion processes or prior to particular laboratory analyses so as to curb the influence of minerals or ash. The chemical treatment is also conducted to reduce environmental implications emanating from coal usage, as well as to increase the efficiency.

The heterogeneous nature of coal requires extensive characterisation in order to effectively elucidate the structural attributes and how the coal structure influences the formation of subsequent products in the form of chars and volatile species. In order to comprehend the role played by nitrogen in coal conversion processes, its concentration and functionality should be established. Basically there are two techniques that have proven suitable for determining the heterocyclic nitrogen functional forms in carbonaceous materials, that is X-ray photoelectron spectroscopy (XPS) (Buckley, 1994; Davidson, 1994; Gong et al., 1999; Kelemen et al., 1998; Kozłowski, 2004; Pels et al., 1995; Pietrzak, 2009; Stańczyk et al., 1995; Wójtowicz et al., 1995) and X-ray absorption near edge structure spectroscopy (XANES) (Mitra-Kirtley et al., 1993a,b; Mullins et al., 1993; Zhu et al., 1997). Solid state ^{15}N nuclear magnetic resonance (NMR) has also been used to a lesser extent due to its inherent shortcomings (Kelemen et al., 2002; Knicker et al., 1995, 1996; Solum et al., 1997). In general, four heterocyclic nitrogen functional groups have been identified by XPS in carbonaceous materials like coal and its derivatives, these are pyridinic-, pyrrolic-, quaternary-, and protonated- and/or oxidised pyridinic-N (Kapteijn et al., 1999; Zhang et al., 2011).

1.2.1 Coal Devolatilisation

Coal combustion is a complex process which involves chemical and physical changes. The process is characterised by drying and heating, devolatilisation, oxidisation of volatiles and oxidisation of the residual char (Wu, 2005). During combustion, pyrolysis or gasification, volatile species are liberated together with nitrogenous components in the first few milliseconds, a phenomenon described as devolatilisation (Wu, 2005). Devolatilisation (pyrolysis) is an important preliminary step in most coal transformation processes, it can account for as much as 70% weight loss of the coal (Serio et al., 1987). In general, the quantity, composition, and the rate of release of volatile matter do not only depend on type of coal but also on the conditions of devolatilisation. The devolatilisation behaviour is influenced by the heating rate, which in turn, is also reliant on size of particle as well as the surrounding temperature, the atmosphere; whether it is oxidising, neutral or reducing, and the absolute pressure (Anthony and Howard, 1976; Gibbins and Kandiyoti, 1989; Suuberg et al., 1979). Figure 1.2 illustrates a hypothetical parent coal molecule undergoing primary and secondary pyrolysis Solomon et al. (1988).

Char is the solid carbonaceous material that is formed from coal as light gases and tar are driven off due to heat treatment. Tar is generally described as volatiles that condense to either solid or liquid at room temperature. The nitrogen containing compounds released during devolatilisation include tar-N, ammonia (NH₃), hydrogen cyanide (HCN) and nitrogen gas (N₂) (Bassilakis et al., 1993; Kambara et al., 1993; Niksa, 1995). Some of the nitrogen remains in the char (Leppälahti and Koljonen, 1995), and the char-N is subsequently oxidised in the next few seconds during char combustion and released as nitrogen oxides (Johnsson, 1994). HCN and NH₃ are the main precursors of nitrogen oxides in combustion systems (Dagaut et al., 2008; Li and Tan, 2000; Nelson et al., 1991). The evolution of nitrogenous species during pyrolysis and/or combustion of coal have been extensively investigated for at least the past forty years. However, more studies on the matter are required to elucidate particular issues that may restrain prospective nitrogen oxides mitigation.

1.2.2 Environmental Implications

Coal combustion produces substantial amounts of the much needed heat, and unfortunately, an indisputable quantity of various gaseous and solid pollutants. The formed emissions include greenhouse gases, particulate matter, volatile organic compounds and various pollutants, which encompass nitrogen oxides and sulphur oxides. Nitrogen oxides are formed from the fixation of nitrogen in the atmosphere due to extreme high temperatures or from oxidation of chemically bound nitrogen within

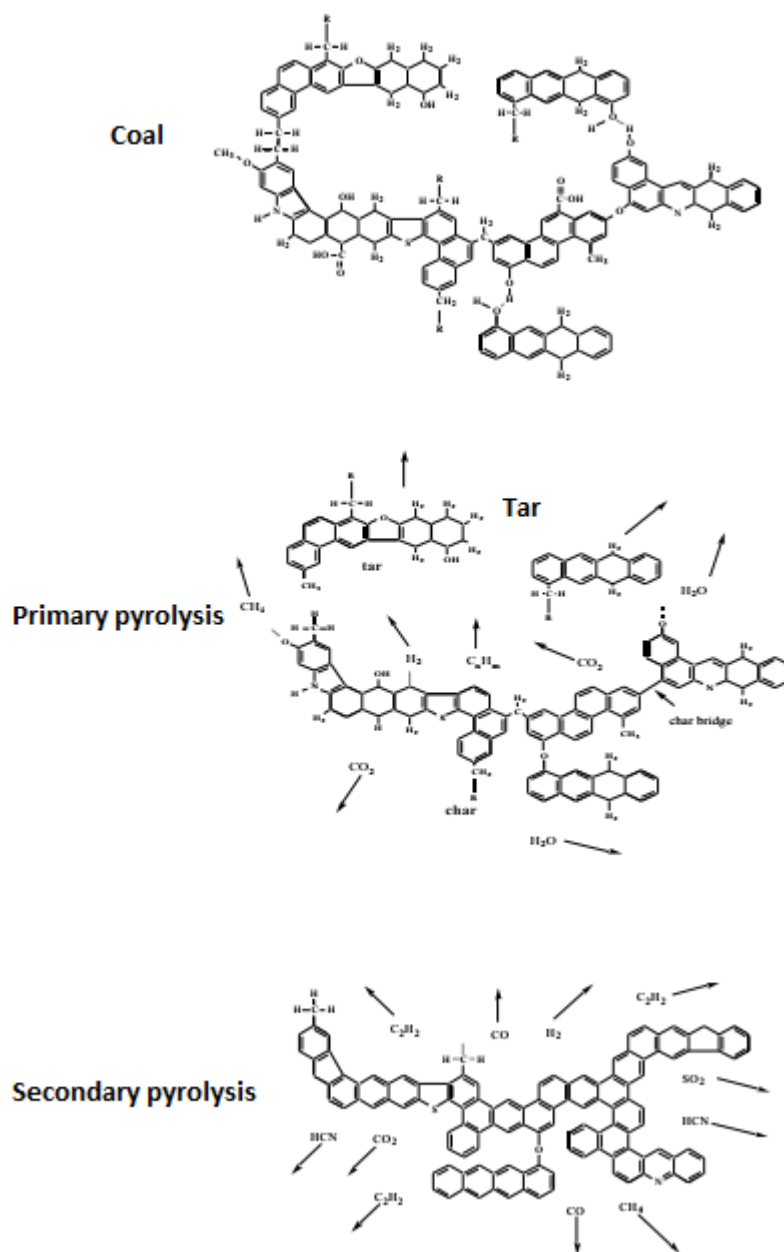


Figure 1.2: Products formed during pyrolysis of a hypothetical parent coal molecule (Adapted from [Solomon et al. \(1988\)](#)).

the coal matrix during combustion ([Boardman and Smoot, 1993](#); [Glarborg et al., 2003](#); [McInnes and Van Wormer, 1990](#)). The pollutants released into the atmosphere subsequently lead to a wide range of environmental repercussions, including destruction of forests, contamination of soils, endangering aquatic life and other living organisms, damaging materials, and putting human health at risk. Trace elements and ultrafine particulates are also liberated from coal combustion, and have been

linked to potentially dangerous carcinogenesis, inflammation and tissue remodelling (Dagouassat et al., 2012; Shoji et al., 2002; Sloss, 2002).

The formed nitrogen oxides are emitted as nitric oxide (NO), nitrous oxide (N₂O) and nitrogen dioxide (NO₂) (Glarborg et al., 2003; Li, 2004). The released NO is subsequently oxidised to NO₂ in the atmosphere. A combination of NO and NO₂ is commonly referred to as NO_x. NO₂ that emanates from anthropogenic activities is the most prevalent form of NO_x in the atmosphere (Environmental Protection Agency, 1999). In addition to their direct effect on human health, NO_x are precursors to acid rain and also take part in the formation of photochemical smog. N₂O is considered a potent greenhouse gas that is also consequently implicated in the reduction of the ozone layer (Glarborg et al., 2003; Kramlich and Linak, 1994; Li, 2004; Rapson and Dacres, 2014; Thomas, 1997). The global warming potential (GWP) exerted by N₂O is 298 times more potent than that effected by CO₂ across a 100-year period. The global warming effect contributed by N₂O is approximated at 6% (Forster et al., 2007; Ravishankara et al., 2009). The combustion of fossil fuels is responsible for more than half of nitrogen oxides emissions around the globe, and up to about 67% of the emissions that emanate from anthropogenic activities (Carpenter et al., 2006). Burning of biomass and use of fertilisers, are among other sources of nitrogen oxides resulting from human activities. Heightened nitrogen accumulation emanating from human activities leads to eutrophication.

1.2.3 Stringent Environmental Legislation

The global power generation from coal combustion is being compelled by environmental legislation to abate levels of pollutant emissions. Stringent emission standards are being imposed all over the globe due to the heightened concerns about the local, regional, and transboundary consequences of emissions from coal-fired plants. The energy industry recognises the need for environmentally friendly coal utilisation, and it is devoted towards the implementation of effective methods for controlling hazardous emissions. It is therefore paramount to have an insight into coal attributes and behaviour to facilitate the development of efficient coal conversion technologies that mitigate pollutants through reduction or conversion into benign by-products or emissions. As regulations become more stringent, the necessity to consider environmental concerns in the operation of combustion systems is also mounting. Among the various environmental laws now affecting coal-fired combustion systems, laws covering abatement of nitrogen oxides emission are especially stringent.

Growing concerns relating to these environmental impacts have prompted the adoption of international legislation and the establishment of national emission standards. The United Nations Economic Commission for Europe (UNECE) Gothenburg

protocol and European Union directives have set national NO_x emission standard at a low 200 mg/m³ for all newly established power stations having a thermal input that exceed 300 MW. International organisations encompassing UNECE and the Inter-governmental Panel on Climate Change (IPCC) have encouraged nations to ascertain their emissions and institute control measures ([Carpenter et al., 2006](#)).

Ecologically friendly use of coal is vital for the long-term acceptance of the world's most abundantly available fossil fuel. Even though renewable sources are an option being given huge consideration to provide a balanced energy mix, South Africa largely places its faith on clean coal technology because coal will remain an indispensable resource as global energy demand rises. The biggest challenge faced by South Africa is compliance with evolving stringent environmental legislation.

1.3 Problem Statement

The evolution of nitrogen containing volatile components in the course of coal pyrolysis and that of other related carbonaceous materials has been under immense investigation over the last four decades. However, more work still needs to be done on the release of volatile nitrogen species from coal with aspirations of establishing efficient utilisation and reduced emissions. Insight on the influence of coal properties on morphological transformations incorporating nitrogen functionality transformations and the concomitant product distribution of nitrogenous species during pyrolysis is important for the conception of effective elemental strategies towards nitrogen oxides reduction. Most of the nitrogen oxides emitted from pulverised and fluidised bed coal combustion systems emanate from nitrogen that is inherent in coal. Therefore, the nitrogen and associated carbon structural transformations occurring in the course coal conversion need to be tracked closely and understood in order to achieve efficient coal utilisation coupled with minimal environmental consequences. The rearrangement of aromatic crystallites occurring simultaneously with the transformation of nitrogen functionalities in the course of pyrolysis have significant practical effects that might lead to the improvement of nitrogen release kinetic mechanisms.

Clear understanding of the influence of coal properties on formation of nitrogenous species remains to be established. South African coals are distinctively high-ash and inertinite-rich compared to other coals around the world especially those in the northern hemisphere which have relatively low ash content and are essentially rich in vitrinite ([Cadle et al., 1993](#); [Everson et al., 2013a, 2008b](#); [Falcon and Ham, 1988](#); [Kaitano, 2007](#); [Rosenberg et al., 1996](#)). Despite this, there has not been much work that seeks to address the influence of these attributes on nitrogen release during coal conversion processes. It is necessary to understand the chemical structure of South

African coals to explain the structural changes which takes place during coal conversion processes like pyrolysis (devolatilisation) in relation to the release of nitrogenous species.

Coals and chars are at times chemically treated, either to increase utilisation efficiency, reduce environmental implications or to minimise disturbance that might emanate from the presence of mineral matter in particular laboratory analyses. Extensive analyses involving a battery of analytical techniques are embarked on to elucidate coal and char properties of which either untreated or demineralised/de-ashed samples are utilised. Therefore it is important to ask the the question; does the adopted systematic HF/HCl pretreatment procedure affect the nitrogen forms in coals and chars? This will assist in establishing whether the acid treatment alters the nitrogen structural attributes or not.

1.4 Objectives and Approach

Coal is a very important energy resource in South Africa. This study intends to contribute towards prolonged usage of this indispensable resource by providing information that could lead towards compliance with stringent environmental requirements related to the abatement of nitrogen oxides. Therefore the primary objectives of this investigation were to:

1. Determine the relation between morphological changes and the concomitant transformations of nitrogen functional forms in chars.
2. Investigate the influence of coal macerals and mineral matter on the evolution of nitrogenous volatile species occurring in the course of pyrolysis.
3. Study the influence of coal properties during pyrolysis on nitrogen product distribution, with emphasis on major precursors of nitrogen oxides, that are HCN and NH_3 .
4. Establish the influence of HF/HCl sequential acid treatment on coal and char nitrogen functional forms.

It is important to increase the understanding of the coal chemical structure and its influence on the subsequent pyrolysis nitrogen distribution products emanating from South African coals. The essence of the study is to ascertain the correlation of the concomitant transformations occurring within the carbon crystallite structure and the nitrogen functionalities, in conjunction with the parallel evolution of nitrogenous volatile species. The partitioning of nitrogen contained in coal into nitrogen retained

in char, and nitrogen emitted within the volatile stream is a significant aspect in establishing the evolution of nitrogen oxides in the succeeding combustion process (Johnsson, 1994; Thomas, 1997). The morphological alterations are most likely to be directly liable for the evolution of the nitrogen contained coal, but this link has not been examined thoroughly so far. Effective use of coal in existing and new applications requires a more definitive, qualitative and quantitative understanding of coal properties compared with performance. The study delves into coal and char chemical-structural transformations, nitrogen functional forms, release of nitrogen volatile species, and the effect of acid treatment. To achieve the stated objectives, the following activities were carried out:

- (a) Pyrolysis experiments in an electrically heated drop tube furnace as well as in a bench-scale bubbling fluidised bed to generate chars and analyse volatile-N species.
- (b) Subjecting the parent coals and the subsequent generated chars to HCl/HF/HCl sequential acid treatment.
- (c) Conventional chemical analyses of coals and the solid products of pyrolysis, as well as the acid treated remnants.
- (d) Detailed petrographic and mineral analyses of the parent coals.
- (e) Determination and quantification of nitrogen functionalities that exist in parent coals, respective chars and acid treated coals/chars using XPS.
- (f) Employing XRD analysis to evaluate carbon structural properties of coals and chars, and use of ^{13}C ss NMR to determine structural properties of raw coals.
- (g) Measuring the NH_3 , HCN, and tar-N that is emitted during pyrolysis experiments.

1.4.1 Scope of Study

Figure 1.3 illustrates the path followed in the activities undertaken and analyses carried out in this study leading to the manifestation of the thesis. A battery of analytical techniques were carried out to establish coal and the respective char attributes. The analyses included conventional techniques, mineral composition, and maceral characteristics. XPS gave the various nitrogen functionalities present in the coal and the subsequent chars. ^{13}C solid state NMR spectroscopy gave the primary carbon structural features of both coal and char. Information from XRD contributed to average aromatic cluster size and staking of aromatic clusters. The thesis contains a review of nitrogen in coal, char and that released into volatile stream mainly due to pyrolysis. Published papers which form the integral part the study are included in the thesis,

furnishing a description of conducted experiments, analytical techniques that were employed, and respective discussions of the results emanating from pyrolysis of the utilised South African coals.

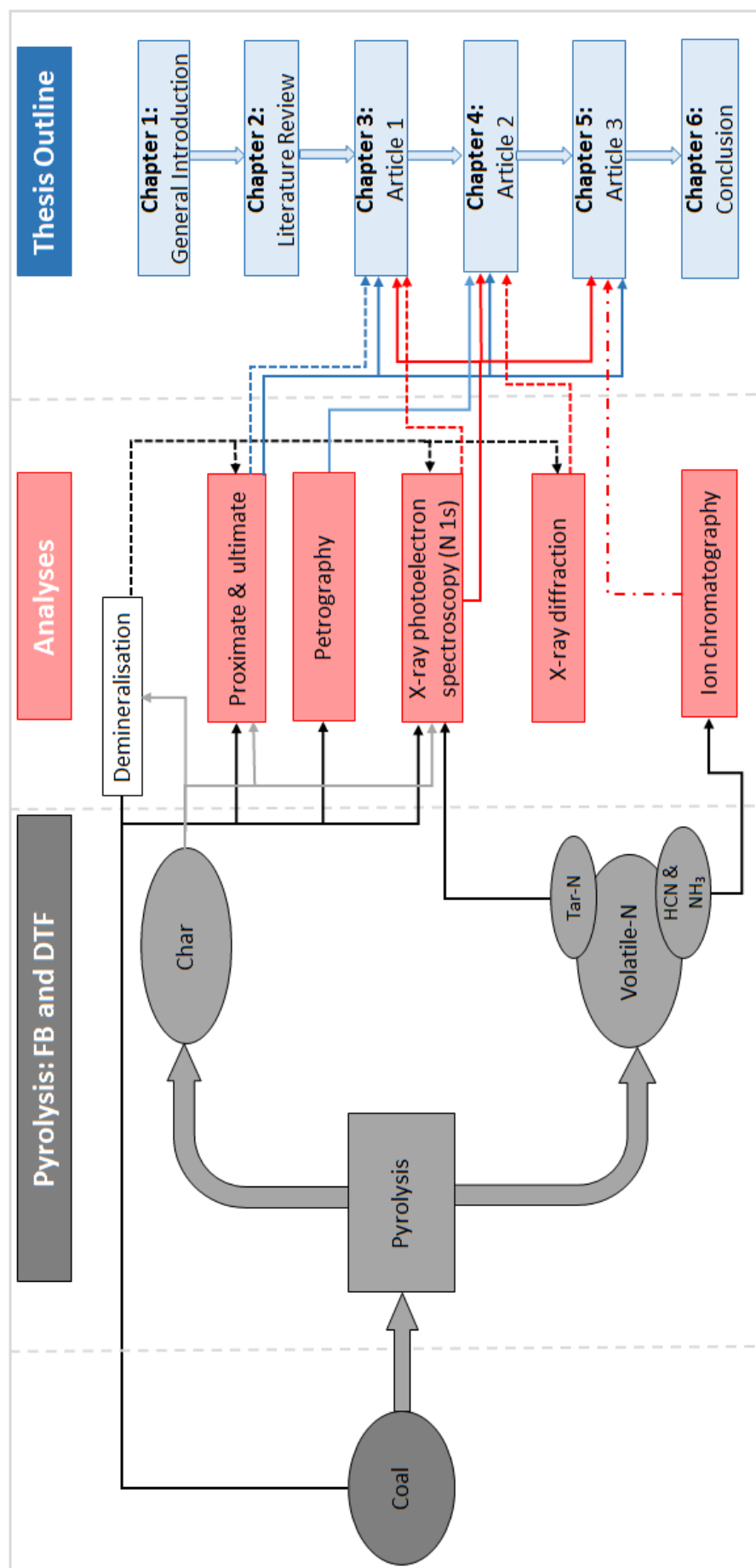


Figure 1.3: A flowchart illustrating the experimental route leading to the compilation of the thesis.

CHAPTER

2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the occurrence of nitrogen in coal, as well as the influence of coal properties on nitrogen transformation in chars, and the subsequent release of volatile nitrogenous species. The changes brought by pyrolysis and chemical treatment are also explored. The literature survey also covers carbon structural properties of coals, and the respective morphological changes that are brought by heat treatment. Focus is also directed towards the influence of chemical treatment on carbonaceous materials. The properties that make South African coals stand out are also discussed.

In an endeavour to determine the influence of coal chemical and physical properties on NO_x release, [Pohl et al. \(1982\)](#) obtained data from field and pilot scale tests that ascertained that fuel properties possessed a great influence on NO_x emissions from boilers. However, operation conditions and the type of reactor also play an essential function towards nitrogen release.

2.2 Coal Nitrogen

The majority of the organic constituent of coal is comprised of carbon, hydrogen and oxygen atomic components, whereas nitrogen and sulphur only make up a very small portion ([Glick and Davis, 1991](#); [Miller, 2005](#)). Proteins of plants and micro-organisms are the original source of nitrogen in coal. The subsequent coalification

process caused the proteins to undergo a series of transformation which resulted in the various nitrogen functional forms found in coal (Flaig, 1968). Generally, the nitrogen in most coals are in the range of 1–2% by weight (wt.%) (Glick and Davis, 1991; Niksa, 1995).

Rigby and Batts (1986) established that there was no orderly variation in nitrogen content with either rank or carbon content in the Australian coals that they studied. Nonetheless, other researchers observed systematic changes with coal rank. Boudou et al. (1984) studied more than 600 coal samples from the Mahakam Delta in Indonesia focusing on total nitrogen variation with coal rank. They noticed that the quantities of total nitrogen increased during the lignite and sub-bituminous coalification stages, subsequently followed by a decrease occurring during the bituminous stage. A significant loss of nitrogen was apparent in anthracites. Burchill and Welch (1989) pointed out that the increase in nitrogen in coals with the range of 80–85 wt.% carbon-content is attributed to loss of oxygen. Decarboxylation generally reaches completion at just over 80 wt.% C, of which any additional loss of oxygen involves dehydroxylation which would not change the C/N ratio substantially. For coals with carbon exceeding 80 wt.%, loss of hydrocarbons would be essential to account for the noticeable increase in nitrogen. Burchill (1987) and Kambara et al. (1993) also reported a similar observation in their findings. Carpenter et al. (2006) mentioned that despite coal nitrogen not being firmly dependent on rank, the O/N ratio appears to correlate with coal rank, while taking note that oxygen is usually calculated by difference.

2.2.1 Organic Nitrogen Structures

Investigations on coal and coal-derived substances have revealed that the organic nitrogen is bonded in stable heterocyclic aromatic structural forms (Davidson, 1994; Kambara et al., 1993; Knicker et al., 1995; Tsubouchi and Ohtsuka, 2008). Attar and Hendrickson (1982) observed that 50–75% of nitrogen in parent coals occurred in the form of pyridine and quinoline derivatives. Modern analytical techniques, principally based on XPS, illustrate that nitrogen in coal primarily exists in pyrrolic form. Elucidation of coal structural properties using XPS investigations have established that nitrogen occurs in heterocyclic aromatic structures, primarily as pyrrolic- (N-5), pyridinic- (N-6), quaternary- (N-Q), and to a smaller margin, if any, as protonated and/or oxidised pyridinic nitrogen (N-X) functional forms (García et al., 2004; Kapteijn et al., 1999; Kelemen et al., 1994, 1998; Leppälahti and Koljonen, 1995). Figure 2.1 shows a simplified schematic illustration of nitrogen functionalities (García et al., 2004). The proof for the presence of amines or anilines in coals still remains ambiguous. The likelihood is that they may be available in minute quantities, largely

in coals of low rank (Carpenter et al., 2006).

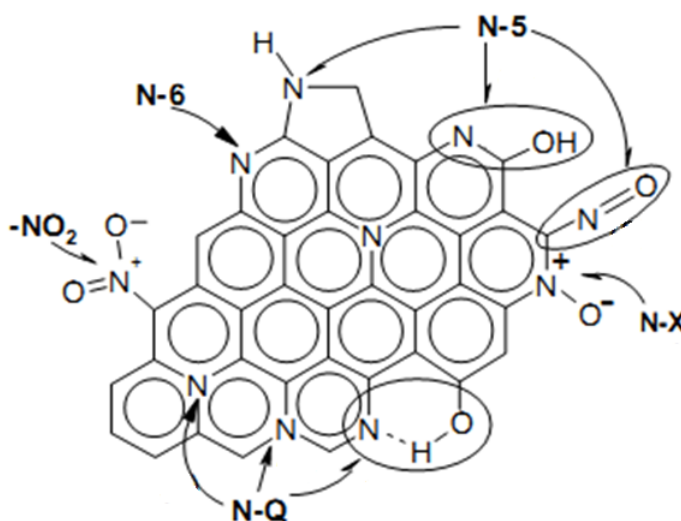


Figure 2.1: A simplified schematic illustration of heterocyclic nitrogen forms present in chars (García et al., 2004).

X-ray absorption near-edge spectroscopy (XANES) (Mitra-Kirtley et al., 1993a,b; Mullins et al., 1993; Zhu et al., 1997), X-ray photoelectron spectroscopy (XPS) (Burchill and Welch, 1989; Kelemen et al., 1994; Pels et al., 1995; Valentim et al., 2011) and, to a smaller extent, ^{15}N solid state nuclear magnetic resonance (ss NMR) (Kelemen et al., 2002; Knicker et al., 1995, 1996; Solum et al., 1997) studies have showed that the predominant nitrogen form in fresh parent coal is N-5, followed by N-6 which tends to increase slightly with coal rank (Thomas, 1997). In fresh coals, N-Q is usually the least, but increases substantially in chars with severity of pyrolysis temperature (Glarborg et al., 2003; Kelemen et al., 1998; Valentim et al., 2011).

Kelemen et al. (1994) observed a decreasing level of N-Q forms along with increasing levels of N-6 with increasing coal rank. Pels et al. (1995) observed that the moieties of nitrogen functionalities changed when coals were put through increasing pyrolysis intensity. Mild pyrolysis of the initially unstable nitrogen functional forms such as the nitro-type complexes in the form of pyridones, protonated pyridinic nitrogen, and nitrogen oxides of pyridinic nitrogen (N-X) are transformed into N-6. They also reported that N-5 was also converted into N-6 due to condensing carbon matrix occurring during pyrolysis. Kelemen et al. (1998) pointed out that before hydrocarbon devolatilisation occurs, quaternary species present in parent coals are lost during mild pyrolysis. These are quaternary species perceived to be associated with hydroxyl groups linked to carboxylic acids or phenols. Kelemen et al. (1998) further reported that severely pyrolysed chars mainly constituted of N-6 and N-Q. At 800 °C, N-5

is converted to N-Q, N-6 and N-X (Jacobson et al., 1958; Patterson and Drenchko, 1962). At temperatures exceeding 450 °C, it is speculated that N-6 is transformed to N-Q through condensation reactions (Pels et al., 1995). The condensation reactions are schematically represented in Figure 2.2. Pels et al. (1995) arrived at a general

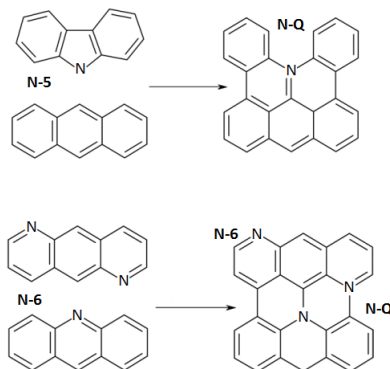


Figure 2.2: Schematic illustration of N-5 and N-6 condensation reactions occurring during pyrolysis.

conclusion that severe pyrolysis cause nitrogen to be in 6-membered rings (N-Q, N-6 and N-X). The fate of nitrogen bound in carbonaceous substances during pyrolysis is shown in Figure 2.3. The transformation of nitrogen functional forms is illustrated in relation to severity of pyrolysis conditions.

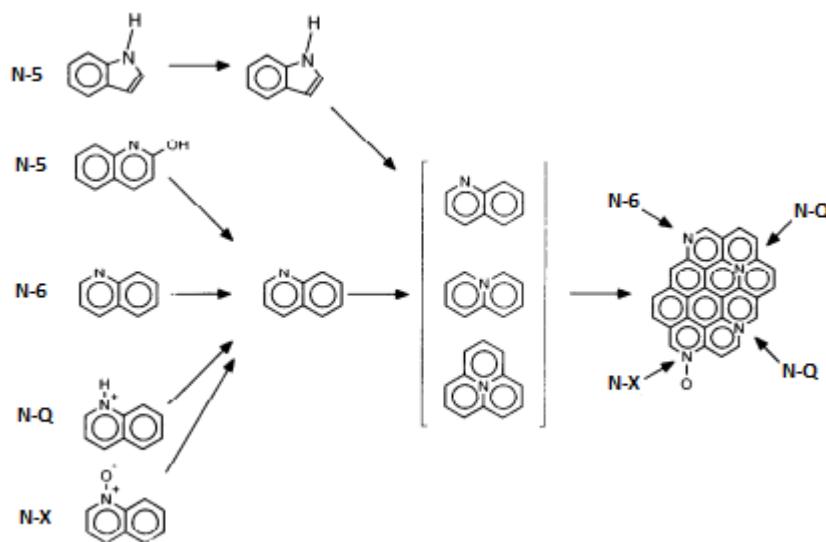


Figure 2.3: Schematic representation of nitrogen functional forms transformation during pyrolysis (Pels et al., 1995).

2.2.2 Inorganic Nitrogen Structures

It is generally agreed that nitrogen exclusively exists in organic form (Burchill and Welch, 1989). This is valid for most coals. However, some inorganic nitrogen may be present as ammonium-rich illite (clay) in semi-anthracite or higher rank coals, of which the amount increases with rank (Buckley, 1994; Dai et al., 2012; Daniels and Altaner, 1990, 1993; Ward and Christie, 1994). The reaction of kaolinite at high temperatures (200 °C) is considered the probable mineral source of NH_4 -illite, attributable to anthracite formation during coalification. Daniels and Altaner (1990, 1993) observed that kaolinite content of the investigated samples decreased as the coal rank increased, and as much as 20% of nitrogen in some samples were obtained in illite interlayers. Nonetheless, the supposition that nitrogen is organic in entirety remains firm for low rank coals. Daniels and Altaner (1993) ascertained that NH_4 -bearing illite authigenesis is exclusively associated with the late-stage coalification process.

2.3 Nitrogen Release

The initial phase of coal nitrogen conversion to nitrogen oxides involves the evolution of coal nitrogen during the first few milliseconds heating stage (Phong-Anant et al., 1985). During devolatilisation, thermal decomposition takes precedence, resulting in the evolution of tar and light gases (Serio et al., 1987). This process is characterised by physical and chemical changes which usually entail the particle becoming plastic then re-hardening (Smith, 1982). Bunt and Waanders (2008) stated that subjecting coal to heat in an inert environment causes the coal to undergo some sort of de-polymerisation reaction resulting in the emergence of a meta-stable intermediate product. The de-polymerisation might be due to the breakage or cleavage of the methylene ($-\text{CH}_2-$) or ether bonds ($-\text{O}-$) between aromatic clusters resulting in the formation of free radical species. The collusion of the free radical components or rearrangement of atoms within a free radical component results in the formation of a stable structure in the form of volatiles (light gases and tar) or depending on vapour pressure they remain as part of the residual char (Elliot, 1981).

In most combustion systems, coal is injected into a hot region. A portion of nitrogen contained in coal is emitted as nitrogenous volatile species (volatile-N) upon rapid heating within an extremely short period (Glarborg et al., 2003; Johnsson, 1994; Wu, 2005). Volatile-N product distribution consists of tar-N (nitrogen in tar), HCN, NH_3 and N_2 (Bassilakis et al., 1993; Kambara et al., 1993; Kidena et al., 2000; Niksa, 1995; Wu et al., 2003). The volatiles, incorporating volatile N are consumed in the flames, and the efficiency of N conversion to NO (with the exception of N_2) is de-

pendent on stoichiometry (Carpenter et al., 2006). Tar is an important intermediate in the evolution process of volatile nitrogen (Kambara et al., 1993). Successive oxidation of released nitrogenous volatile species by O_2 in air results in evolution of nitrogen oxide pollutants in the form of NO_x and N_2O . Almost all the NO_x and N_2O released from fluidised bed combustion emanate from coal-N in entirety (Takeshita et al., 1993; Wójtowicz et al., 1993), while more than 80% of total NO_x emitted from pulverised coal combustion come from coal-N (Boardman and Smoot, 1993; Hjalmarsson, 1990; Tsubouchi and Ohtsuka, 2008; Unsworth et al., 1991). Pohl et al. (1982) made stated that data were not available at the time to ascertain that the partitioning of fuel nitrogen between the char and the volatile matter influenced the release of NO_x . Regardless, considerable evidence supported this rationale, while limited evidence contradicted the hypothesis. Eddings et al. (1994) and Smith et al. (1993) came to a conclusion that a model that is solely based on fuel nitrogen content largely possessed shortcomings. The model assumed that all fuel-N is released as HCN in quantities that are in proportion to the parent coal nitrogen. The model was insufficient due to its inability to distinguish nitrogen that is partitioned into light gases, tars and chars. Fuel-rich conditions promote the formation of N_2 , which forms the basis for air-staging techniques and is applied in low- NO_x burner designs (Nelson et al., 1996). The quantity of volatile matter released during devolatilisation is mainly influenced by coal type, pyrolysis conditions and particle size (Kambara et al., 1993; Kidena et al., 2000; Kobayashi, 1976; Takagi et al., 1999). Previous studies have demonstrated that the quantity of volatile nitrogen liberated is dependent on temperature (Kambara et al., 1993). In a gasification review, Leppälahti and Koljonen (1995) stated that regardless of fuel type, more NH_3 tend to be produced in comparison to other nitrogenous species, and that the NH_3 in the volatile stream appears to be largely reliant on nitrogen content.

2.3.1 Conditions Influencing N Release

The evolution of nitrogenous species in the course of coal combustion occurs in two stages (Johnsson, 1994); the first stage constitutes the release of light gases and tar in the volatile stream during devolatilisation. This is subsequently followed by the combustion of light gases and tar in the presence of oxygen, wherein the nitrogenous species may be oxidised to various nitrogen oxides; NO , N_2O or NO_2 , and/or reduced to N_2 depending on combustion conditions. The second stage of nitrogen release takes place as the char burns and nitrogen in the char is oxidised to nitrogen oxides.

HCN and NH_3 are intermediately formed during combustion and have been identified as the two main precursors of nitrogen oxides in quite a number of studies (Chang et al., 2003; Dagaut et al., 2008; Deng et al., 2013; Hämäläinen and Aho,

1996; Johnsson, 1994; Ledesma et al., 1998; Leppälahti and Koljonen, 1995; Li and Tan, 2000; Nelson et al., 1991; Tan and Li, 2000a,b; Tian et al., 2002, 2005; Xie et al., 2001). The ratio of HCN to NH_3 released is dependent upon several parameters; which include heating rate, residence time, chemical structures present in the coal and the nature of the coal (Aho et al., 1993; Chang et al., 2005; Chang et al., 2004, 2003; Glarborg et al., 2003; Hämäläinen et al., 1994; Leppälahti, 1995; Leppälahti and Koljonen, 1995; Niksa, 1995). A review by Leppälahti and Koljonen (1995) echoed that the formation of HCN is favoured by conditions that include elevated heating rates as well as temperatures that exceed 725 °C. In addition, the coal properties that promote HCN liberation include high coal rank (high proportion of nitrogen is bonded to aromatic structures), together with raised equivalence ratios. On the other hand, low rank coal, which is related to a large proportion of coal-N that is bonded to amine structures, as well as elevated pressure, together with extended secondary reactions duration tend to favour the formation of NH_3 .

A lot of research has been done to understand the chemistry that leads to the evolution of HCN, NH_3 , tar-N, and char-N as the major precursors of NO_x and N_2O (Axworthy et al., 1978; Bassilakis et al., 1993; Baumann and Möller, 1991; Kambara et al., 1993; Nelson et al., 1991; Phong-Anant et al., 1985; Solomon and Colket, 1978; Tsubouchi and Ohtsuka, 2008). However, more studies are required to further elucidate the coal-N chemistry in an endeavour to meet the emerging more stringent regulations, and so as to ultimately achieve zero emissions in coal usage. Solomon and Colket (1978) conducted pyrolysis with a wire mesh heater at a slow heating rate (600 °C/s) and a solid residence time of 80 s. At temperatures less than 350 °C, more than 80% of coal-N was retained in the chars, while the remainder was released as tar-N in heterocyclic forms (Nelson et al., 1991; Solomon and Colket, 1978; Zhang and Fletcher, 2001). Increasing the temperature to 500 °C caused an increase in tar-N and a subsequent concomitant decrease in char-N. The reported increase in tar-N and the reduction in char-N within the specified temperature range almost remained unchanged, implying that coal-N is released primarily as tar-N during primary pyrolysis. However, minute quantities of other nitrogenous volatile species in the form of NH_3 and HCN may also be produced (Johnsson, 1994; Li, 2004). Raising the temperature from 500 °C to 900 °C did not alter the release of tar-N significantly, nonetheless, an appreciable decrease in char-N yield was witnessed. The obtained results suggest the release of other nitrogenous volatile species other than tar-N and char-N.

Chen et al. (1992) carried out pyrolysis of a subbituminous coal at a rapid heating rate at 690 °C and established that approximately 80% of coal-N was converted to tar-N and char-N. Their results correlated to those obtained by Solomon and Colket

(1978) at 700 °C. Concomitantly, a marked increase in HCN with temperature was witnessed, nonetheless, they reported that no measurable NH_3 could be detected. [Chen et al. \(1992\)](#) also observed a similar trend on rapid pyrolysis of a bituminous coal. The increase in HCN yield at 690–1060 °C was comparable to the magnitude of the declining sum of tar-N and char-N. [Tsubouchi and Ohtsuka \(2008\)](#) pointed out that this observation strongly suggests that the formed HCN emanates from both tar-N and char-N. [Li and Tan \(2000\)](#) reported that the yields of NH_3 and HCN are altered significantly when coal is pyrolysed in fluidised bed. They highlighted that more HCN was produced at higher temperatures. NH_3 also displayed an increasing trend, reaching a maximum at about 800–850 °C, followed by a decline as temperature increased. [Chen et al. \(1992\)](#) observed that yields of HCN at 1000 °C were ranged between 10% and 20%, which is much lower than the yields at 1060 °C which stood at 40%. During rapid heating rate, about 20–65% HCN yields were reported within the same temperature range ([Kambara et al., 1993](#)). This variation implies that a portion of the released HCN is converted into other gaseous nitrogenous species that incorporate NH_3 and N_2 ([Tsubouchi and Ohtsuka, 2008](#)). Figure 2.4 shows the formation of HCN from the thermal cracking of N-6, while a plausible mechanism for formation of NH_3 is highlighted by the presence of $\text{H}\cdot$ radicals.

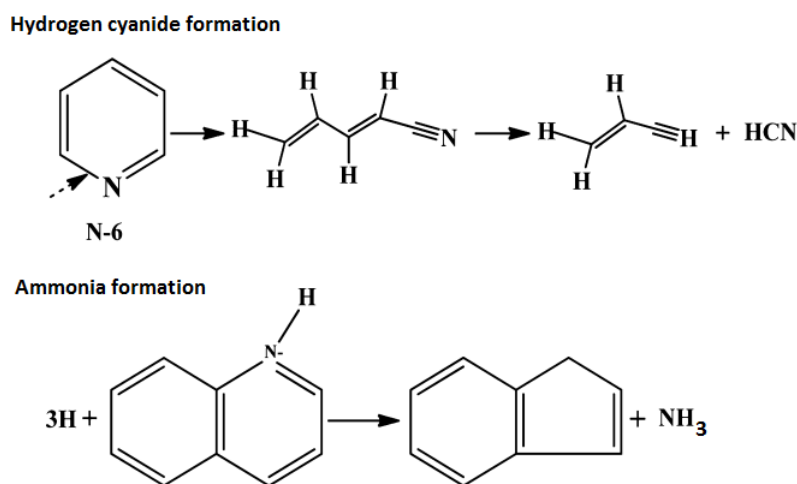


Figure 2.4: Plausible HCN and NH_3 formation reaction paths during pyrolysis ([Wei et al., 2015](#)).

The conversion of nitrogen in coal to NH_3 is necessitated by hydrogen ([Li and Tan, 2000](#)). There is quite a number of theories in literature pertaining to the mechanisms of the formation of NH_3 during pyrolysis ([Bassilakis et al., 1993](#); [Baumann and Möller, 1991](#); [Kambara et al., 1993](#)). The hypotheses appear to be contradictory and seem not to explain the experimental data adequately ([Li, 2004](#); [Li and Nelson, 1996](#);

Li et al., 1996; Li and Tan, 2000). The factors determining whether the release of HCN becomes predominant over NH_3 , or the other way round, are still not clear and require further analysis and exploration. In addition, the role played by free radicals during coal pyrolysis towards nitrogen release is also still obscure (Li et al., 1998; Li et al., 1996).

Considerable pyrolysis studies have been conducted on simple N-containing model compounds with the hope of understanding parallel reactions occurring during the pyrolysis of complex heterogeneous coal (Axworthy et al., 1978; Deng et al., 2013; Doughty and Mackie, 1992; Hämäläinen et al., 1994; Kapteijn et al., 1999; Kelemen et al., 1994, 1998; Lifshitz et al., 1989; Pels et al., 1995; Solum et al., 2001; Stańczyk et al., 1995). Typical examples are illustrated by Mackie et al. (1990, 1991), who conducted pyrolysis of pyrrole and pyridine in shock-tube reactors in which the released HCN was the major N-containing volatile component formed, while NH_3 was not detected. However, Axworthy et al. (1978) performed pyrolysis of pyridine in a quartz capillary reactor which resulted in substantial NH_3 being formed. Furthermore, Sugiyama et al. (1978) carried out pyrolysis of pyridine in a tube reactor and showed that NH_3 was the main volatile-N species formed. In other demonstrations (Doughty and Mackie, 1992, 1994; Doughty et al., 1994; Mackie et al., 1990, 1991; Terentis et al., 1992), pyrolysis of low concentrated pyrrole, pyridine, 2-picoline, and butenenitriles in shock-tube reactors resulted in insignificant formation of NH_3 as N-containing species. Nonetheless, pyrolysis of high concentrated pyridine and benzonitrile by Axworthy et al. (1978) carried out in a quartz capillary reactor released a significant proportion of NH_3 . The availability of hydrogen rich condensed carbonaceous material is a favourable condition needed for the formation of NH_3 during pyrolysis of the mentioned model compounds (Li and Tan, 2000). Sugiyama et al. (1978) reported that the presence of carbonaceous materials, such as soot, which catalyse the additional formation of further carbonaceous materials, enhances the formation of NH_3 from pyridine pyrolysis at 680 °C.

Li and Nelson (1996) reported that model compounds begin to decompose at around 800 °C under conditions similar to those in a fluidised bed pyrolysis. The thermal cracking temperature seemed to correlate to that for N-containing heterocyclic volatile species released during coal pyrolysis (Li and Tan, 2000). Thermal cracking of N-containing tars released from pyrolysis of a bituminous coal were studied by Li et al. (1998). Decomposition of tar samples was conducted at different temperatures using XPS. The results obtained from XPS revealed that nitrile functional groups were neither existing in raw coal nor in tars released at temperatures below 700 °C. However, the nitrile groups started to emerge as the temperature increased to 700–800 °C. The generation of nitrile functional groups signifies the tearing apart of

N-containing heterocyclic rings. The nitrile groups are the intermediates towards the formation of HCN (Axworthy et al., 1978; Doughty and Mackie, 1992, 1994; Doughty et al., 1994; Ikeda et al., 2000; Lifshitz et al., 1993, 1989; Mackie et al., 1990, 1991; Terentis et al., 1992). The findings of these researchers were confirmed by Li et al. (1998) who illustrated through XPS that the concentration of nitrile groups increased with temperature. Li et al. (1998) alluded that there was no convincing evidence pointing at the presence of amines in tar samples. The production of nitrile intermediates in gas phase is crucial during the decomposition of heterocyclic N-containing species towards the formation of HCN (Li and Tan, 2000). Ledesma et al. (1998) and Li et al. (1998) investigated the thermal cracking products of coal pyrolysis in a fluidised bed reactor that was connected in-line with a plug-flow reactor. The results showed that HCN was the main nitrogen containing component in the gas phase, even though the total concentration of N-containing species was quite low. The formation of HCN also began in the range of 700 °C to 800 °C. Nonetheless, trace amounts of NH₃ were reported as well.

The discussion above suggests that it is highly unlikely to generate NH₃ from pyrolysis of model compounds containing pyrrole or pyridinic heterocyclic structures. Nevertheless, the pyrolysis of coal and biomass yields substantial quantities of NH₃. This implies that the formation of HCN and NH₃ from pyrolysis of solid fuels underwent different mechanisms to that of pyrolysis of model compounds in gas phase (Aho et al., 1993; Jones et al., 1999; Kambara et al., 1995, 1993; Li, 2004; Li and Nelson, 1996; Li et al., 1996; Li and Tan, 2000; Schäfer and Bonn, 2000, 2002; Stańczyk, 1999; Tan and Li, 2000a,b; Yuan et al., 2012). The most likely explanation for the formation of NH₃ from pyrolysis of solid fuels is that it emanates from the direct and/or indirect hydrogenation of the nitrogen contained in heterocyclic structures. Experimental results presented by Tan and Li (2000b) which illustrated that the indirect path occurred via heterogeneous hydrogenation on the char surface (Bassilakis et al., 1993) or via homogeneous hydrogenation of HCN in the gaseous phase (Baumann and Möller, 1991), is a very unlikely rationale for the witnessed yields of NH₃ emanating from pyrolysis of inherently hydrogen rich brown coal. The hydrogenation chances of HCN are much less on the char surface to be considered as a primary path for the formation of NH₃ during pyrolysis of high rank coals. Therefore, direct hydrogenation of nitrogen that is contained in coal/char undergoing pyrolysis is regarded as the primary path for NH₃ formation (Li and Tan, 2000; Schäfer and Bonn, 2000, 2002). The hydrogen that leads to hydrogenation is generated in-situ during thermal cracking reactions which occur during pyrolysis of the solid fuels. The generation of hydrogen may occur through the breaking off of hydro-aromatic structures, dehydrogenation of aliphatic structures, or condensation taking place be-

tween aromatic structures. The $\text{H}\cdot$ radicals produced in-situ subsequently react with the N-containing heterocyclic species, resulting in the initial activation of the cyclic structure (Li and Tan, 2000). The $\text{H}\cdot$ is perceived to be much more active in initiating the shattering of the N-containing heterocyclic structures compared to other radicals such as $\cdot\text{CH}_3$ (Li et al., 1998; Li and Nelson, 1996). The sequence continues with the $\text{H}\cdot$ radical migrating to the nitrogen containing sites, leading to the hydrogenation of the N site and subsequent release of NH_3 .

2.3.2 Influence of Metal Cations on N Release

The inherent alkali, alkaline earth and transition metal cations in coal can catalyse the devolatilisation of coal-N into volatile-N (Deng et al., 2013; Tsubouchi, 2014; Tsubouchi et al., 2003a; Tsubouchi and Ohtsuka, 2002a,b, 2008; Tsubouchi et al., 2003b; Tyler and Schafer, 1980). Subsequently, the metal cations influence the distribution of volatile-N into tar-N, NH_3 , HCN and N_2 (Hayashi et al., 1995; Ohtsuka et al., 1997; Wu et al., 2000, 2003). Bituminous coals contain appreciable amounts of Ca, Fe, Mg, K, and Na cations in ion exchange forms (Brockway et al., 1991; Hüttinger and Michenfelder, 1987; Tsubouchi and Ohtsuka, 2008). It has been found that char-N is the primary origin of N_2 , and the process is catalysed by Fe, Ca and Na cations (Mori et al., 1996; Ohtsuka et al., 1994; Tsubouchi et al., 2001; Tsubouchi and Ohtsuka, 2002a, 2008). Pronounced conversion of char-N to N_2 during pyrolysis of coal might result in substantial reduction of NO_x and N_2O emissions (Tsubouchi and Ohtsuka, 2008).

Several studies have been conducted to determine the influence of inherent minerals on the release and distribution of volatile-N species through acid demineralisation and subsequent doping of specific metal additives. Friebe and Köpsel (1999) demonstrated the effect of demineralisation on the release of NH_3 and HCN emanating from pyrolysis of a German brown coal. They reported that the emission of HCN began at 400 °C and it was the primary gaseous nitrogen product during the pyrolysis of raw coal at temperatures less than 600 °C. However, the release of NH_3 only started at 500 °C and became the predominant volatile-N species at temperatures exceeding 600 °C. The observed results imply that the formation of NH_3 occurs through secondary pyrolysis involving hydrogenation of HCN. The acid demineralisation process reduces the minerals in coal substantially, and that altered the HCN and NH_3 release patterns significantly. HCN became the major product within the temperature range of 400 °C to 800 °C and was appreciably higher than that released by raw coal. However, the release of NH_3 only began at 700 °C and the yield was much less than HCN.

Wu and Ohtsuka (1997) and Tsubouchi and Ohtsuka (2008) reported on the in-

fluence of demineralisation and the successive doping of Ca or Fe on the distribution of HCN, NH₃ and tar-N released during pyrolysis of low rank coals in a fixed bed reactor at 1000 °C and a heating rate of 400 °C/s. Pyrolysis of almost all the raw coal released NH₃ as the major volatile-N species, followed by tar-N and HCN, respectively. An analogous pattern for volatile-N components was also witnessed by [Tsubouchi and Ohtsuka \(2002b\)](#) during pyrolysis of 10 coals at 1350 °C and 400 °C/s in a fixed bed reactor. An apparent reduction of NH₃, and a noticeable increase in HCN and tar-N were observed due to the reduction of minerals caused by acid demineralisation. The doping of 1% (mass, dry) Fe³⁺ ions by [Wu and Ohtsuka \(1997\)](#) to a demineralised coal produced an apparent reduction in NH₃, tar-N and HCN, resulting in an increase in the yield of N₂. These findings imply that Fe cations that are naturally contained in coals have a catalytic effect on the breakdown of nitrogenous volatile species to N₂. Addition of 3% (mass, dry) Ca²⁺ ions to demineralised coals resulted in a pronounced increase in NH₃, as well as a decrease in HCN and tar-N. The doping of Ca²⁺ ions into demineralised coals produced a distribution of volatile-N species that is similar to that of raw coals. The same was also witnessed during pyrolysis of demineralised coals that were doped with smaller amounts of Ca cations (0.5–1%). This suggests that minute quantities of inherent Ca in coals can promote the formation of NH₃ from HCN and tar-N.

Further pyrolysis conducted in a fixed bed at temperatures exceeding 1000 °C, doping of Ca²⁺ ions into a demineralised Chinese lignite coal resulted in a steady increase of NH₃ yield with increasing temperature, despite the fact that tar-N and HCN yields did not change appreciably ([Tsubouchi and Ohtsuka, 2002a](#)). However, pyrolysis of the demineralised counterpart at 1000–1350 °C produced volatile-N species that remained almost constant. The obtained results indicate that the Ca²⁺ cations that are inherently present in coal do play a role of catalysing the formation of NH₃ from the nitrogen in chars.

Quite a number of researchers ([Baumann and Möller, 1991](#); [Freihaut et al., 1982](#); [Kambara et al., 1993](#); [Kidena et al., 2000](#); [Phong-Anant et al., 1985](#); [Tsubouchi, 2014](#); [Tsubouchi and Ohtsuka, 2002b](#)), have reported the substantial release of N₂ emanating from coal pyrolysis. Some researchers have not paid much attention to the evolution N₂ from coal pyrolysis since it is not a precursor of nitrogen oxides (NO_x and N₂O) originating from fuel nitrogen. Nonetheless, [Tsubouchi and Ohtsuka \(2008\)](#) highlighted the need to focus on the release of N₂; the effective conversion of char-N and volatile-N to N₂ will substantially reduce the levels of fuel NO_x and N₂O. [Tsubouchi \(2014\)](#) pointed out that small quantities of inherent Ca and Fe seemed to enhance the formation of N₂ from devolatilised char-N. Tsubouchi and co-workers ([Tsubouchi et al., 2001](#); [Tsubouchi and Ohtsuka, 2002a,b](#)) also demonstrated that

Ca^{2+} ions doped in low rank coals promoted the formation of N_2 from char-N during pyrolysis of coals at temperatures exceeding $1000\text{ }^\circ\text{C}$, regardless of the heating rate.

Nonetheless, there has been limited information on the influence of these metal cations emanating from typical high-mineral matter South African coals. SA coals are characterised by high mineral matter content, and the majority are also rich in inertinites. The respective substantial quantities of inherent minerals that are present in SA coals play a vital role towards the partitioning of coal-N as projected and corroborated in open literature. A closer look at the nitrogen product distribution from a pyrolysis experiment at $1300\text{ }^\circ\text{C}$ by [Tsubouchi \(2014\)](#), shows that coals (BR and LP) with the least ash content (both 3.1%) emitted the most HCN (approximately 15% and 12%, respectively), followed by coal IL which contained 9.0% ash and subsequently released about 10% HCN, while coal OM possessing the highest ash content (13.3%) released the least amount of HCN ($\approx 8\%$). Under similar experimental conditions ($10^4 - 10^5\text{ }^\circ\text{C/s}$, $1300\text{ }^\circ\text{C}$), [Tsubouchi et al. \(2003a\)](#) earlier reported that coal AD containing 1.4% ash released $\approx 15\%$ HCN, while coal ZN with 4.0% ash released a comparatively low yield of about 10%. The apparent trend highlights that HCN yields decrease with increasing ash content. The ash content of most of the SA coals ranges from around 20% to 40%, therefore the influence of the inherent minerals is expected to be quite significant as well. For example, applying projections and postulations based on results reported by [Tsubouchi \(2014\)](#) and [Tsubouchi et al. \(2003a\)](#), it may be expected that SA coals release much less HCN, depreciated char-N, and much more N_2 at high temperatures.

2.4 Char Nitrogen

After the release of nitrogen into the volatile stream, a fraction of the coal-N remains in the char matrix as char-N ([Bassilakis et al., 1993](#); [Kambara et al., 1993](#); [Niksa, 1995](#)). [Kelemen et al. \(1998\)](#) reported that the char and tar produced upon devolatilisation contained predominantly N-5 and N-6 functional forms. They also observed that a fraction of N-Q that was initially present in trace amounts in coal appeared significantly in the char and tar. Through a series of rapid pyrolysis investigations involving 20 coals, [Kambara et al. \(1993\)](#) observed that quaternary nitrogen is finally converted to NH_3 and some fraction of pyrrolic and pyridinic nitrogen is converted to HCN.

[Zhang et al. \(2013\)](#) stated that pyrolysis induced the conversion of N-5 to N-Q and N-6, whereby slow heating rates favoured the formation of quaternary nitrogen, whereas the fast heating rate tended to result in relatively high pyridinic nitrogen content in char. This evolution of organic nitrogen speciation is analogous to meta-

morphism, as described by [Boudou et al. \(2008\)](#), who stated that the relative amount of nitrogen replacing carbon in condensed, as well as partly aromatic structures, by which nitrogen is covalently bonded to three carbon atoms (N-Q) exhibits exponential increments with developing metamorphic grade.

2.5 Coal and Char Structure

Characterisation techniques are analytical methods that are used to measure particular physical and chemical characteristics. The composition of coal and its respective products has a determining effect on their properties which influences the efficiency of utilisation. In this study, several characterisation techniques were employed for structural elucidation of coal and the respective chars, encompassing physical and chemical analyses, petrographic analysis, X-ray photoelectron spectroscopy (XPS), solid-state nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and X-ray fluorescence (XRF). The analytical techniques are primarily based on coal parameters which have been predefined by the authorities of internationally recognised organisations for standardisation, such as the International Organisation for Standardisation (ISO) or the American Society for Testing and Materials (ASTM). Characterisation of coal provides information that assists in the prediction of behaviour of coal utilisation processes like pyrolysis, combustion or gasification.

Coal attributes that are used to establish the grade of coal include the behaviour of ash at high temperatures, sulphur content, and the amount of trace elements. However, formal classification systems entailing grade of coal have not been developed. The coal grade is a very crucial attribute for determining coal feed stock for power plants. Volatile matter, carbon and hydrogen content are usually used in the classification of coals.

2.5.1 Conventional Chemical Analyses

Proximate and ultimate analyses of coal provide valuable information incorporating specific energy, fixed carbon, ash (inert portion), moisture, volatile matter, and elementary constituents ([Speight, 2012, 2015](#)).

2.5.1.1 Proximate Analysis

Proximate analysis is conducted to establish the quantities of total moisture, inherent moisture, volatile matter, ash, and fixed carbon. The quantity of moisture in coal gives an indication of the drying needed in the handling and pulverising sections of the boiler coal feeding system ([Miller and Tillman, 2008](#)). Volatile matter content is

deduced from the fraction that is released as gas or vapour form, with the exclusion of moisture. Volatile matter principally comprises oxygen, hydrogen, carbon monoxide, methane, other hydrocarbons, and the fraction of moisture that is generated by chemical reaction during coal thermal decomposition. Volatile matter is also utilised as a determining factor of the ease of coal ignition, as well as an indication on whether supplemental fuel will be required for flame stabilisation. Volatile matter content is also used as the basis for buying and selling of coal. Ash is principally generated from mineral matter during coal combustion, and the ash results are generically lower than that of the source minerals. The quantity of mineral matter in coal is often utilised as a measure for determining coal quality. The ash content influences the optimum load in the operation of the collection system of boiler bottom ash and fly ash. The ash content is also used as a yardstick for the evaluation of shipping and handling charges (Miller and Tillman, 2008). Fixed carbon is the remaining carbonaceous residue resulting from the driving off of volatile matter. Hence it is deduced by difference through the subtraction of the sum of moisture, ash and volatiles. Fixed carbon can be utilised as a guide towards the choice of fuel-firing equipment.

2.5.1.2 Ultimate Analysis

The proportions of elemental constituents of the organic portion that encompass carbon, hydrogen, nitrogen, oxygen, and sulphur are determined through ultimate analysis by standard laboratory methods (ASTM D3176-15, 2015; ISO 29541, 2010). Oxygen is determined by difference due to the complexity of analysing oxygen directly. For that reason, the calculated value for oxygen embodies the cumulative errors emanating from analysis of other elements. The ultimate analysis may be utilised in conjunction with the calorific value of coal to carry out combustion calculations that include the determination of coal feed rates, combustion air requirements, and weight of products of combustion to determine fan sizes, boiler performance, and sulfur emissions (Miller and Tillman, 2008).

2.5.2 Coal Petrology

Coal petrology relates to the analysis of coal, including interpretation of obtained data to provide meaningful information concerning organic composition, extent of maturation, and the linkage of the organic matter and minerals that are contained in coal (du Cann, 2012). Macerals are microscopically distinct organic components of coal which are analogous to minerals in inorganic rocks. The word “maceral” was first coined by Stopes (1935), due to the analogous or parallel nature of macerals to minerals in rocks. At a later stage, Spackman (1958) gave a revised definition of a

maceral as “an organic substance, or optically homogeneous aggregates of organic substances, possessing distinctive physical and chemical properties, and occurring naturally in the sedimentary, metamorphic, and igneous materials of the earth”.

Coals may be classified in accordance to basic and autonomous parameters which include organic composition, rank, as well as grade (du Cann, 2012). The organic composition primarily relates to three major maceral groups which are identified as vitrinite, liptinite, and inertinite. Vitrinite and liptinite are reactive macerals and play a very important role during combustion compared to inertinite (Kizgut and Yilmaz, 2003; Su et al., 2001). However, this phenomenon cannot be generalised for coals of different origin, inertinite in Gondwana coals tends to behave differently (Borrego et al., 1997; Choudhury et al., 2007; Diessel, 1983; Oka et al., 1987). The Gondwana coals can contain substantial amounts of reactive semifusinite together with the inertodetrinite which are reactive sub-macerals of inertinite. The rank of coal is considered to be the extent of maturation of coal. Coals are categorised in decreasing order of rank as anthracites, bituminous coals, sub-bituminous coals, and lignites, respectively. The position of a coal in the coalification sequence from brown coal (low rank) to anthracite (high rank) can be directly determined by reflectance analysis. Coal rank, which is a measure of degree of maturity, is based on vitrinite random reflectance. Coal grade generally relates to the presence of impurities, which is conveniently associated with the ash content.

Gondwana coals belong to the Permian age to a large extent, and are ranked as bituminous coals, with limited occurrence of anthracites (Cai and Kandiyoti, 1995; Cairncross, 2001). This explains the similarities among Southern Africa coals and those in the domains which were part of Gondwana (Cai and Kandiyoti, 1995; Falcon and Ham, 1988). The coals are generally known for having a large portion of minerals, as well as the dominance of the inertinite maceral (Cadle et al., 1993; Cairncross, 2001). On the other hand, Laurasian coals of the Carboniferous age typically constitute of an appreciable portion of vitrinite along with a minimal mineral matter content (Snyman and Botha, 1993). A great part of South Africa contains coals of the Permian age and a small Molteno region with Tertiary age coals. SA coals are typically rich in inertinites as well as contain high mineral matter content.

2.5.3 Advanced Characterisation

Carbonaceous substances such as coal and char are non-hydrolysable. Therefore, wet chemistry methods cannot be utilised to determine nitrogen forms as when applied to hydrolysable substances for the determination of amino acids, amino sugars and other related nitrogen containing biomolecules like uric acid, chlorophyll phospholipid-amines (Valentim et al., 2011). Coal has been analysed using destruc-

tive techniques and non-destructive methods such as spectroscopic techniques. Modern analytical techniques such as XPS, XANES, XRD and ss NMR have been used to study nitrogen as well as the carbon structural properties in coal and/or char. These characterisation techniques have been employed to identify and in some instances to quantify these nitrogenous compounds in non-volatile complex solids and carbonaceous systems (Genetti and Fletcher, 1999).

2.5.3.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), which is conjointly referred to as electron spectroscopy for chemical analysis (ESCA), is a surface analytical method which is widely used to examine both elemental and chemical composition of the outermost surfaces (Moulder et al., 1992). The analysis gives information about the position of the energy levels of the outermost atomic layers of a solid substance (Frost and Kloprogge, 2008; Wagner et al., 1979). It entails measurement of kinetic energies of core and valence electrons normally photo-emitted from a sample when irradiated by soft X-rays (Mg $K\alpha$ or Al $K\alpha$ is often used) in a vacuum system of less than 1×10^5 Pa (Moulder et al., 1992; Wagner et al., 1979). Photons with a particular energy are collided with an atom, molecule or solid substance. The photons then cause one of the electrons within the atom to be excited from a low energy orbital. Each element possesses a unique elemental spectrum. The core electrons possess characteristic binding energies, therefore the photoelectron spectrum gives an analysis of all the elements with the exception of hydrogen and helium (Lampman, 2003).

The detected electrons are emitted only from the outermost surface up to 7–10 nm of the solid (Valentim et al., 2011; Wagner et al., 1979), implying that the analysis is only a few atomic layers from the outer surface. The acquired spectrum is obtained from plotting the number of emitted electrons per given energy interval against the kinetic energy they possess (Moulder et al., 1992). Equation 2.1 depicts the kinetic energy (KE) that is possessed by an emitted electron.

$$KE = hv - BE - \phi_s \quad (2.1)$$

Whereby hv represents the characteristic energy of the incident X-ray photon, BE marks the binding energy of the atomic orbital where the electron emerges from, and ϕ_s serves as the spectrometer work function (Moulder et al., 1992; Wagner et al., 1979).

Different functional groups or various oxidation states bring about chemical shifts in the typical binding energies of the associated elements. In coal, the presence of carbon-oxygen or carbon-nitrogen functional groups results in chemical shifts of

carbon (1s) spectra peak broadening to higher binding energies. The resultant broadened peak envelop which is assumed to be a summation of individual components can be deconvoluted (resolved) into corresponding components of functional groups.

With regard to nitrogen, XPS reaction entails the ejection of an energised electron from the K shell, hence it is referred to as XPS N 1s. The utilisation of XPS N 1s analysis to elucidate the nitrogen functionalities in coal dates back to 1981 by [Jones et al. \(1981\)](#). [Burchill and Welch \(1989\)](#) also utilised the XPS N 1s analysis in one of the inception investigations to determine nitrogen structural attributes of three anthracite coals. XPS is distinguished by high surface sensitivity, hence the information on coal is usually deduced from samples that are pulverised to very small particle size ($<100\text{ }\mu\text{m}$). Another limitation of XPS data is that the interpretation of nitrogen moiety depends highly on curve resolution of the nitrogen (1s) spectrum and it seldom possesses well-resolved peaks. This implies that curve resolving of the XPS N 1s spectra may lead to substantial quantitative error and uncertainty in analysis of projected results ([Bartle et al., 1987](#); [Kelemen et al., 2002, 2007, 1999](#); [Knicker et al., 1995](#); [Patience et al., 1992](#); [Vairavamurthy and Wang, 2002](#)). This uncertainty in peak deconvolution arises from lack of the definition of the fundamental spectral peak for each functional group component. The binding energy of functional group components has been extensively deduced from model compounds, therefore the accuracy of deconvolution of peaks produced by a complex substance like coal is dependent upon the suitability of transferring chemical shifts from these simple model compounds ([Pels et al., 1995](#); [Stańczyk et al., 1995](#)). The consistent sensitivity of XPS towards the element rather than the functional group implies that the functional group analysis is quantitative within the precision of peak deconvolution routine. Recent progress in software applications such as CasaXPS offers powerful data processing environments, bringing about amplified and effective peak deconvolution in a way that essentially annuls the hindrance.

The use of XPS technique to determine forms of nitrogen in coal along with the respective solid derivatives attracted enormous attention in the 1990s through to the 2000s ([Glarborg et al., 2003](#); [Kambara et al., 1995, 1993](#); [Molina et al., 2000](#); [Stańczyk, 1999](#); [Thomas, 1997](#); [Wójtowicz et al., 1993, 1995](#); [Zhu et al., 1997](#)). The interest was propelled by endeavours and aspirations to establish relationships between coal nitrogen functionalities and the subsequent nitrogen oxides released in the course of combustion. The curve resolution of XPS N 1s spectra emanating from coal analysis illustrated that coal constitutes of N-5, N-6 and N-Q ([Bartle et al., 1987](#); [Kelemen et al., 1999](#); [Pels et al., 1995](#); [Zhang et al., 2013](#)). In other carbonaceous materials like chars a fourth additional heterocyclic nitrogen functional group representing protonated- and/or oxidised pyridinic nitrogen (N-X), has also been iden-

tified (García et al., 2004; Kapteijn et al., 1999; Kelemen et al., 1999, 1998; Suzuki et al., 1994; Valentim et al., 2011). Binding energy ranges for the respective nitrogen functionalities that were obtained from open literature are given in Table 2.1. A description of peak assignment from the XPS N 1s spectrum is outlined in Section 3.2.5.

Table 2.1: Respective XPS N 1s binding energy ranges obtained from literature.

	Nitrogen functional forms				References
	N-5	N-6	N-Q	N-X	
Binding energy, (eV)	400.4(±0.1)	398.7(±0.1)	401.4(±0.1)	403(±0.5) -NO; 405(±0.5) -NO ₂	Suzuki et al. (1994)
	400.4(±0.3)	398.7(±0.3)	401.4(±0.3)	402-404	Pels et al. (1995)
	400.2(±0.1)	398.8(±0.1)	401.4(±0.1)		Kelemen et al. (1999, 1998)
	400.3(±0.3)	398.7(±0.3)	401.4(±0.5)	402-405	Kapteijn et al. (1999)
	400.2	398.8	401.4	402.9	Kozłowski (2004)
	400.2(±0.3)	398.7(±0.3)	401.7	403.1(±0.3)	Garcia et al. (2004)
	400.6(±0.3)	398.9(±0.3)	401.3(±0.3)	402-405	Valentim et al. (2011)

2.5.3.2 X-ray Absorption Near Edge Structure

X-ray absorption near edge structure (XANES) is also referred to as near edge X-ray Absorption Fine Structure (NEXAFS) and entails the analysis of spectra that is acquired in X-ray absorption spectroscopy experiments. Spectroscopic analysis is distinct to a particular element, and it is responsive to the immediate bonding environment that establishes the partial density of the empty states of a molecule (Koningsberger and Prins, 1988). The fundamental principle is based on the fact that as X-ray radiation energy scans through the binding energy zone of a core shell, an abrupt increase of absorption is experienced, and that phenomenon is equivalent to the absorption of X-ray photon by a distinct type of core electrons (for example; 1s electrons of N). This brings about an absorption edge in the XAS spectrum by virtue of its vertical appearance. The absorption edges are primarily allocated according to the principle quantum number of the excited electrons.

Nitrogen X-ray absorption near-edge structure spectroscopy (N-XANES) is specifically utilised to determine organic nitrogen components. However, the technique possesses some inherent limitations that still need to be addressed. N-XANES penetrates further into the surface of the analyte unlike XPS, thereby yielding additional data from the available internal nitrogenous components (Mitra-Kirtley et al., 1993a,b). However, N-XANES has a major drawback of not being able to detect quaternary nitrogen in carbonaceous materials (Kelemen et al., 1994; Pels et al., 1995). In addition, N-XANES also suffers from an inherent limitation with respect to the in-

interpretation of background that respectively influences measuring of nitrogen functionality. Additionally, N-XANES is confined to a narrow energy range among the prominent edge peaks for every form of nitrogen (Zhu et al., 1997).

2.5.3.3 X-ray Diffraction

The utilisation of X-ray diffraction (XRD) was originally confined to the evaluation of minerals and/or low- and high-temperature ash in coal (Maity and Mukherjee, 2006). However, the technique has since developed into a principal procedure for determination of carbon structural properties. Structural parameters which include the degree of ordering, interlayer spacing (d_{002}), and crystallite size (L_a , L_c) have been used for evaluation of carbon staking in remarkably crystalline carbonaceous materials (Iwashita and Inagaki, 1993).

The microtextural and microstructural attributes of carbon incorporated in carbonaceous materials define the crystallite structure. XRD has been utilised extensively to analyse the structure of carbonaceous substances at atomic level (Ergun and Tiensuu, 1959; Everson et al., 2013b; Feng et al., 2003; Franklin, 1950, 1951; Lu et al., 2002, 2001; Sharma et al., 2002; Takagi et al., 2004; Trejo et al., 2007). The crystallite of carbonaceous materials like coal and char constitutes of polyaromatic basic structural units that are approximately 1 nm, made of polyaromatic layers that comprise of 4 to 10 aromatic rings in isolation or stacked by 2 or 3.

The XRD spectra emanating from materials illustrate diffuse peaks at (002), (10) and (11) bands that resemble the (002), (100) and (110) reflections of graphite respectively, and strong low-angle or background scattering (Franklin, 1951; Lu et al., 2002, 2001; Takagi et al., 2004; Wu et al., 2008). The diffuse peaks of the (002), (10) and (11) reflections indicate the presence of small graphite-like domains. The (002), (10) and (11) peaks of diffuse nature signify the existence of tiny graphite-like structures (Franklin, 1950, 1951; Lu et al., 2001). The amorphous or non-crystalline carbon produces the background intensity of X-ray diffraction pattern. Some of the crystallographic parameters that can be evaluated from the XRD pattern include aromaticity (f_a), fraction of amorphous carbon (X_A), crystallite height or aromatic layer stacking height (L_c), average crystallite size or diameter (L_a) and the inter-layer spacing or inter-planar distance (d_{002}).

L_c and L_a parameters (Equations 2.2 and 2.3, respectively) can be evaluated by the empirical equation that was initially developed by Scherrer (Davis et al., 1995; Everson et al., 2013b; Feng et al., 2003; Kashiwaya and Ishii, 1991; Lu et al., 2001; Takagi et al., 2004; Trejo et al., 2007).

$$L_c = \frac{K\lambda}{\beta_{002} \cos \theta_{002}} \quad (2.2)$$

$$L_a = \frac{K\lambda}{\beta_{10} \cos \theta_{10}} \quad (2.3)$$

Braggs Equation (Equation 2.4) is applied to determine the interlayer spacing (d_{002}) between aromatic sheets (Everson et al., 2013a; Lu et al., 2001; Takagi et al., 2004).

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (2.4)$$

Equation 2.5 is utilised to evaluate the average number of crystallites in a stack (N_{ave}) (Everson et al., 2013b; Trejo et al., 2007).

$$N_{ave} = \frac{L_c}{d_{002}} + 1 \quad (2.5)$$

The respective corresponding areas beneath the (002) band and γ band (A_{002} and A_γ) are proportional to the aromatic and aliphatic carbon structures. Therefore, Equation 2.6 can be employed for determination of aromaticity of carbonaceous substances (Everson et al., 2013b; Kawakami et al., 2006; Lu et al., 2002, 2001; Trejo et al., 2007).

$$f_a = \frac{A_{002}}{A_{002} + A_\gamma} \quad (2.6)$$

2.5.3.4 Solid State Nuclear Magnetic Resonance

Solid-state nuclear magnetic resonance (ss NMR) spectroscopy is a form of the NMR spectroscopy method that is utilised for resolving molecular structure, in which the analyte is held in medium with limited or no movement, like, a crystalline or powder state, membrane-bound system or aligned solution. In contrast to XRD, NMR is responsive to the local chemical environment and thus can also be applied to the characterisation of amorphous compounds.

(a) Coal characterisation by solid state ^{13}C NMR

Cross-polarisation magic angle spinning (CP MAS), and Dipolar Dephasing (DD) are the techniques usually employed during ss NMR analysis experiments and are often utilised to evaluate structural parameters of coal as well as related carbonaceous materials. In general, the CP MAS technique relies on the power of dipolar coupling which exists between the proton and carbon atoms, hence the proton density and spatial closeness to the carbon nucleus is paramount (Causemann, 2012a). Any parameter that depreciates the intensity of dipolar coupling such as distance as well as the ascribed motion subsequently decreases the CP efficiency resulting in respective

decreased peak intensity within the spectrum (Okolo et al., 2015). The CP efficiency is governed by CP rate (T_{CH}) together with proton relaxation time ($T_{1\rho}^H$). Supaluknari et al. (1990) expounded that the $T_{1\rho}^H$'s of primary carbon moieties available in coals fall within same ranges. The respective CP rates illustrate that the highest rate emanates from aliphatic carbons, followed by aromatics, and carbonyls. These findings imply that the aromatics and carbonyls are overlapped by aliphatics resulting in systematic errors on the derived carbon structural parameters. On the other hand, direct polarisation (DP, single pulse) MAS is a quantitative analytical tool, thereby providing a good estimation of the ratio of aromatic- to aliphatic-structures. In a typical laboratory analysis of structural parameters of two coals, the DP MAS results were put in comparison to those obtained through CP MAS. The results depicted that CP MAS undervalues aromaticity by a magnitude of 10–15%. Nonetheless, the inherently low ^{13}C leads to extended analysis periods in in DP MAS. Analyses of coal may exceed 48 hours, whereas CP MAS can be conducted within a time frame of 2–6 hours. The respective accuracy and speed of analyses lead to a combination of both techniques being broadly utilised in the coal characterisation fraternity.

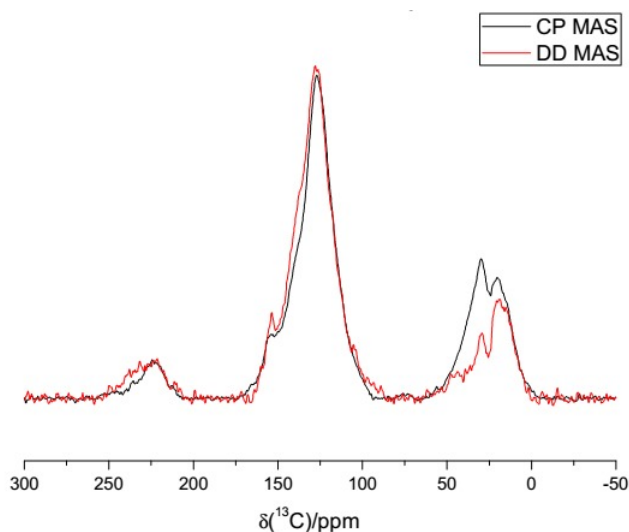


Figure 2.5: Typical CP MAS and DD MAS spectra from coal analysis (Causemann, 2012a).

The dipolar dephasing (DD MAS) technique is utilised to differentiate intensely proton coupled carbons apart from carbons that are protonated mildly, or not at all. In the unavailability of ^1H decoupling, the process of magnetising ^{13}C that are associated with intensely ^1H coupled carbons dipphase quicker in comparison to the mildly coupled counterparts (Okolo et al., 2015). This implies that a DD spectrum obtained from elongated dephasing delays, such as $40\ \mu\text{s}$, is bound to predominantly possess signals from carbons that are mildly or not protonated (Supaluknari et al., 1990).

Figure 2.5 illustrates the superimposed CP- and DD MAS spectra of a particular coal, highlighting the loss of intensity of aliphatic carbons. That being the case, the DD procedure facilitates the determination of mildly coupled carbons that are in existence in bridgehead aromatic structures. Utilisation of an integral acquired from a DD plot leads to the evaluation of fraction of bridgehead carbons (f_a^B), and thus mole fraction of aromatic bridgehead carbons (X_b) and average number of clusters per 100 carbon atoms (C) parameters.

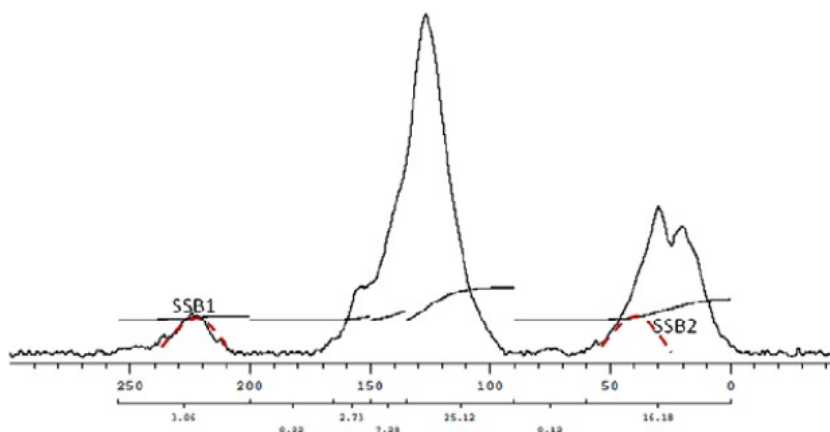


Figure 2.6: A typical CP MAS spectrum of a coal sample measured at a MAS frequency of 12kHz with integration reset points (Causemann, 2012a).

Figure 2.6 displays a typical CP MAS spectrum from coal, along with the integration reset points as well as the respective integrals used for the evaluation of coal structural parameters. The apparent peak at 225 ppm emanates from the chemical shift anisotropy (CSA) linked to aromatic carbons, and it is labelled as the first spinning sideband (SSB1). The eminent peak at approximately 120 ppm is a result of the presence of aromatic structures, and it is referred to as an isotropic line (Causemann, 2012a; Okolo et al., 2015). Spinning sidebands emerge at spinning frequency intervals of 12 kHz, this results in a second spinning sideband (SSB2) which overlaps on the aliphatic peak emerging at 0–60 ppm. The respective integrals of aromatic and SSB2 peaks are significant towards the evaluation of structural parameters.

(b) Coal characterisation by solid state ^{15}N NMR

Solid state ^{15}N NMR is a non-destructive analytical technique applied to characterise the chemical nature of nitrogen present in non-soluble materials. In general nitrogen has two NMR-active isotopes: ^{14}N and ^{15}N (Causemann, 2012b). Both nuclei have low sensitivity due to their low gyromagnetic ratios. ^{14}N has a high natural abundance

of 99.6% as compared to ^{15}N has a low natural abundance of 0.4%. Despite its low natural abundance ^{15}N SS NMR studies are more common than ss ^{14}N NMR owing to the fact that ^{14}N is a quadrupolar nuclei ($I=1$), which is usually surrounded by non-spherical electronic environments. As a consequence ss ^{14}N NMR spectra experience prevalent quadrupolar interaction resulting in a line broadening in the order of several MHz, which cannot be detected due to technical limitations. ^{15}N on the other hand has a nuclear spin of $I=\frac{1}{2}$. Consequently, ss ^{15}N NMR spectra are not affected by quadrupolar interaction and different nitrogen environments can be distinguished from each other. The challenge of the low sensitivity due to the low natural ^{15}N abundance can be overcome by using ^{15}N enriched samples as well as the application of $^{15}\text{N}\{^1\text{H}\}$ CP MAS technique. During the course of ^{15}N CP MAS procedure, magnetisation of protons is transferred to ^{15}N and subsequently the ^{15}N signal is detected. As protons have very good NMR properties like a natural abundance of almost 100%, a large gyromagnetic ratio as well as short relaxation times, the application of the CP MAS technique results in enhanced quality of the spectrum as depicted by improved signal to noise ratio.

[Knicker et al. \(1995\)](#) demonstrated that solid state ^{15}N NMR can be applied to whole coal samples despite the low natural abundance of the ^{15}N isotope and its low sensitivity. Solid state ^{15}N NMR suffers a major flaw in its severe sensitivity problems. This is attributed to the more abundant ^{14}N nucleus which possesses a quadrupole moment and the small magnetogyric ratio of ^{15}N resulting in poorly resolved spectra with very broad resonance lines ([Kelemen et al., 2002](#); [Knicker et al., 1995](#)). [Kelemen et al. \(2002\)](#) further pointed out that another drawback facing solid-state ^{15}N NMR is that complex carbonaceous materials usually have broad resonances that make peak position assigning tedious. For instance, the peak position for some nitrogen forms and amides are very close to each other, making clear peak assignment a difficult task.

2.5.4 X-ray Fluorescence

X-ray fluorescence spectroscopy (XRF) is a non-destructive analytical technique utilised to establish the elemental constituents of a substance. When a substance is subjected to a primary X-ray source, it emits a fluorescence X-ray (also known as secondary X-ray). Each particular element that is present in an analyte emits a characteristic fluorescence that is specific and unique. Therefore XRF spectroscopy can qualitatively and quantitatively determine the composition of a material. XRF is widely used to deduce major and minor elements of coal ashes ([Vassilev et al., 2003](#)).

2.5.4.1 Coal Mineral Matter

The level of different minerals in coal depends on the origin, and varies from one coal to another. Mineral matter in coal comprises of distinct particles of minerals, inorganic elements which are amalgamated with organic compounds, dissolved salts, as well as other inorganic substances incorporated in coal pore water (Ward, 2002). The prevalent minerals in coal consist of quartz, clay minerals (particularly kaolinite, illite, and mixed-layer illite-smectite), sulphide minerals (for instance, pyrite and marcasite), and carbonates (especially siderite, calcite, and dolomite) (Dai et al., 2012; Harvey and Ruch, 1986; Palmer and Lyons, 1996; Yu et al., 2007). Potent but negligible minerals have also been established in coal (Belkin et al., 2010; Kalaitzidis et al., 2010; Koukoulas et al., 2010; Wang, 2009).

2.6 Coal and Char Chemical Treatment

The inorganic matter that is present in coal markedly affects the chemical attributes and the subsequent potential utilisation. Coals and the respective chars are chemically treated by an alkaline and/or acidic lixiviants before particular conversion processes or laboratory analytical techniques to appreciably minimise the presence of minerals or ash. Reducing the influence of mineral interference in certain laboratory techniques, mitigation of coal utilisation environmental impact, and improving the efficiency of coal utilisation are among other major reasons for chemical pre-treatment. It is paramount to know the implications of coal or char chemical treatment with regard to chemical structural attributes transformation. The exercise of demineralising coal or char de-ashing is usually carried out through the usage of a single or combination of HCl, HF, NaOH, H_2SiF_6 and HNO_3 (Steel and Patrick, 2001).

Chemical treatments have been utilised in an endeavour to produce ultra clean coal (UCC), that is, coal possessing <0.1 wt.% mineral matter (Steel and Patrick, 2001). The mineral matter in coal limits the suitability of coal to be utilised as a possible substitute for oil and natural gas to produce a variety of fuels, chemicals and materials. A typical example involves the usage of coal instead of petroleum coke for aluminium electrodes, coal must contain <0.5 wt.% to be usable. A number of researchers have reported on leaching methods that have exhibited appreciable reduction in minerals or ash (Benson and Holm, 1985; Demirbaş, 2002; Durand and Nicaise, 1980; Liu et al., 2014; Mursito et al., 2011; Robl and Davis, 1993; Steel and Patrick, 2001; Wijaya and Zhang, 2011). Currently, chemical pre-treatment technologies aiming to produce clean coal are not yet feasible on commercial basis. However, a number of applicable patents are available (Kindig and Reynolds, 1987; Lloyd and Turner, 1986; Reggel et al., 1976; Waugh and Bowling, 1987; Yang, 1979). In some

laboratory analytical techniques, mineral matter in coal or ash in char results in interference thereby compromising the integrity of results (Everson et al., 2013b; Okolo et al., 2015; Roberts et al., 2015b; Roets et al., 2015; Strydom et al., 2011). However, an analytical technique such as XPS has an advantage in that it can be utilised in the analyses of both demineralised/de-ashed and untreated samples without limitations. Analytical techniques that need input samples without minerals or ash include XRD (for the determination of carbon crystallites and amorphous fractions), NMR, and HR-TEM. Typical data deduced from these techniques may be utilised as a building block in operations such as molecular modelling. It is important to ascertain that essentially no substantial changes in organic constitution and structural attributes occur during chemical treatment. Reactions encompassing ester hydrolysis and Friedel-Crafts may occur due to the interaction of coal or char with an acid (Larsen et al., 1989). Lixivants like LiAlH_4 , HNO_3 , and NaBH_4 have been observed to result in chemical structural transformations to organic substances (Chen et al., 1999).

Kelemen et al. (1995) subjected coals to three organic acids of different concentrations, and then analysed the demineralised remnants using XPS to determine nitrogen structural transformations. The proportion of N-Q increased considerably in the two coals that were treated in highly concentrated p-toluenesulfonic acid. Nonetheless, no notable nitrogen structural alterations occurred through exposing the coals to the comparatively low concentrations of 2-naphthol-, and octanoic acid, respectively. In another study, Kelemen et al. (2002) observed that the fraction of N-Q appreciated when a kerogen was washed with an acid. In an endeavour to prevent inorganic nitrogen interference that might arise from trace ammonium salts during XPS N 1s analysis, Boudou et al. (2008) pretreated high rank coal samples with HF and HCl. Larsen et al. (1989) noted that the systematic demineralising procedure involving HF and HCl produced insignificant impact on the organic macromolecular structure of coal. However, Rubiera et al. (2002) pretreated coals with a concoction of HF and H_2SiF_6 , as well as after-washing with HNO_3 , and reported that the procedure induced notable changes to chemical composition. They witnessed notable increase in nitrogen, oxygen, and volatile matter. Through XRD analysis of coal remnants from acid washing, Takagi et al. (2004) stated that the washing procedure had insignificant effect on parameters for stacking-structure. Strydom et al. (2011) carried out respective sequential HF/ HNO_3 , and HF on coal. They reported that the systematic HF/ HNO_3 chemical treatment technique introduced nitrogen and oxygen containing components, whereas, the HF/HCl procedure did not cause notable changes apart from negligible augmentation of carboxylic functionalities.

CHAPTER

3

THE EFFECT OF ACID DEMINERALISING BITUMINOUS COALS AND DE-ASHING THE RESPECTIVE CHARs ON NITROGEN FUNCTIONAL FORMS

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<https://doi.org/10.1016/j.jaap.2017.04.009>.

Highlights

- South African bituminous coals were pyrolysed, acid treated and analysed using XPS.
 - Demineralising parent coals had no significant effect on nitrogen functionalities.
 - De-ashing chars derived from inertinite-rich coals had no effect on nitrogen forms.
 - De-ashing high-temperature chars from vitrinite-rich coal induced extra N moieties.
-

Abstract

An opportunity presented itself to compare changes in nitrogen functional forms brought by the acid treatment of South African bituminous coals and their respective chars. X-ray photoelectron spectroscopy (XPS) was used to determine functional forms of the raw coals, acid-treated coals, respective chars prepared at 740 and 980 °C in a bench-scale fluidised-bed (FB), and at 1000 and 1400 °C in a drop-tube furnace (DTF), as well as their corresponding de-ashed remnants. The XPS N 1s spectra for the raw coals were typically similar to previous widely reported bituminous coals, of which pyrrolic nitrogen was the predominant form of organically bound nitrogen, followed by pyridinic and quaternary nitrogen. In pyrolysed chars, quaternary nitrogen was the dominant form followed by pyridinic, pyrrolic and protonated-/oxidised heterocyclic nitrogen forms respectively. Nonetheless, XPS N 1s analysis for DTF severely pyrolysed chars (1000 and 1400 °C) prepared from high ash and vitrinite-rich coal, and also a char (1400 °C) from a relatively low ash and inertinite-rich coal, gave a spectra with only two sub-peaks corresponding to quaternary and pyridinic nitrogen. It seems that the HCl/HF/HCl sequential demineralising/de-ashing process had no effect on the nitrogen functional forms of raw coals and the entire chars prepared from the FB. De-ashing of DTF severely pyrolysed chars emanating from high ash and inertinite-rich coal exhibited no marked change to the nitrogen functional forms. However, acid treatment of DTF chars derived from a high ash and vitrinite-rich coal, a char from relatively low ash and inertinite-rich coal, which initially contained pyridinic and quaternary nitrogen resulted in additional nitrogen moieties of pyrrolic and protonated/oxidised nitrogen.

Keywords

Nitrogen functionality; XPS; Pyrolysis; Coal demineralisation; Char de-ashing; South African coals

3.1 Introduction

Nitrogen constitutes a relatively small organic portion in coal in the order of 2% or less, with the bulk organic component comprising of carbon, hydrogen and oxygen atomic components, while sulphur also makes up a very small portion (Glick and Davis, 1991; Miller, 2005). Coal is principally comprised of tiny aromatic structures (Solum et al., 1989) and almost all the nitrogen in coal exists as heterocyclic nitrogen functional forms (Davidson, 1994; Pels et al., 1995). The inorganic portion mostly comprises of various minerals whose concentration differ from coal to coal, depending on source. The bulk of minerals present in coal comprise of kaolinite, quartz, illite, montmorillonite, siderite, calcite, gypsum, pyrite, dolomite and feldspars (Yu et al., 2007).

The presence of inorganic matter in coal notably influences its chemical attributes and potential utilisation. Prior to certain laboratory analytical techniques or conversion processes, coals and chars are leached by an acid or alkali solution to reduce mineral or ash content significantly. Increasing the efficiency of coal usage and the call to mitigate environmental implications of coal combustion are some of the major reasons for the need for coal chemical pre-treatment. It is therefore of paramount importance to be equipped with knowledge on whether the leaching procedure modifies the coal or char structure in addition to the intended minerals or ash removal. The demineralisation or de-ashing process is often conducted by utilising one or more of a combination of HCl, HF, NaOH, H₂SiF₆ and HNO₃ (Steel and Patrick, 2001).

Several other aspects of leaching processes which proved to reduce mineral matter in coals and ash content in chars appreciably have been demonstrated (Benson and Holm, 1985; Demirbaş, 2002; Durand and Nicaise, 1980; Liu et al., 2014; Mursito et al., 2011; Robl and Davis, 1993; Steel and Patrick, 2001; Wijaya and Zhang, 2011). At present, there are no commercially viable technologies for clean coal production. Nevertheless, there is quite a number of pertinent patents in this regard (Kindig and Reynolds, 1987; Lloyd and Turner, 1986; Reggel et al., 1976; Waugh and Bowling, 1987; Yang, 1979). In laboratory analyses, the presence of mineral matter in coal or ash in char causes interference in certain analytical techniques (Everson et al., 2013b; Okolo et al., 2015; Roberts et al., 2015b; Roets et al., 2015; Strydom et al., 2011). X-ray photoelectron spectroscopy (XPS) can be used on characterising and identifying the chemical forms of nitrogen in both raw and acid-treated samples without limitations. However, a number of coal and/or char analytical techniques such as X-ray diffraction (XRD) to analyse carbon crystallites and amorphous fractions, solid state ¹³C or ¹⁵N nuclear magnetic resonance (ss-NMR), high resolution

transmission electron microscopy (HR-TEM) require the use of demineralised coal samples or de-ashed char samples. The information obtained from these analyses may be used as input data in exercises like molecular modelling. It is therefore important to ensure that there is no significant alteration of the organic composition and structure. Structural changes as a result of acid-induced chemistry, like ester hydrolysis and Friedel-Crafts reactions might be expected to occur during acid treatment of coals or chars (Larsen et al., 1989). Chemical methods that involve the usage of leaching agents such as HNO_3 , LiAlH_4 and NaBH_4 are noted for causing chemical changes to organic matter (Chen et al., 1999).

Kelemen et al. (1995), treated coals with 3 organic acids of different strengths and then subsequently carried out XPS nitrogen 1s analysis. In 2 of the 3 coals that were subjected to a strong acid, p-toluenesulfonic acid, the level of quaternary nitrogen species increased substantially. However, treatment of the coals with relatively weaker acids (2-naphthol and octanoic acid) resulted in no significant changes in nitrogen functional forms. In a different investigation, Kelemen et al. (2002) reported that the level of quaternary nitrogen feature increased upon treatment of a kerogen with acid. In their work on kerogens, Boudou et al. (2008) treated high rank samples with HF/HCl prior to XPS analysis to curb the possible contribution from mineral nitrogen in the form of ammonium salt traces. Larsen and co-workers Larsen et al. (1989) found that the HCl/HF demineralisation technique does not seem to alter the macromolecular organic structure of coal considerably. Rubiera et al. (2002) used a mixture of HF/ H_2SiF_6 with HNO_3 being used as a pretreatment or after-wash and they reported that the demineralisation process altered the chemical composition; volatile matter, oxygen and nitrogen content increased. Takagi et al. (2004) reported that the acid treatment had little influence on stacking-structure parameters as determined by XRD. Strydom et al. (2011) compared the effect of the HF/ HNO_3 and HCl/HF method on the chemical structure of the demineralisation remnants. They observed that oxygen and nitrogen bearing species were integrated into the coal structure in the course of HF/ HNO_3 leaching procedure. However, they did not observe any of these modifications on the product of HCl/HF/HCl leaching process, besides a slight increase in the carboxylic functional groups.

XPS currently offers the best approach to access organic nitrogen transformation-related changes. XPS N 1s has been used extensively to determine and quantify the heterocyclic nitrogen functional forms in carbonaceous materials (Buckley, 1994; Davidson, 1994; Gong et al., 1999; Kelemen et al., 1998; Kozłowski, 2004; Pels et al., 1995; Pietrzak, 2009; Stańczyk et al., 1995; Wójtowicz et al., 1995). In coal and other carbonaceous materials like chars, XPS N 1s spectra studies have shown that these heteroatomic structures mainly exist in the form of pyrrolic, pyridinic, quaternary

and to a lesser extent as protonated and/or oxidised heterocyclic nitrogen structures (Boudou et al., 2008; Kapteijn et al., 1999; Kelemen et al., 1994, 1998; Leppälahti and Koljonen, 1995; Zhang et al., 2011). Pels et al. (1995) reported that upon subjecting coal to increasing severity of the pyrolysis conditions, the chemical speciation of organically bound nitrogen changes. Severely pyrolysed chars principally comprise of pyridinic and quaternary nitrogen forms (Kelemen et al., 1998; Pels et al., 1995). The high levels of quaternary nitrogen emerging from high temperature pyrolysis has been associated with nitrogen being incorporated into the resultant large polynuclear aromatic carbon structures (Kelemen et al., 1998; Pels et al., 1995; Wójtowicz et al., 1995). Thermal transformation of coal entail stages of enhanced elimination of organic nitrogen until finally resulting in graphite containing traces of nitrogen (Boudou et al., 2008).

In as much as XPS offers the most viable method in analysing organic nitrogen species in carbonaceous materials, it has the limitation of only examining the outermost surface to about 2-7 nm into the analyte (Valentim et al., 2011). In addition, the curve deconvolution of the N 1s spectrum in some instances does not possess well-resolved peaks, making the interpretation of the particular XPS data obtained under such circumstances to be subjective, resulting in appreciable quantitative error and ambiguity in interpretation (Bartle et al., 1987; Kelemen et al., 2002, 1999; Patience et al., 1992; Vairavamurthy and Wang, 2002). Nonetheless, recent developments in instrumentation and advancements in software applications have improved the peak resolution capabilities such that this drawback is almost adequately addressed. In addition to XPS, other non-destructive analytical techniques that have been utilised to characterise organic nitrogenous species, with limitations, are nitrogen X-ray absorption near-edge structure spectroscopy (N-XANES) and ss ^{15}N NMR (Kelemen et al., 2006; Knicker et al., 1995, 1996). The relatively low natural abundance of ^{15}N isotope as well as its small magnetogyric ratio are responsible for the intrinsic low sensitivity experienced by the cross polarisation ss ^{15}N NMR analysis of carbonaceous materials (Bartle et al., 1987; Kelemen et al., 2002; Knicker et al., 1995; Vairavamurthy and Wang, 2002). This phenomenon causes difficulty in identifying other nitrogen forms above the noise level besides pyrrolic and pyridinic nitrogen forms (Kelemen et al., 2002, 2007). N-XANES have more penetrating power into the sample surface as compared to XPS, hence giving more information on interior nitrogen species in coal or char (Mitra-Kirtley et al., 1993a,b). However, N-XANES has an inherent limitation of not detecting quaternary nitrogen in carbonaceous substances (Kelemen et al., 1994; Pels et al., 1995). In addition, N-XANES encounters a drawback in evaluation on background which subsequently impact quantification of functional forms present, furthermore, a narrow energy range exist in N-XANES for the leading edge peaks for

each type of nitrogen functionality (Zhu et al., 1997). The findings between N-XANES and XPS imply that quaternary nitrogen only exists in the surface layers of coals and chars, while protonated/oxidised heterocyclic nitrogen is only concentrated on the outer surface of chars. Further investigations are necessary in that regard.

Nonetheless, only limited data are available on treatment effects on nitrogen functional groups in coals and chars. To investigate the possible effects of acid treatment on organic nitrogen speciation, a series of chars were produced from 3 South African bituminous coals using a laboratory scale bubbling fluidised-bed (FB) and drop-tube furnace (DTF). The influence of HF and HCl sequential leaching of the coals and respective chars on nitrogen functional forms (N 1s sub-peaks) was investigated and reported in this study. XPS was utilised to speciate and quantify nitrogen functionalities initially present in bituminous coals, in subsequent resultant chars to track the nitrogen functional form transformations and primarily the influence brought by HCl and HF sequential demineralising/de-ashing on the fate of nitrogen functionalities.

3.2 Materials and methods

Three South African bituminous run-of-mine (ROM) coals were used in this study, namely Glisa, Lethabo and Matimba coals. A set of four chars from each coal were prepared and analysed, of which two chars were made from a 50 mm bench-scale bubbling fluidised bed and the other two were produced from a drop-tube furnace. Pyrolysis of the coals in a bench-scale bubbling fluidised bed was carried out at 740 & 980 °C, while in the drop-tube furnace it was conducted at temperatures of 1000 & 1400 °C. Part of the raw coals were demineralised and a portion of generated chars were de-ashed according to the procedure that is outlined in Section 3.2.3. This was followed by XPS analysis on parent coals, prepared chars, and their acid-treated counter parts.

3.2.1 Bubbling Fluidised-Bed

Experiments were conducted in an electrically heated laboratory-scale bubbling fluidised bed of silica sand. The reactor comprised of a 50 mm internal diameter ceramic tube and a total height of 1550 mm. Coal samples of ± 1 mm were pyrolysed at 740 and 980 °C at a heating rate of $>10^4$ °C/s, under a N₂ (99.995%) atmosphere. Prior to the tests, about 200 g of silica sand (fluidising material) was fed into the system and then heated to the required temperature. The fluidised bed was operated continuously with a 1:1 mixture of ± 1 mm coal and 0.3-0.65 mm silica sand fed with a screw feeder at a rate of 21 g/min. The char/silica sand mixture was collected at

the bottom of the reactor. Nitrogen gas was flown over the produced chars to restrain oxidation until the temperature had dropped close to ambient temperature. The char and sand mixture was then separated by sieving.

3.2.2 Drop-tube furnace

The second set of pyrolysis experiments were carried out in an electrically heated drop-tube furnace. Dilute coal particle suspensions ($-75\ \mu\text{m}$) aided by 99.995% N_2 (primary gas) were continuously fed at a rate of about 1 g/min into the heated section of the DTF which comprises of a 70 mm internal diameter and a 1.8 m vertical ceramic tube and were pyrolysed at 1000 and 1400 °C at a heating rate of $>10^4\ ^\circ\text{C/s}$ in N_2 . The relatively low fuel feed rate necessitated a quasi-single particle analysis, of which each particle is considered to be discrete and has negligible effect on other particles. The apparatus and conditions were set such that an average residence time of 1.8 s was attained throughout the entire experiments. The char particles were collected by a water-cooled collection probe.

3.2.3 Acid treatment procedure

The well established acid treatment technique which involve the sequential use of HCl and HF as lixiviants was adopted in this study. It has been widely utilised by several other researchers for the reason that it does not significantly change the molecular structure of coal or char (Everson et al., 2013b; Hattingh et al., 2013; Louw et al., 2015; Okolo et al., 2015; Roberts et al., 2015b; Roets et al., 2015; Strydom et al., 2011; Takagi et al., 2004; Van Niekerk and Mathews, 2010).

Approximately 50 grams of finely pulverised ($-75\ \mu\text{m}$) coal or char was stirred in 200 ml of 5 N hydrochloric acid in a beaker for 24 hours using a magnetic stirrer. The mixture was filtered with the aid of a vacuum pump, of which the coal or char residue was added to 200 ml of 5 N hydrofluoric acid in a polyethylene beaker and the mixture was agitated for 24 hours. The acid was separated from the mixture through vacuum filtration, of which the coal or char residue was again mixed with 200 ml of 5 N HCl and stirred for 24 hours. The HCl treatment enhanced the removal of carbonates and acid-removable calcium (Önal and Ceylan, 1995), while HF was responsible for the removal of predominant quartz and alumino-silicates (Wijaya and Zhang, 2011). The acid filtrate was separated from the coal/char by vacuum aided filtration. The coal/char residue was washed several times with de-ionised water to ensure that all the acid had been drained off. The washed and filtered coal/char was then dried at 60 °C in a vacuum oven until there was no noticeable weight change.

The effectiveness of demineralising or de-ashing, E_d , illustrated on Equation

3.1, was used to determine the extent or efficiency of the demineralising/de-ashing exercise (Okolo et al., 2015). E_d , given as a percentage, denotes the ratio of the ash component (as measured by proximate analysis) eliminated to the initial ash composition on dry basis (d.b).

$$E_d = \left[\frac{A_i - A_d}{A_i} \right] \cdot 100\% \quad (3.1)$$

of which A_i represents the ash content of the initial coal or char sample and A_d is the remaining ash component in demineralised coal or de-ashed char sample (wt. %, d.b).

3.2.4 Standard coal and char analyses

Proximate analyses were conducted using appropriate standards; ash content was determined in accordance with ISO 1171 (2010), volatile matter content was evaluated through ISO 562 (2010) and fixed carbon content was deduced by difference. Ultimate analysis was performed in line with the ISO 29541 (2010) guidelines.

With regard to petrographic analysis, the coal samples were milled to a particle size of -3 mm. A petrographic block of each sample was prepared and polished in accordance with the ISO 7404: 2 (1985), and then subsequently examined using a microscope. Vitrinite random reflectance measurements to determine the rank of coals were taken (100 readings on vitrinites in each coal sample) in accordance with the ISO 7404: 5 (1994). Coal maceral point-count analyses, to determine the petrographic compositions, were accomplished by using the ISO 7404: 3 (1994) standard.

3.2.5 XPS N 1s spectra acquisition and processing

The XPS analyses were conducted at The University of Queensland's Centre for Microscopy and Microanalysis. XPS N 1s signals were acquired and recorded using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was Monochromatic Al K α X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) high resolution scans at 40 eV. Survey scans were carried out over 1200-0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was $1.0 \cdot 10^{-9}$ torr and during sample analysis it was $1.0 \cdot 10^{-8}$ torr. Due to the very low level of N in some of the char samples, especially very high-temperature char samples (inclusive of the corresponding de-ashed remnants), it was necessary to increase the X-ray

power from 225 to 300 W and the number of sweeps over the N 1s was increased from 6 to 9.

Relative amounts of nitrogen functional forms were calculated, the process entailed peak fitting of the high-resolution data using the CasaXPS version 2.3.14 software application and a linear baseline with Kratos library Relative Sensitivity Factors (RSFs). In all instances, to determine relative amount of species comprising of the N 1s photoelectron spectrum, resolving the XPS N 1s signal was performed using a mixed 70-30% Gaussian-Lorentzian peak shapes and full width at half-maximum (FWHM) was fixed at $1.3(\pm 0.1)$ eV while the N peaks were defined but not fixed. The curve fitting was carried out with the only constraint being that all the peaks have a FWHM of $1.3(\pm 0.1)$ eV. In all instances, an energy correction was done to account for sample charging based on the C 1s peak at 284.8 eV (Gong et al., 1999; Kelemen et al., 2006, 1999; Kozłowski, 2004). To obtain a best fit, the positions and intensities of peaks were left unconstrained (Boudou et al., 2008). An average chi square value of ≈ 0.8 was attained during the curve fittings, this value is indicative of a good fit. Chi square is a measure of the goodness of fit, basically, a chi square value between 1 and 2 relates to a relatively good efficacy of curve fitting.

The allocation of sub-peaks within a peak envelop was guided by the binding energies of known nitrogen species that could have contributed towards the resultant peak envelop (Pels et al., 1995). To evaluate the relative quantities of species comprising of N 1s spectrum, curve resolution procedure similar to the one described by Kelemen et al. (1994, 1995) for quantification of organically bound nitrogen forms in coal and high-temperature coal chars, was followed. Nitrogen in model compounds with well known binding energies was instrumental in chemical-structural allocations of XPS N 1s sub-peaks, data on coal/char nitrogen from literature also served as a yardstick in that regard (Kapteijn et al., 1999; Kelemen et al., 1999, 1998; Kozłowski, 2004; Suzuki et al., 1994; Valentim et al., 2011), in addition, information in the NIST X-ray Photoelectron Spectroscopy Database (Naumkin et al., 2015) and the Handbook of X-ray Photoelectron Spectroscopy (Moulder et al., 1995) also gave direction in the sub-peak placement during the deconvolution process. A maximum of 4 or 5 sub-peaks have a possibility of emanating within the XPS N 1s spectra of N-containing carbonaceous materials due to the different binding energies of various present nitrogenous species.

Upon severe pyrolysis, the electronic properties of the carbon matrix changes significantly which in-turn calls for changes in the relaxation and chemical shift contributions to the N 1s binding energy of the mentioned nitrogen functional forms (Kelemen et al., 1998). So deductively using the given binding energies and considering the effect brought by high temperature phenomenon, the N 1s peaks for pyri-

dic, pyrrolic and quaternary nitrogen functional forms of chars in this study were allocated to 398.6(± 0.2), 400.3(± 0.3) and 401.4(± 0.4) eV, respectively. Whereas the binding energy for protonated and/or pyridinic N-oxide complexes ranged from 402 to 405 eV, other allocations in this wide range are characteristic of nitrogen atoms that have replaced an inner C atoms within the graphene layers, resulting in some sort of quaternary nitrogen. This wide zone is also attributable to ammonium fixed in clay and other nitrogen forms (Boudou et al., 2008; Valentim et al., 2011).

Besides these major peaks, Kelemen et al. (1999) pointed out the presence of low levels of amino species with binding energy of 399.4 eV which cannot be clearly distinguished from pyridinic forms. Furthermore, XPS measurements cannot differentiate between pyrrolic, pyridone, amine and amide nitrogen because the binding energy of amides and pyridone nitrogen all fall within the pyrrolic nitrogen region and hence only referred to as the pyrrolic peak (Hansson et al., 2003; Kelemen et al., 2006, 2002, 1999; Zhu et al., 1997). The N-6 peak is explicitly attributed by pyridinic nitrogen. The quaternary nitrogen sub-peak which appears at ≈ 401.1 eV in the N 1s curve resolved spectra can be associated with ammonium salts (Gong et al., 1997), pyridinium ion and bridgehead nitrogen in aromatic structures (Kelemen et al., 2002) and protonated amino acids (Boudou et al., 2008; Hansson et al., 2003). N-X may be due to oxidised nitrogen, pyridinic-N-oxide functional forms, or other forms of nitrogen (Garcia et al., 2004; Zhang et al., 2011). There has been a general consensus on the absence of inorganic nitrogen (NH_4^+ ions) in bituminous and sub-bituminous coals (Buckley, 1994; Buckley et al., 1995; Daniels and Altaner, 1990, 1993; Juster et al., 1987), however, Gong et al. (1997) were unequivocally adamant on the presence of ammonium-bearing clay in a bituminous coal they studied. Nitro type complexes ($-\text{NO}_2$) have been reported to possess high binding energy exceeding 405 eV (Pels et al., 1995; Senō and Tsuchiya, 1976; Suzuki et al., 1994), a value of 406.2(± 0.1) eV was obtained for a 1-nitropyrene model compound by Bartle et al. (1987).

3.3 Results and discussion

3.3.1 Characterisation

Standard methods and procedures were used for the conventional chemical analyses. The results for proximate and ultimate analyses are given in Table 3.1. The nitrogen analyses results shown in Table 3.1 indicate that the relative amount of nitrogen present in the coal remains the same in subsequent FB chars produced at 740 and 980 °C; however, an apparent steady decrease occurs in DTF chars produced at 1000 and 1400 °C. Almost all the nitrogen in the coals and chars was retained in the

CHAPTER 3. THE EFFECT OF ACID DEMINERALISING BITUMINOUS COALS AND DE-ASHING THE RESPECTIVE CHARS ON NITROGEN FUNCTIONAL FORMS

remnants of the de-ashing process. The N/C atomic ratios derived from ultimate analysis (daf) are similar with the atomic ratios derived from XPS analysis, and to a large extent among the coals.

The HCl and HF sequential de-ashing process carried out on coals and the respective chars reduced the ash content appreciably as shown by high de-ashing efficiencies (E_d). Traces of oxygen were reintroduced by the acid treatment in chars. Strydom et al. (2011) attributed a similar change in their study to a slight increase in the carboxylic functional groups.

Table 3.1: Proximate and ultimate analyses results for raw coals, subsequent chars from FB & DTF, and the respective de-ashed samples.

Samples	Pyrolysis Temp*	Proximate Analysis (wt %, d.b.)			Ultimate Analysis (wt %, d.a.f.) ^d					Atomic Ratios		Demin/De-ash, E_d
		Ash % ^a	VM % ^b	FC % ^c	C	H	N	S	O	N/C _{ulti}	N/C _{xps}	
Glisa Coal	(-) ^{raw}	19.9	23.6	56.4	80.7	4.5	1.9	1.1	11.9	0.020	0.017	89.4
	(-) ^{dem}	2.1	22.7	75.2	83.0	3.9	2.0	0.8	10.3	0.020	0.018	
Glisa Chars	740	21.8	5.6	72.7	94.3	0.9	2.1	1.2	1.5	0.019	0.012	95.4
	740 ^{dem}	1.0	8.8	90.2	90.7	1.4	1.9	0.8	5.2	0.015	0.015	
	980	23.1	1.6	75.3	96.6	0.1	2.0	1.3	0.0	0.018	0.008	95.2
	980 ^{dem}	1.1	5.2	93.7	94.2	0.2	1.7	0.3	3.6	0.015	0.012	
	1000	24.8	2.2	73.0	96.2	0.3	1.8	1.7	0.0	0.016	0.006	94.1
	1000 ^{dem}	1.5	5.7	92.9	90.4	0.6	1.4	0.8	6.8	0.013	0.004	
	1400	25.3	0.2	74.5	97.4	0.2	0.5	1.9	0.0	0.005	0.006	93.5
	1400 ^{dem}	1.6	2.8	95.6	94.6	0.1	0.8	0.6	3.9	0.007	0.006	
Lethabo Coal	(-) ^{raw}	39.8	21.6	38.5	74.9	4.0	1.7	1.0	18.4	0.019	0.019	96.7
	(-) ^{dem}	1.3	28.2	70.6	77.4	3.5	1.2	1.9	16.0	0.013	0.022	
Lethabo Chars	740	49.8	4.3	45.9	95.6	1.0	1.8	1.4	0.2	0.016	0.012	94.0
	740 ^{dem}	3.0	9.9	87.1	89.2	1.6	1.8	1.0	6.5	0.017	0.016	
	980	48.9	0.7	49.3	96.6	0.1	2.0	1.3	0.0	0.018	0.007	95.5
	980 ^{dem}	2.2	5.8	92.0	93.2	0.5	1.4	0.7	4.1	0.013	0.006	
	1000	49.7	2.9	47.5	93.0	0.2	1.5	1.3	4.1	0.013	0.004	93.7
	1000 ^{dem}	3.2	6.5	90.3	89.6	0.6	1.5	0.6	7.6	0.014	0.006	
	1400	54.0	0.0	45.8	97.4	0.0	0.9	1.7	0.0	0.008	0.004	97.9
	1400 ^{dem}	1.1	4.0	94.8	93.2	0.0	0.7	0.5	5.6	0.007	0.005	
Matimba Coal	(-) ^{raw}	33.2	26.9	39.9	79.4	5.1	1.7	2.0	11.8	0.019	0.020	93.7
	(-) ^{dem}	2.1	32.0	65.9	79.7	4.8	1.7	2.2	11.6	0.018	0.019	
Matimba Chars	740	52.8	3.6	43.6	95.0	1.1	2.0	1.9	0.0	0.018	0.013	97.2
	740 ^{dem}	1.5	8.6	89.9	86.8	1.0	1.6	1.5	9.1	0.015	0.014	
	980	56.4	0.8	42.8	95.9	0.3	1.6	2.1	0.0	0.014	0.005	96.6
	980 ^{dem}	1.9	5.0	93.1	88.6	0.2	1.3	0.7	9.1	0.013	0.007	
	1000	43.2	1.0	55.8	94.5	0.1	1.5	1.5	2.3	0.013	0.004	94.7
	1000 ^{dem}	2.3	5.1	92.6	90.5	0.5	0.9	0.9	7.2	0.008	0.003	
	1400	46.2	0.5	53.3	97.5	0.3	0.5	1.2	0.4	0.005	0.003	91.4
	1400 ^{dem}	4.0	2.2	93.8	94.5	0.1	0.5	0.8	4.0	0.005	0.003	

*Pyrolysis temperature (°C); ^{raw}-Raw coal; ^{dem}-Demineralised coal or De-ashed char.

^aAnalyses conducted according to ISO 1171 (2010); ^bAnalyses conducted according to ISO 562 (2010).

^cAnalyses conducted by difference; ^dAnalyses conducted according to ISO 29541 (2010).

^eN/C_{ulti} and N/C_{xps} are evaluated from ultimate analysis (daf) and XPS respectively.

Proximate results are reported on dry basis (d.b), while elemental results are reported on dry ash free basis (d.a.f).

E_d represents demineralisation or de-ashing efficiency given by Equation 3.1.

The vitrinite random reflectance data showed that the coal samples are classified as bituminous, medium rank C coals, according to ISO 11760 (2005) classification of coals. The mean random reflectance for Glisa, Lethabo and Matimba coals were 0.75%, 0.60% and 0.72% respectively. Each of the three raw coals contained 3% (vol., mmb) liptinite. Glisa (69% inertinite & 18% Vitrinite, vol., mmb) and Lethabo

(46% inertinite & 15% vitrinite, vol., mmb) coals were predominantly composed of inertinite which is a typical macerals attribute of most of South African coals (Everson et al., 2008a; Phiri, 2010; Roberts et al., 2015b). However, Matimba coal constituted 50% vitrinite and 23% inertinite (vol., mmb). The vitrinite-class distributions showed standard deviations (σ) of <0.1 , which is typical of single seam, non-blend coals, according to the terminology of the ECE-UN International Codification System for Medium and High Rank coals (1988).

3.3.2 XPS N 1s analyses of coals and chars

The relative quantities of nitrogen functional forms present in the coals, demineralised coals, subsequent chars and the de-ashed counterparts were acquired through the deconvolution of the XPS N 1s spectra. For the sake of brevity, as it has been done before by several other researchers (Boudou et al., 2008; García et al., 2004; Pels et al., 1995; Valentim et al., 2011; Wójtowicz et al., 1995; Zhang et al., 2011), the nitrogen functional forms namely pyrrolic, pyridinic, quaternary and oxidised/protonated nitrogen shall be referred to as N-5, N-6, N-Q and N-X respectively.

The XPS N 1s spectra for Glisa, Lethabo and Matimba raw coals and their corresponding demineralised samples are presented in Figure 3.1. The three sub-peaks obtained from the deconvoluted XPS N 1s spectra corresponded to the energy positions of N-5 as the major sub-peak, followed by N-6 and N-Q, respectively. This trend is consistent with widely published results for raw or fresh coals (Kelemen et al., 2002, 1999, 1998; Pels et al., 1995; Valentim et al., 2011; Zhang et al., 2013). There was no marked effect resulting from the HCl/HF sequential treatment of the raw coal samples as deduced from the respective curve fitting of N 1s spectra. The spectra of demineralised samples were similar to that of untreated raw coals, implying that pyrrolic nitrogen was the most abundant form of organically bound nitrogen followed by pyridinic and the least being quaternary nitrogen. The accompanying relative distribution of nitrogen functionalities in coals, subsequent chars and acid treated counterparts, resulting from the XPS N 1s curve fitting process, are shown in Figure 3.1 through 3.4. Plots illustrating the XPS N 1s transformation as a result of heat treatment of the three coals and leaching on coal and subsequent chars are shown in Figure 3.5.

Heat treatment of coal samples introduced changes in nitrogen functional forms which are evident from the curve-resolved XPS N 1s spectral shapes in Figure 3.2 to 3.4 which represent a series of Glisa, Lethabo and Matimba chars and their corresponding de-ashed samples, respectively. The transformation brought by severe pyrolysis was accompanied by a substantial increase in relative amount of N-Q while N-5 decreased substantially, and a slight decrease in N-6 was also encountered. The

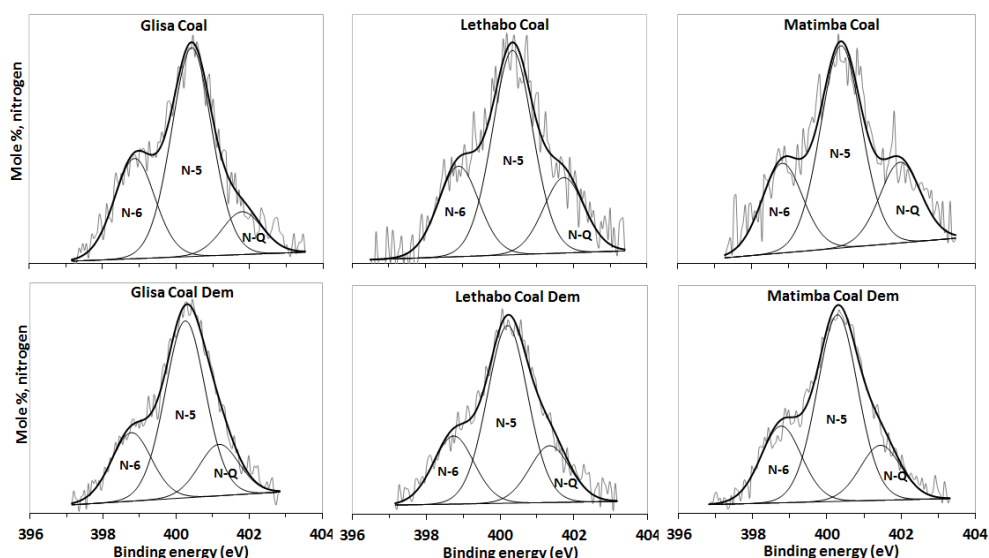


Figure 3.1: Nitrogen functional forms in the 3 raw coals and the respective demineralised coals as deduced from the N 1s XPS spectra. The XPS N 1s spectra of the untreated and acid treated char samples are shown in the same figure. Each figure illustrates the spectra for the de-ashed sample placed right below its untreated counterpart and its name has a **Dem** affix.

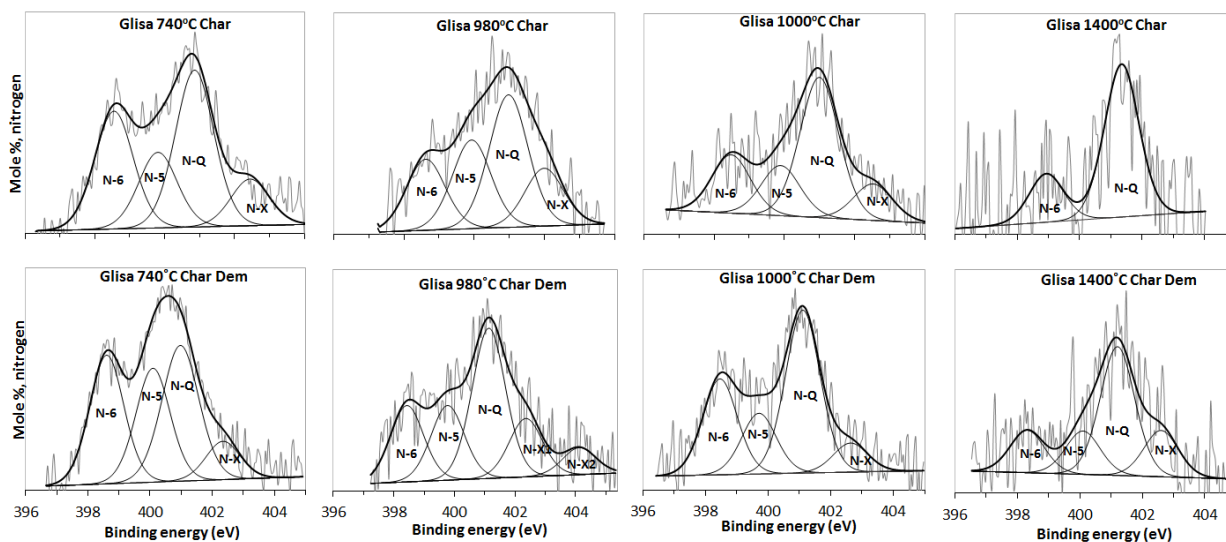


Figure 3.2: XPS N 1s spectra of Glisa chars prepared at various temperatures and their de-ashed counterparts.

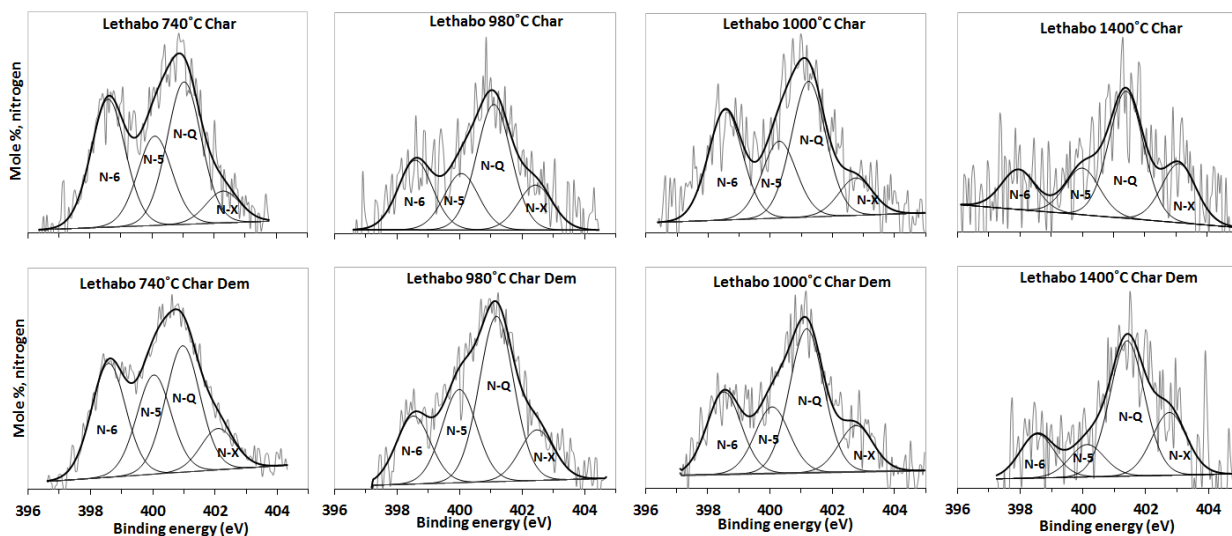


Figure 3.3: XPS N 1s spectra of Lethabo chars prepared at various temperatures and their de-ashed counterparts.

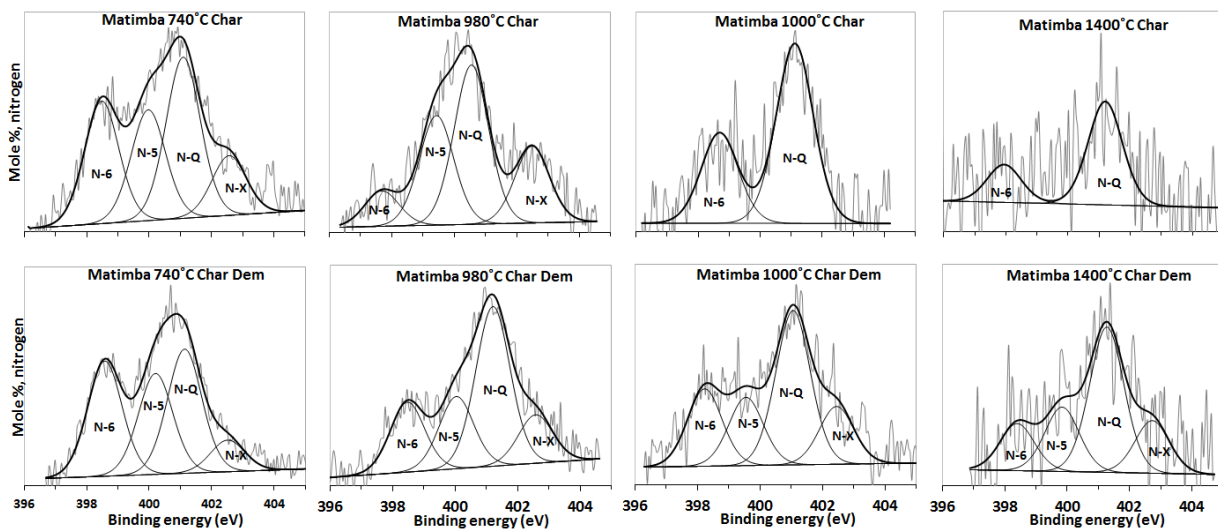


Figure 3.4: XPS N 1s spectra of Matimba chars prepared at various temperatures and their de-ashed counterparts.

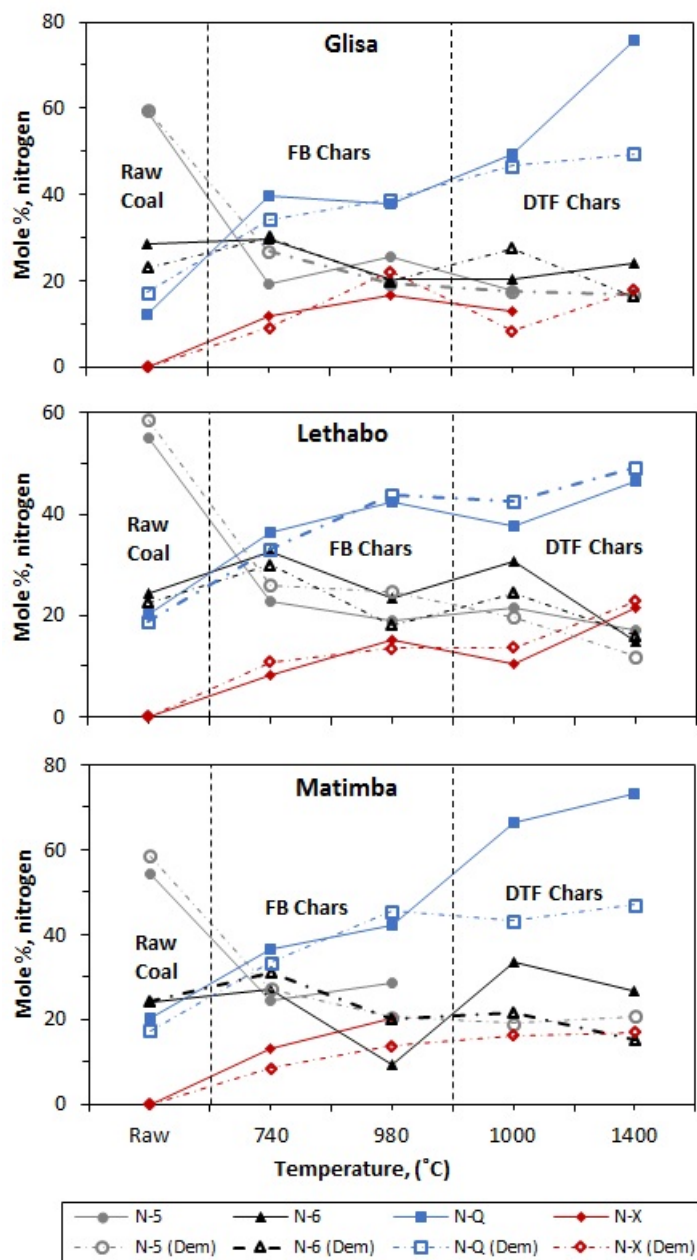


Figure 3.5: XPS N 1s transformations as a result of temperature and acid treatment.

abundance of N-Q sub-peak in chars is a result of nitrogen substituting for carbon in condensed polynuclear aromatic structures, partially aromatic/heterocyclic systems resulting in N being covalently bonded to three C atoms (N-Q) (Boudou et al., 2008). The heat treatment caused N positioned on the edges of the graphene layers to change location towards the inner parts of the graphene structures as result of condensation and/or polymerisation of polynuclear aromatic structures (Casanovas et al., 1996; Kelemen et al., 1999, 1998; Pels et al., 1995; Stańczyk et al., 1995; Valentim et al., 2011; Xiao et al., 2005). Therefore, the relatively high amount of N-Q in chars indicate that very large polynuclear aromatic structures were developed under the given pyrolysis conditions. In a parallel reaction, elevated temperatures resulted in elimination of edge-located N (N-5 and N-6) which was transported away as volatiles, either in the form of tar molecules or released in light gases as NH_3 and HCN (Bassilakis et al., 1993; Genetti and Fletcher, 1999; Jones et al., 1981; Niksa, 1995; Wójtowicz et al., 1995). Pels et al. (1995) attributed the diminishing of N-5 with increasing severity of pyrolysis as a result of the conversion of nitrogen present as pyridones into N-6, which takes place simultaneously with the reduction of oxygen associated with nitrogen. The apparent decrease in N-6 sub-peak was also brought by the oxidation of pyridine N resulting in N-X sub-peak emerging (Valentim et al., 2011). The fourth sub-peak, N-X, emerged in all the chars prepared from the FB at 740 and 980 °C although the peak was relatively lower in abundance as compared to the other three sub-peaks. The N-X sub-peak also appeared in the DTF chars curve resolved XPS N 1s spectra for Glisa 1000 °C, Lethabo at 1000 and 1400 °C chars.

The chars produced in a DTF at 1000 and 1400 °C had nitrogen content substantially decreased as indicated in Table 3.1. Some char samples had a N content as low as ~0.5 atom % (5 in 1000 atoms) which resulted noisy spectra being obtained. This phenomena is clearly illustrated by the noisy raw XPS N 1s signal of 1400 °C chars of Glisa, Lethabo and Matimba coals in Figures 3.2, 3.3 and 3.4, respectively. Nonetheless, N-5 and N-X peaks were not observed in all the deconvoluted XPS N 1s spectra for Matimba DTF chars and 1400 °C Glisa char. The absence of the N-5 and N-X peaks is clearly evident in the N 1s spectrum for Glisa 1400 °C char as shown in Figure 3.2. The N-5 and N-X sub-peak absence is also evident in all N 1s spectra of Matimba DTF chars (1000 and 1400 °C) as illustrated in Figure 3.4. N-Q and N-6 are the only remaining sub-peaks in the Glisa char prepared at 1400 °C, Matimba chars produced 1000 and 1400 °C, respectively. Pels et al. (1995) and Wójtowicz et al. (1995) attributed the occurrence of N-X sub-peak in chars due to high reactivity of severely heat-treated chars towards oxidation resulting in the formation of N-oxides. Stańczyk et al. (1995) proposed that this transformation occurs at high temperatures through the transformation of quaternary nitrogen to N-oxides.

Acid treatment did not cause any significant changes in nitrogen functional forms in all chars prepared from the fluidised bed as illustrated on Figure 3.5. However, apparent changes occurred in the N 1s XPS spectra for severely pyrolysed DTF Glisa and Matimba chars after acid treatment. The XPS N 1s spectra of Glisa and Matimba chars produced under severe pyrolysis conditions were quite different (1400° for Glisa; 1000°C and 1400°C for Matimba), all the pyrrolic nitrogen present in raw coals and the subsequent FB chars disappeared at this stage, of which most of it was converted to N-Q and N-6, with the former being the major constituent. This behaviour has been reported in other studies for coals of different ranks (Pels et al., 1995; Wójtowicz et al., 1995). In spite of that, the XPS N 1s spectra for corresponding de-ashed chars, Glisa 1400 °C, Matimba 1000 and 1400 °C respectively, revealed that the acid treatment caused some organic structural changes to the nitrogen functional forms characterised by the conversion of some of the inherent N-6 and N-Q to N-5 and N-X. However, quaternary nitrogen remained the predominant nitrogen functional form in all the remains of de-ashed char samples.

The XPS N 1s spectrum for de-ashed Glisa 980°C char in Figure 3.2 shows two sub-peaks within the N-X N 1s electron binding energy range (Valentim et al., 2011), hence the reported relative mole % represents the summation for the two N 1s sub-peaks with a binding energy of 402.4 and 404.1 eV respectively. Suzuki et al. (1994) and Valentim et al. (2011) attributed these two sub peaks which are mostly encountered in chars between 402 and 405 eV to pyridinic N-oxide complexes (N-X). De-ashed char contains very little or no silicate minerals that can host ammonium, therefore the N 1s XPS N-X sub-peak at 404.1 eV of the de-ashed char in this instance cannot be due to the presence clay-bound NH_4^+ but N-Q.

The chars derived from the high ash and inertinite-rich Lethabo coal displayed greater resilience towards drastic N 1s transformations within the high DTF temperatures as shown in Figures 3.3 and 3.5, compared to the other two coals. A steady increase of N-X was attained with increasing temperature, such that the N-X in Lethabo char prepared at 1400 °C (Lethabo 1400 °C in Figure 3.3) exceeded the relative quantities of N-5 and N-6, it was however still lower compared to the relative amount of N-Q. The Lethabo char produced at 1400°C and its respective de-ashed remnant (Figure 3.3) had the largest relative abundance of N-X compared to all other chars. This could be caused by the presence of substantial amounts of ash and the high temperature employed. Acid treatment of all the respective Lethabo chars caused no marked change towards the nitrogen functionality. On the other hand, Glisa coal, which is also inertinite-rich but having relatively low ash displayed enormous nitrogen functional form transformation at 1400 °C resulting in a char with only quaternary and pyridinic nitrogen. However, the acid treatment of these chars

with only N-Q and N-6 peaks led to the introduction of a considerable relative amount of N-5 and N-X such that the relative quantity of N-5 and N-6 were virtually equal in the de-ashed remnants as depicted by Glisa 1400 °C Char Dem in Figure 3.2, Matimba 1000 and 1400 °C Char Dem in Figure 3.4.

Louw et al. (2015) pointed out that inertinite-rich coal undergoes limited fluidity during heat treatment, however, chars derived from vitrinite-rich coals displayed more significant structural transformations. These are some of the differing attributes of chars emanating from heat treated vitrinite- and inertinite-rich coals. The structural changes could be one of the reasons rendering the chars prepared from vitrinite rich chars at extremely high temperatures to be susceptible to nitrogen functional form changes after acid treatment. The inducement of N-5 in the de-ashed chars which are derived from severely pyrolysed Matimba DTF chars may be attributed to the conversion of N-6 to pyridones. The same argument applies to the Glisa char produced at 1400°C and its de-ashed counterpart. Pyridinic nitrogen structures are found on the edge of the graphitic polynuclear structures, the most likely explanation towards the emergence of N-X sub-peak from de-ashed char remnants is through oxidation of the pyridinic nitrogen. The emergence of the N-X sub-peak in these chars is most probably as a result of the oxidation of char surface by HCl and HF.

After acid treatment, Kelemen et al. (1995) observed that quaternary nitrogen species increased in abundance in two of the coals they worked on, whereas no change was witnessed on the third sample. They further reported that on treatment of the coals with a strong organic acid, more than 50% of the observed level of pyridinic nitrogen forms in one of the coals were converted into quaternary nitrogen species. However, no significant changes emanated from the treatment of coals by weak organic acids.

3.4 Conclusions

The effect of acid treatment on nitrogen functional forms on South African bituminous coals and the subsequent chars produced during pyrolysis was studied. The HCl/HF sequential demineralisation procedure had no significant effect on the nitrogen functional forms in all the three bituminous raw coals. Acid treatment of chars prepared from the FB and the entire set of chars derived from high ash and inertinite-rich coal (Lethabo) caused no marked change to the nitrogen functional forms. Severely pyrolysed chars prepared from high ash and vitrinite-rich coal by the DTF only constituted of quaternary and pyridinic nitrogen, however acid treatment changed the organic nitrogen structural forms by inducing a portion of pyrrolic and

oxidised-pyridinic/protonated nitrogen. Severely pyrolysed char (1400 °C) from a relatively low ash and inertinite-rich, of which also had only two sub-peaks representing quaternary and pyridinic nitrogen also underwent similar organic nitrogen structural changes after de-ashing. This revelation of the non-altering nature of nitrogen functional forms in coals, chars produced within the FB temperature range and some of the high temperature DTF chars (derived from high ash and inertinite-rich coal) after acid treatment is very important on the prospects of conducting exercises like molecular modelling.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this Chapter is outlined below, and it is also available on the online version of the article at: <http://dx.doi.org/10.1016/j.jaap.2017.04.009>.

Abstract

The supplementary Table 3.2 contains information that was obtained from Figure 3.1 to 3.4 in the main body of the Chapter 3 “The effect of acid demineralising bituminous coals and de-ashing the respective chars on nitrogen functional forms”. The data relates to the distribution of nitrogen functional forms in coals, demineralised coals, subsequent chars and de-ashed counterparts, emanating from the XPS N 1s curve fitting exercise. The data in the supplementary Table was used to plot Figure 3.5.

References

Please note that references for this chapter are consolidated in the main references on page 113.

CHAPTER 3. THE EFFECT OF ACID DEMINERALISING BITUMINOUS COALS AND DE-ASHING THE RESPECTIVE CHARS ON NITROGEN FUNCTIONAL FORMS

Table 3.2: Comparison of nitrogen functional forms as detected from N 1s XPS spectra in raw coal, respective chars and acid treated counterparts.

N-Functional Forms	Binding Energy (eV)	Glisa Coal		Glisa 740°C		Glisa 980°C		Glisa 1000°C		Glisa 1400°C	
		Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed
Pyrrolic (mol %)	400.3±0.2	59.31	59.60	19.05	26.67	25.33	19.32	17.59	17.43	-	16.63
Pyridinic (mol %)	398.6±0.2	28.51	23.08	26.69	30.14	20.31	17.76	20.46	27.52	24.11	16.29
Quaternary (mol %)	401.4±0.3	12.08	17.32	39.51	34.22	37.84	38.84	49.18	46.71	75.89	49.34
N-oxide (mol %)	402.4±0.4	-	-	11.75	8.97	16.52	15.10	19.73	8.34	-	17.74

N-Functional Forms	Binding Energy (eV)	Lethabo Coal		Lethabo 740°C		Lethabo 980°C		Lethabo 1000°C		Lethabo 1400°C	
		Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed
Pyrrolic (mol %)	400.3±0.2	55.18	58.71	22.81	26.05	19.03	24.73	21.35	19.63	17.09	11.82
Pyridinic (mol %)	398.6±0.2	24.45	22.53	32.69	29.91	23.49	18.05	30.60	24.34	14.70	16.03
Quaternary (mol %)	401.4±0.3	20.37	18.76	36.37	33.19	42.34	43.81	37.67	42.41	46.61	49.29
N-oxide (mol %)	402.4±0.4	-	-	8.13	10.85	15.15	13.41	10.38	13.63	21.61	22.86

N-Functional Forms	Binding Energy (eV)	Matimba Coal		Matimba 740°C		Matimba 980°C		Matimba 1000°C		Matimba 1400°C	
		Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed	Raw	De-ashed
Pyrrolic (mol %)	400.3±0.2	54.26	58.60	24.40	27.12	28.75	20.62	-	19.08	-	20.82
Pyridinic (mol %)	398.6±0.2	24.08	24.11	27.01	30.99	9.29	19.98	33.52	21.63	26.81	15.23
Quaternary (mol %)	401.4±0.3	20.37	18.76	36.37	33.19	42.34	43.81	66.48	42.41	73.19	46.95
N-oxide (mol %)	402.4±0.4	-	-	13.13	8.5	20.18	13.84	-	16.14	-	17.00

CHAPTER

4

TRANSFORMATION OF NITROGEN FUNCTIONAL FORMS AND THE ACCOMPANYING CHEMICAL-STRUCTURAL PROPERTIES EMANATING FROM PYROLYSIS OF BITUMINOUS COALS

Note: *This chapter has been published as:*

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<https://doi.org/10.1016/j.apenergy.2018.02.107>.

Highlights

- Transformations in N functionalities and carbon crystallite structures were examined.
 - Pyrolysis caused the change in aromaticity to correlate with quaternary-N of chars.
 - Diminishing pyrrolic-N in chars correlated with the degree of disorder index (DOI).
 - Total reactive macerals in coal influence morphological changes at high temperatures.
 - Vitrinite- and inertinite-rich coal chars displayed similar and varying N forms.
-

Abstract

Characterisation of simultaneous changes in nitrogen functionalities and condensed aromatic crystallites during pyrolysis of bituminous coals was conducted. X-ray photoelectron spectroscopy (XPS) was utilised to determine nitrogen functional forms in three South African bituminous coals and the subsequent transformation in respective chars. Corresponding structural properties of coal and char were deduced through X-ray diffraction (XRD) analysis. Carbon structural properties in parent coals were also determined by solid state ^{13}C nuclear magnetic resonance (ss NMR). The chars were prepared by pyrolysis at 740-980 °C in a bench-scale fluidised-bed (FB) and at 1000-1400 °C in a drop-tube furnace (DTF). The changes in XPS N 1s spectra of the coals through the respective chars were used to determine the nitrogen functionality transformations. Deconvolution of the XPS N 1s spectra revealed that pyrrolic nitrogen decreased with increasing pyrolysis temperature while quaternary nitrogen increased appreciably. Simultaneously, information deduced from XRD spectra showed that aromaticity (f_a) and average crystallite diameter (L_a) increased with severity of pyrolysis temperature in all the chars, while the fraction of amorphous carbon (X_A) and degree of disorder index (DOI) decreased significantly. Chars derived from the vitrinite-rich (also high in total reactive macerals) coal were more susceptible to thermal treatment with regard to nitrogen functional forms and other carbon crystallite transformations; high temperature chars only contained pyridinic and quaternary nitrogen, and exhibited a significant increase in crystallite height (L_c) and the average number of aromatic carbons (N_{ave}). Aromaticity of coals determined from ss ^{13}C NMR and XRD corresponded. Comparison of structural changes brought by pyrolysis, as measured by XPS and XRD, showed that a good correlation existed between increasing quaternary nitrogen and f_a . In a marked contrast, the diminishing of pyrrolic nitrogen displayed a good efficacy with DOI and X_A . The reported concomitant transformations of nitrogen functional forms with char morphological

changes are considered precursors to nitrogen release. This will inform future detailed studies on the conversion of coal nitrogen in solid fuel fired systems, such as in the applications of low-NO_x burner technologies towards the release and reduction of nitrogen oxides in pulverised coal combustion.

Keywords

Nitrogen forms transformation; Carbon crystallite; Pyrolysis; XPS; XRD; Char morphology

4.1 Introduction

Coal is integral to the economies of several countries and regions around the world as it provides reliable and affordable power required to meet electricity demand and fuel economic growth. Bituminous coals are mostly used for steam production in the electric power generation industry across the globe. When coal is introduced into a combustion or gasification chamber it goes through pyrolysis (devolatilisation) during the primary stage of combustion or gasification which results in coal nitrogen to be partitioned into char nitrogen and volatile nitrogen, of which the volatile-N consist of NH₃, HCN and tar-N (Johnsson, 1994; Solomon and Colket, 1978; Tsubouchi, 2014; Yuan et al., 2012). Nitrogen oxides are formed during the subsequent combustion. Coal-N is the dominating source of nitrogen oxides in most solid fuel combustion systems (Glarborg et al., 2003), contributing more than 80% from pulverised coal combustion (Tsubouchi and Ohtsuka, 2008), and almost all the NO_x (NO and NO₂) and nitrous oxide (N₂O) emissions from fluidised bed combustion (Wójtowicz et al., 1993). Once devolatilisation is complete, char-N becomes the source of subsequent nitrogen release during pyrolysis/combustion/gasification (Thomas, 1997; Tsubouchi, 2014). NO_x has been condemned for causing acid rain, ground level ozone and photochemical smog, while N₂O is a potent greenhouse gas that has been blamed for indirectly depleting the ozone layer (Carpenter et al., 2006).

The complexity and heterogeneity of coal and its subsequent products presents the most persistent difficulty in characterisation endeavours. A variety of coal structural models have been proposed as a result of its inherent heterogeneous nature (Mathews and Chaffee, 2012). Hence the need to employ different conventional and novel advanced characterisation techniques to elucidate the structure of coal and related substances. Some of the advanced analytical techniques that have been utilised by many researchers to elucidate coal or char molecular chemical structure include XPS, solid state nuclear magnetic resonance (ss ¹³C and ¹⁵N NMR), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Fourier transform

infrared spectroscopy (FTIR) and Raman spectroscopy. These analytical methods have been applied on coal and char analyses with variable outputs ([Almendros et al., 2003](#); [Compagnini et al., 1997](#); [Dun et al., 2013](#); [Kelemen et al., 2007](#); [Knicker et al., 1996](#); [Okolo et al., 2015](#)). Nonetheless, coal structure and related substances which include coal chars are still yet to be fully understood. The comprehension of chemical and physical processes that determine formation of nitrogen oxides during combustion of solid fuels continue to pose a challenge despite considerable research having been conducted in the past four decades ([Glarborg et al., 2003](#)). Quite a number of studies have tried to correlate NO_x emissions to coal properties, however, so far there is no generic relationship or model that precisely predicts the level of nitrogen oxides beyond the data set upon which it was established. Almost all of the correlations were dependent on the application of basic coal attributes determined by the standard proximate and ultimate analyses ([ISO 1171, 2010](#); [ISO 29541, 2010](#); [ISO 562, 2010](#)). There are issues that limit the potential reduction of nitrogen oxides that still require to be resolved. Further enlightenment of nitrogen chemistry in solid fuel fired systems is beneficial towards the improvement of primary measures for the control of nitrogen oxides.

In general, coal contains about 1–2% nitrogen by weight (daf) ([Davidson, 1994](#); [Niksa, 1995](#)), most of which exists as organically bound N-containing heteroatomic ring structures ([Davidson, 1994](#); [Knicker et al., 1995](#)). Nitrogen in coal organic fraction originates from proteins of plants and micro-organisms, of which most of the proteins were transformed by biological reactions during the early stages of coalification resulting in different types of nitrogenous compounds being formed ([Flaig, 1968](#)). X-ray photoelectron spectroscopy (XPS) analyses on coals and chars have revealed that these heteroatomic structures mainly exists in the form of pyrrolic (N-5), pyridinic (N-6), quaternary (N-Q) and to a lesser extent, as protonated and/or oxidised pyridinic (N-X) nitrogen structures ([Kelemen et al., 1998](#); [Leppälahti and Koljonen, 1995](#); [Pels et al., 1995](#)). In exceptional circumstances a fifth nitrogen form, nitro type complexes (-NO₂), with binding energy above 405 eV has been reported in chars and model compounds ([Pels et al., 1995](#); [Valentim et al., 2011](#)).

XRD has traditionally been utilised for qualitatively and quantitatively analysing the mineral constitution of coal. However, the technique has also proven to be a powerful tool in elucidating carbon crystallite properties of demineralised coals and structural transformations occurring in respective de-ashed chars due to heat treatment ([Feng et al., 2003](#); [Hattingh et al., 2013](#); [Lu et al., 2002](#); [Maity and Mukherjee, 2006](#); [Roberts et al., 2015a](#)). ¹³C NMR spectroscopy has been utilised to elucidate the structural differences between coals, tar and char ([Genetti et al. \(1999\)](#); [Lin et al. \(2014\)](#); [Sun et al. \(2003\)](#)). XPS has been widely utilised for determining and quanti-

fying nitrogen functional forms in complex solid and non-volatile carbonaceous systems, including in the transformation of nitrogen species during pyrolysis of coal and model compounds (Boudou et al., 2008; Kelemen et al., 1994, 1998; Pels et al., 1995; Stańczyk et al., 1995; Valentim et al., 2011). The distribution of nitrogen functional forms varies with increasing intensity of pyrolysis conditions (Pels et al., 1995; Zhang et al., 2013).

During pyrolysis, the heteroatoms are removed through devolatilisation of nitrogen, sulphur, and oxygen compounds, decreasing the number of these edge-located atoms and causing carbon structure rearrangement (van Heek and Mühlen, 1991). In high temperature chars, N-Q becomes the prominent form of nitrogen. The edge-located nitrogen species (N-5 and N-6) are liberated into the volatile stream as NH₃, HCN, N₂ or conveyed as part of the tar molecules (Deng et al., 2013; Genetti and Fletcher, 1999; Kambara et al., 1993). Pels et al. (1995) showed that carbazole, a rich source of N-5, at temperatures exceeding 800 °C a significant portion of N-5 was transformed into N-6 and N-Q. In addition, acridine which is a source of N-6, lead to the conclusion that heat treatment transforms a portion of N-6 into N-Q. Quaternary nitrogen can emanate from both organic and inorganic origins (Buckley et al., 1995; Dai et al., 2012; Daniels and Altaner, 1993).

A great portion of Gondwana coals of the Permian age are bituminous coals and an infrequent existence of anthracites (Cai and Kandiyoti, 1995; Cairncross, 2001). Some of the coals in the southern Africa region share similar attributes with the coals that also emanated from the splinter Gondwana regions that encompass India, Madagascar, Australia, Antarctica and South America (Cai and Kandiyoti, 1995; Falcon and Ham, 1988). These coals are characterised by high levels of mineral matter and inertinite content (Cadle et al., 1993; Cairncross, 2001). However, there is contrast that is exhibited by the age and basins of the coals. The Carboniferous coals of the Laurasian region (northern hemisphere) are generally high in vitrinite and contain low mineral matter (Snyman and Botha, 1993). The North Atlantic coals of the Palaeozoic and Mesozoic age show an average petrographic composition that is dominated by vitrinite with averages of 70% and 74% (mmf) respectively. Nonetheless, the Gondwana counterparts of the same age also displayed maceral compositions dominated by vitrinite, but much less, averaging 52% and 65% (mmf) respectively (de Sousa e Vasconcelos, 1999). In further comparisons, de Sousa e Vasconcelos (1999) stated that coals of the Tertiary emanating from both the North Atlantic and Gondwana territories have similar petrographic compositions with vitrinite ≈80% and inertinite ≈10% (mmf). Generally, coals in South Africa (SA) are Permian, apart from a very small deposit in the Molteno area, which is Tertiary. The Main Karoo Basin hosts the Free State-, Witbank-, Highveld-, Ermelo- and KZN coal deposits, which

formed around a large inland delta. Coals are typically inertinite-rich and mineral matter content that is quite high (Falcon and Ham, 1988). The Limpopo Province Coalfields, which includes the Waterberg Coalfield, were formed in small basins tectonically different in that they were half grabens or grabens (Cairncross, 2001). The coals in these coalfields are typically vitrinite-rich and high in mineral matter content. South Africa is one of the countries that are heavily dependent on coal, a substantial portion of the SA's liquid fuels are produced from bituminous coals, the coals are also utilised to generate more than 90% of the country's electricity (Hancox, 2016).

The behaviour of nitrogen that is inherently present in coal, which is the major source of nitrogen oxides, needs to be closely monitored during coal conversion processes to enable coal optimum utilisation with minimum environmental implications. The manifestation of such achievements, that will ensure prolonged usage of coal, require close examination on the transformation of nitrogen within the immediate carbonaceous environment of coal-chars towards aspirations to gain an in-depth insight into the release of nitrogen species. There appear to be a need for systematic studies that simultaneously monitor the association of nitrogen functional forms with the accompanying changes of carbon crystallite properties during coal pyrolysis. Previous studies by other researchers were exclusively focusing on either nitrogen functionalities using XPS or the elucidation carbon structural properties deduced from XRD. This study aims at evaluating the simultaneous transformation of nitrogen functionalities and condensed aromatic crystallites during pyrolysis of SA bituminous coals in a bench-scale bubbling fluidised bed (FB) and drop-tube furnace (DTF) through the application of a battery of analytical methods, mainly incorporating XPS and XRD, respectively. The crux of the matter is to establish an insight on the relationship between the changes in carbon crystallite structure and the concomitant transformation of nitrogen functional forms. The partitioning of nitrogen in coal (coal-N) into volatile-N and char-N is one of the important aspects determining the formation of nitrogen oxides (NO_x and N₂O) in the successive combustion process (Johnsson, 1994; Thomas, 1997). Nitrogen constitutes a small portion of coal (1-2 wt.%, daf), while carbon forms the largest component, hence the need to consider a holistic approach by factoring in carbon structural attributes and their relation to N transformations. The chemistry of this association might be a key factor towards the release of precursors of nitrogen oxides (tar-N, HCN and NH₃) during devolatilisation (pyrolysis), which is the initial stage that precedes combustion. It is perceived that the morphological rearrangements are probably directly responsible for coal-N release, and also this connection has received little, if any, detailed monitoring in the past. Char-N becomes the only source of nitrogen release during the later stages of pyrolysis/combustion/gasification (Thomas, 1997; Tsubouchi, 2014), hence the im-

portance of its monitoring within the condensed aromatic structures. The changes in aromatic crystallites during pyrolysis and the accompanying transformation of N functional forms has important practical implications and may ultimately lead to improved kinetic mechanisms for coal-N release in solid fuels fired systems.

4.2 Material and methods

4.2.1 Origin of coal samples and char preparation

Run-of-mine coal samples that were utilised by [Phiri et al. \(2017\)](#) were also used in this study, viz. Glisa, Lethabo and Matimba. Glisa coal originates from Glisa Colliery in the Witbank Coalfield, in South Africa's Mpumalanga Province. Lethabo coal was extracted from New Vaal Colliery which is situated in the Sasolburg Coalfield stretching in the north of Free State Province. These two respective coalfields exist within rocks of the Main Karoo Basin and the coals are typically inertinite-rich, with high mineral matter. Matimba coal sample was obtained from Grootgeluk Colliery in the Waterberg Coalfield, located in Limpopo Province. The Waterberg Coalfield was formed in small basins tectonically different in that they were half grabens or grabens. The coals here are typically vitrinite-rich and contains high mineral matter. These three coals are mainly used as fuel feed stock in power plants. Typical SA coals are uniquely distinguished by a well defined rank, maceral composition and mineral content ([Everson et al., 2008b](#); [Roberts et al., 2015a](#)).

The description of FB and DTF, and detailed char preparation procedure, were furnished by [Phiri et al. \(2017\)](#). Pyrolysis in the FB were carried out by feeding ± 1 mm coal particles which were premixed at 1:1 ratio with fluidising material (silica sand) into the preheated reactor at 21 g/min. Devolatilisation took place in 99.995% N₂ at a heating rate of $>10^4$ °C/s at 740, 820, 900 and 980 °C respectively. Pulverised coal with size particles of $-75\text{ }\mu\text{m}$ were fed into the DTF at 1 g/min aided by 99.995% N₂ primary gas. The pyrolysis experiments were conducted at 1000, 1130, 1270 and 1400 °C respectively, the coal particles experienced a heating rate of $>10^4$ °C/s as they traversed down the heated zone of the reactor. A residence time of 1.8 s for each DTF experimental run was achieved through appropriately positioning the water cooled collection probe in conjunction with predetermined experimental conditions.

4.2.2 Sample preparation

The HCl/HF/HCl sequential demineralising of coals and de-ashing of the respective chars was performed ([Everson et al., 2013b](#); [Phiri et al., 2017](#)), to curb the interference that might occur in some analytical techniques due to the presence of mineral

matter or ash (Boral et al., 2015; Maity and Choudhury, 2008; Maity and Mukherjee, 2006; Strydom et al., 2011). The resultant demineralised coal samples were treated with samarium (II) iodide (SmI_2) prior to ss ^{13}C NMR analysis (Molander, 2004; Muntean and Stock, 1991). The selective chemical reduction by SmI_2 treatment results in partial elimination of free radicals and hence improving the quantifiable fraction of observable carbon, thus improving structural information attainable by ^{13}C NMR analysis (Muntean et al., 1988).

4.2.3 Conventional coal and char analyses

Proximate and ultimate analyses of coals and the respective chars were carried out by Bureau Veritas Testing and Inspections SA. The procedures followed and standards adhered to are outlined by Phiri et al. (2017). Petrographics SA conducted the petrographic analysis of the parent coals. Petrographic sample preparation was conducted using the guidelines of ISO 7404: 2 (1985) while the group maceral analysis was performed according to ISO 7404: 3 (1994). The reactive inertinite macerals were determined as outlined by Steyn and Smith (1977). Both commercial laboratory facilities are situated in Pretoria, South Africa.

4.2.4 XPS N 1s spectra acquisition and processing

X-ray photoelectron spectroscopy was used to determine and quantify organically bound nitrogen functional forms present in parent coals and the respective transformation in chars brought by pyrolysis. The analyses were conducted at the Centre for Microscopy and Microanalysis (The University of Queensland, Australia). XPS N 1s signals were acquired and recorded using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer that incorporate a 165 mm hemispherical electron energy analyser. Phiri et al. (2017) furnished the detailed equipment specifications, conditions utilised, and the deconvolution procedure applied on the XPS N 1s spectra to determine sub-peaks that in essence serve as the identification and quantification of nitrogen functionalities.

4.2.5 XRD analysis of coals and chars

X-ray diffraction of demineralised coals and de-ashed chars was performed by a commercial laboratory facility, XRD Analytical and Consulting in Pretoria, South Africa (Everson et al., 2013b; Roberts et al., 2015a). Demineralised coal and de-ashed char samples were used to curb the noise effects on the diffractogram resulting from the presence of mineral matter (Everson et al., 2013b; Okolo et al., 2015; Roberts et al., 2015a). Carbon crystallite analysis was performed in line with the ASTM D-5187

(2002) standard and also as described by [Everson et al. \(2013b\)](#) and [Iwashita et al. \(2004\)](#). Approximately 2 g of demineralised coal or de-ashed char samples were prepared for XRD analysis using a backloading preparation method. The samples were analysed by a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation at ambient temperature. The X-ray intensities were detected in a continuous scan over a range of $4.0^\circ \leq 2\theta \leq 120^\circ$ with a scan step time of 13.3 s and a step size (2θ) of 0.017° .

Figure 4.1 illustrates corrected and smoothed diffractograms for Glisa coal and the respective FB chars prepared at different temperatures. The small spikes appearing on the coal diffractogram represent traces of mineral remnants in the analysed sample ([Everson et al., 2013b](#)). The peak positions, indicated by (002), (10) and (11) on the diffractograms provide useful information towards the determination and calculation of crystallite lattice parameters. In carbonaceous crystallites, the (002) and (10) peaks are ascribed to the stacking of the graphitic basal planes and the hexagonal ring structure, respectively ([Zhang et al., 2008](#)). Coal and chars are made up of different carbon structures hence the normalised (002) peak of the XRD spectra were deconvoluted into Gaussian curves as shown in Figure 4.2, illustrating the determination of the amorphous carbon fraction (X_A) in 740 °C Glisa char. The ratio of carbon atoms in aliphatic side chains against aromatic rings gives the aromaticity of carbonaceous materials ([Lu et al., 2001](#)). The HighscorePlusTM application was utilised to determine the aromaticity (f_a) of coal and char samples through the distinctive areas under the (002) peak. The area under the left-most part of the γ -band represents the portion of aliphatic carbon atoms, while the area under the remaining section of (002) peak corresponds to the aromatic carbons ([Lu et al., 2002, 2001; Sahajwalla et al., 2004](#)). The degree of disorder index (DOI), which express the disorderliness of carbon crystallites, was evaluated from f_a and X_A using a relationship that is outlined by Equation 4.1 ([Everson et al., 2013b](#)).

$$DOI = X_A + (1 - X_A)(1 - f_a) \quad (4.1)$$

The carbon crystalline structure parameters of coals and chars were deduced from the XRD diffractograms. Carbon crystallite lattice parameters which incorporate inter layer spacing (d_{002}) and crystallite height (L_c) were deduced from the crest and the full width at half maximum (FWHM) of the (002) peak respectively ([Everson et al., 2013b](#)). L_c was calculated from the XRD diffractograms using the Scherrer equation ([Cullity, 1978](#)). The average number of aromatic layers per carbon crystallite (N_{ave}) was derived from the calculated values of d_{002} and L_c in accordance with the procedure developed by [Trejo et al. \(2007\)](#). The crystallite diameter (L_a) is inversely proportional to the width of the (10) peak ([Zhang et al., 2008](#)). There were no struc-

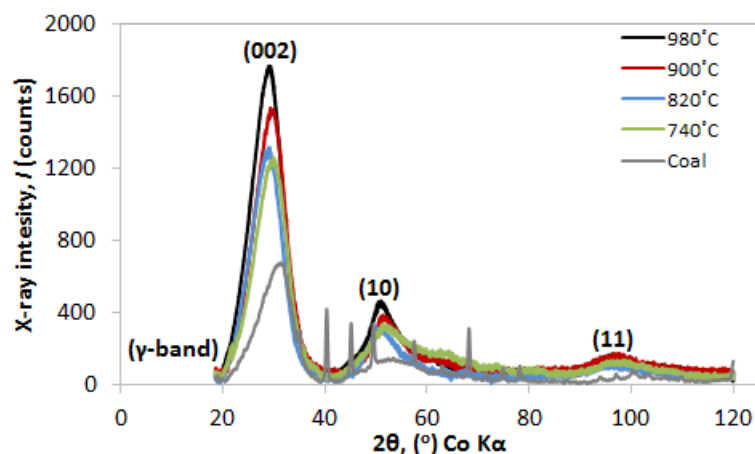


Figure 4.1: Baseline corrected and smoothed XRD diffractogram of Glisa coal and the respective FB chars.

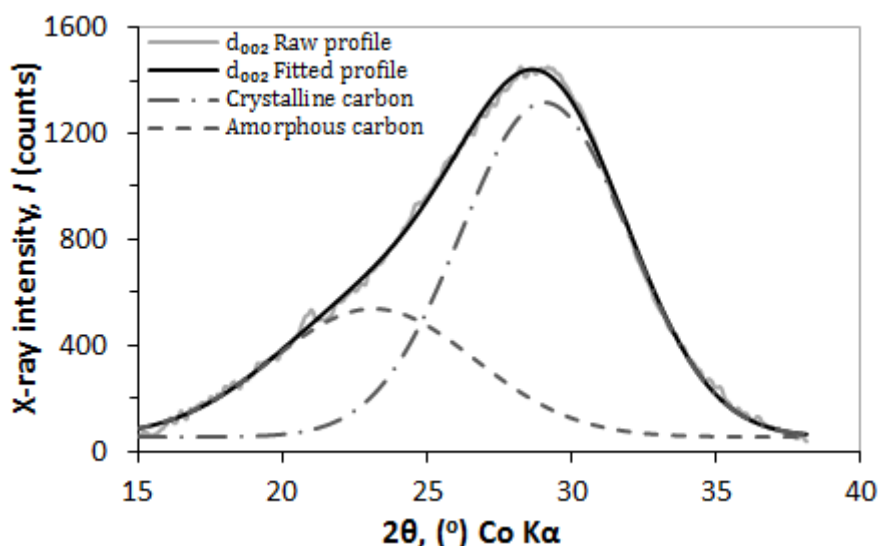


Figure 4.2: Determination of amorphous carbon fraction (X_A) through the Gaussian curve deconvolution of the (002) peak of Glisa 740°C char.

tural properties that were determined from the (11) peak because of its spread out and inconspicuous nature.

4.2.6 Solid state ^{13}C NMR spectroscopy

To determine the structural parameters of coal samples, NMR analyses, which encompass cross-polarisation magic angle spinning (CP MAS) and dipolar dephasing (DD), were conducted at Stellenbosch University in South Africa. The ss ^{13}C NMR spectra were obtained from the Varian VNMRs 500 MHz two-channel spectrometer which consists of 4 mm zirconia rotors and a 4 mm ChemagneticsTM T3 HX MAS

probe. The CP spectra were acquired at ambient temperature with proton decoupling, and employing a relaxation delay of 3.0 s and executing 8000 scans to achieve a tolerable signal-to-noise ratio. The Hartmann-Hahn match power parameters were fine-tuned as follows; radio frequency fields set at $\gamma C B_{1C} = \gamma H B_{1H} \approx 56$ kHz, where γC and γH represent the magnetogyric ratios of carbon and proton respectively, and their corresponding radio field strengths which are B_{1C} and B_{1H} (Roberts et al., 2015a). Cross-polarization contact time was pegged at 2.0 ms. The free induction decay was 3500 points and Fourier transformed with a 50 Hz line broadening. The MAS was carried out at 12 kHz and Adamantane was employed as an external chemical shift standard, by which the methyl peak was referenced to 38.4 ppm. The DD analyses (Hatcher, 1987), were conducted under similar conditions of which the interrupted decoupling time constant, $t_{1Xidref}$, was fixed at 40 μ s after evaluating an array of time constants. Prior to integration, the spectra were individually phased and baseline corrected. The adjustments of integration reset points and coal structural parameters evaluation from integral values were in line with Solum et al. (1989). To reduce operator bias, all spectra were processed in the same way, concurrently.

4.3 Results

4.3.1 Proximate and ultimate analyses

The results for proximate and ultimate analyses are shown in Table 4.1. Substantial decrease of volatile matter was witnessed with increasing pyrolysis temperature with respect to all the three coals. Elemental analysis showed that the proportion of nitrogen that was retained in FB chars is similar to that initially present in parent coals. However, under DTF conditions, there was a significant loss of nitrogen into the volatile stream leaving char remnants with low nitrogen content as pyrolysis temperature increased, as elaborated by the absolute nitrogen ($|N|$). The content of fixed carbon increased appreciably on devolatilisation.

4.3.2 Petrographic properties

Maceral analysis results are furnished in Table 4.2. The three coals were classified as bituminous, Medium Rank C coals according to vitrinite random reflectance. About 96% of SA coals are bituminous, 2% are anthracite and the remaining are basically coking coals. In summary, the 3 coals were mainly distinguished by mineral matter content and maceral composition; of which Glisa coal is inertinite-rich and has relatively low mineral matter content (compared to the other two coals), Lethabo coal is predominantly inertinite and high in mineral matter. These are typical attributes

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Table 4.1: Chemical properties of raw coals and respective chars from the FB and DTF.

Sample ID	Devol Temp ^a	Proximate Analysis (wt %, d.b.)			Ultimate Analysis (wt %, d.a.f.) ^d					N/C ^e	N ^f	
		Ash % ^a	VM % ^b	FC % ^c	C	H	N	S	O			
Glisa	Coal	–	19.9	23.6	56.4	80.6	4.5	1.9	1.1	11.9	0.020	1.9
	FB Chars	740	21.8	5.6	72.7	94.3	0.9	2.1	1.2	1.5	0.019	1.69
		820	22.1	3.6	74.2	95.7	0.5	2.2	1.2	0.4	0.020	1.66
		900	20.9	2.1	76.7	95.2	0.3	2.2	1.1	1.2	0.020	1.77
		980	23.1	1.6	75.3	96.6	0.1	2.0	1.3	0.0	0.018	1.57
	CDTF Chars	1000	24.8	2.2	73.0	96.3	0.3	1.8	1.7	0.0	0.016	1.36
		1130	25.4	0.6	74.0	97.1	0.0	1.1	1.8	0.0	0.010	0.80
		1270	24.9	0.5	74.5	97.2	0.2	0.8	1.8	0.0	0.007	0.60
		1400	25.3	0.2	74.5	97.4	0.2	0.5	1.9	0.0	0.005	0.37
	Lethabo	Coal	–	39.8	21.6	38.5	74.9	4.0	1.7	1.0	18.4	0.019
FB Chars		740	49.8	4.3	45.9	95.6	1.0	1.8	1.4	0.2	0.016	1.20
		820	48.7	3.4	47.3	95.7	0.8	2.3	1.2	0.0	0.021	1.60
		900	50.3	2.0	43.8	96.0	0.4	2.1	1.5	0.0	0.019	1.37
		980	48.9	0.7	49.3	96.6	0.1	2.0	1.3	0.0	0.018	1.38
CDTF Chars		1000	49.7	2.9	47.5	92.9	0.2	1.5	1.3	4.1	0.013	1.00
		1130	50.3	2.0	47.6	94.1	0.0	1.8	1.4	2.7	0.016	1.18
		1270	53.6	0.5	45.9	96.7	0.3	1.4	1.6	0.0	0.012	0.80
		1400	54.0	0.0	45.8	97.4	0.0	0.9	1.7	0.0	0.008	0.51
Matimba		Coal	–	33.2	26.9	39.9	79.4	5.1	1.7	2.0	11.8	0.019
	FB Chars	740	52.8	3.6	43.6	95.0	1.1	2.0	1.9	0.0	0.018	0.89
		820	53.8	2.2	44.0	95.4	0.7	1.9	2.0	0.0	0.017	0.81
		900	56.7	1.1	42.2	95.6	0.5	1.7	2.2	0.0	0.016	0.65
		980	56.4	0.8	42.8	96.0	0.3	1.6	2.1	0.0	0.014	0.61
	DTF Chars	1000	43.2	1.0	55.8	94.6	0.1	1.5	1.5	2.3	0.014	0.98
		1130	43.5	0.3	56.1	95.9	1.4	1.1	1.6	0.0	0.010	0.71
		1270	49.0	0.1	50.9	97.0	0.0	0.9	2.1	0.0	0.008	0.47
		1400	46.2	0.5	53.3	97.6	0.3	0.5	1.2	0.4	0.005	0.29

*Devolatilisation temperature (°C); FB-fluidised bed; DTF-drop-tube furnace; ^aAnalyses done using [ISO 1171 \(2010\)](#)

^bAnalyses conducted according to [ISO 562 \(2010\)](#) guidelines; ^cAnalyses conducted by difference;

^dAnalyses conducted according to [ISO 29541 \(2010\)](#); ^eAtomic ratio; ^fAbsolute nitrogen content (wt. %, d.a.f)

Proximate results are reported on dry basis (d.b), while elemental results are reported on dry ash free basis (d.a.f).

of most SA coals. Glisa coal has higher total reactivities than Lethabo coal, this is attributed to the contribution by the reactive- semifusinite and inertodetrinite. However, Matimba coal is relatively vitrinite-rich and high in mineral matter. Besides the high mineral matter, Matimba coal possess similar attributes to the northern hemisphere Laurasian coals that have typical high levels of vitrinite. Due to the high temperature effects, maceral composition were not performed on chars.

4.3.3 XPS N 1s of coals and chars

Evaluation of coals and chars using XPS provided information relating to changes in surface nitrogen functional forms ([Kelemen et al., 2007, 1994](#)). The XPS N 1s spectra obtained from the three parent coals were deconvoluted into three sub-peaks which appeared at approximately 398.5, 400.1 and 401.1 eV. These peaks correspond to the binding energy positions of pyridinic, pyrrolic, and quaternary nitrogen, respectively. The sub-peak representing pyrrolic nitrogen is most dominant, followed by pyridinic

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Table 4.2: Maceral compositions for the three parent coals.

Coal	Macerals (% volume, mineral matter basis)													Total Reactives	Visible Minerals
	Vitrinite			Liptinite			Inertinite								
	VIT	PV	TV	S/R/C	ALG	TL	RSF	ISP	F/SC	MIC	R/IN	I/IN	TI		
Glisa	16	2	18	3	0	3	17	19	5	2	10	16	69	48	10
Lethabo	15	0	15	3	0	3	6	14	3	1	8	14	46	32	36
Matimba	48	2	50	3	0	3	3	6	4	1	1	8	23	57	24

Terms and abbreviations used:

VIT - vitrinite; PV - pseudovitrinite; TV - total vitrinite; S/R/C - sporinite/resinite/cutinite; ALG - alginite;

TL - total liptinite (formerly referred to as exinite); RSF - reactive semifusinite; ISP - inert semifusinite;

F/SC - fusinite/secretnite; MIC - micrinite; R/IN - reactive inertodetrinite; I/IN - inert inertodetrinite; TI - total inertinite

Total Reactives = vitrinite + liptinite + reactive semifusinite + reactive inertodetrinite

and quaternary nitrogen functional forms respectively, this is corroborated by widely published materials (Boudou et al., 2008; Kelemen et al., 2007, 1994, 1995, 1998; Phiri et al., 2017; Valentim et al., 2011). Four sub-peaks were fitted onto the XPS N 1s spectra of all FB chars, the fourth sub-peak (402-405 eV), which was not encountered in the N 1s spectra of parent coals, is attributed to oxidised and/or protonated pyridinic nitrogen (Kapteijn et al., 1999). The N 1s spectra for Glisa FB and DTF chars illustrating the fitted peaks are shown in Figures 4.3 and 4.4 respectively. The relative amount of the nitrogen functional forms deduced from the deconvolution of the N 1s spectra are presented in Table 4.3. Relative nitrogen species present in the three coals and their subsequent transformation in chars due to pyrolysis are illustrated in Figure 4.5. Regardless of pyrolysis conditions, the relative quantity of pyridinic nitrogen remained within a fairly small range. The XPS N 1s spectra of severely pyrolysed Glisa DTF char (1400 °C) and all DTF chars generated from the vitrinite-rich Matimba coal was deconvoluted into two sub-peaks representing N-Q and N-6. The oxidised pyridinic nitrogen complexes in FB chars displayed a slight ascending trend with increase in temperature. The slight increase of N-X with increasing pyrolysis temperature in Lethabo DTF chars occurred at the expense of pyridinic nitrogen which displayed a subtle decrease. From the parent coals, the ratio N-6/N-5 increased slightly followed by a subtle decrease at high temperatures (Table 4.3), displaying a small variation, highlighting an initial decrease of N-5 due to heat treat and remaining almost constant within the FB temperature range while N-6/N-Q ratio exhibited a clearly noticeable variation, illustrating the dominance of N-Q.

The respective chars emanating from the entire pyrolysis temperature range contained more quaternary nitrogen than the parent coals. Marked changes in nitrogen functional forms in chars occurred as a result of pyrolysis, a considerable decrease in pyrrolic nitrogen sub-peak in the N 1s spectra occurred in all other chars, and was completely unavailable in the Glisa 1400 °C char and all the Matimba DTF chars (Phiri et al., 2017). A distinct feature of most of the chars, with the exception of all Matimba DTF chars and Glisa 1400 °C, was the significant emanation of N-X. The

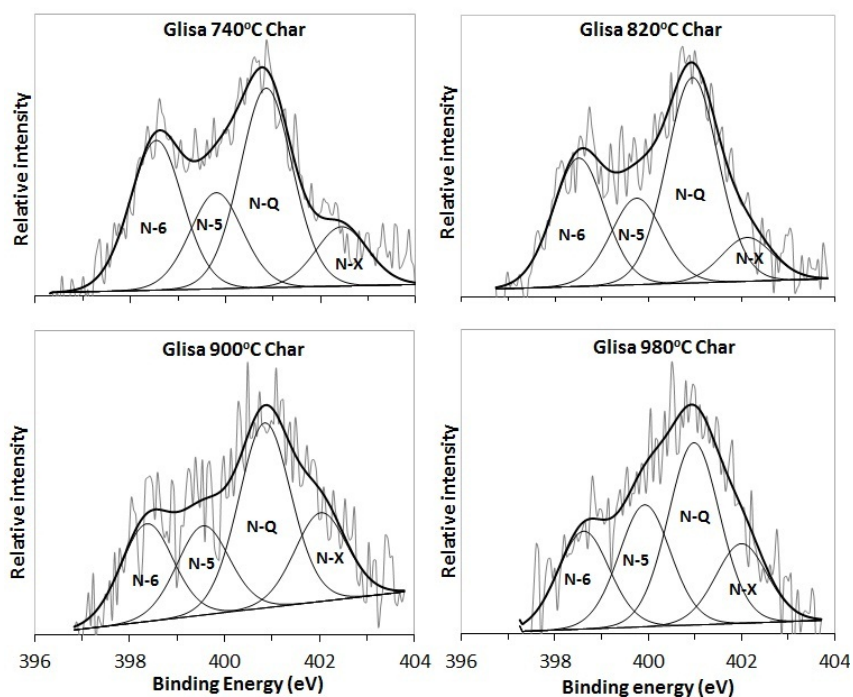


Figure 4.3: XPS N 1s spectra for Glisa chars prepared using FB displaying four sub-peaks that represent pyrrolic (N-5), pyridinic (N-6), quaternary (N-Q) and protonated &/or pyridinic N oxide complexes (N-X).

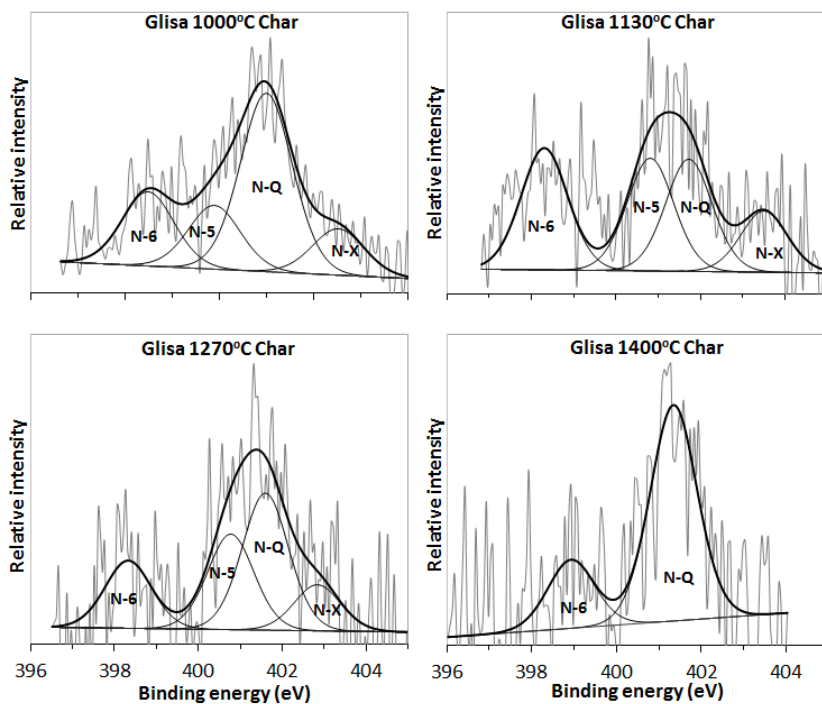


Figure 4.4: XPS N 1s spectra for Glisa chars prepared using DTF showing nitrogen functionality depicted by N-5, N-6, N-Q and N-X.

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Table 4.3: Results from XPS nitrogen (1s) spectra of coals and chars.

Sample ID	(°C)	*N/100 C's	N-5	N-6	N-Q	N-X	N-6/N-5	N-6/N-Q	
Glisa	Coal	–	1.7	59.3	28.5	12.2	–	0.5	2.3
	FB Chars	740	1.2	19.1	29.7	39.5	11.8	1.6	0.8
		820	1.0	18.6	27.7	44.3	9.4	1.5	0.6
		900	0.9	19.4	21.2	40.1	19.3	1.1	0.6
		980	0.8	25.3	20.3	37.8	16.5	0.8	0.5
	DTF Chars	1000	0.6	17.6	20.5	49.2	12.8	1.2	0.4
		1130	0.4	29.9	27.5	29.9	15.0	0.9	0.9
		1270	0.2	27.6	19.6	39.5	13.3	0.7	0.5
		1400	0.2	–	24.1	75.9	–	–	0.3
Lethabo	Coal	–	1.9	55.2	24.5	20.4	–	0.4	1.2
	FB Chars	740	1.2	22.8	32.7	36.4	8.1	1.4	0.9
		820	1.0	30.3	25.0	35.4	9.3	0.8	0.7
		900	0.8	26.5	22.4	38.5	12.6	0.9	0.6
		980	0.7	19.0	23.5	42.3	15.2	1.2	0.6
	DTF Chars	1000	0.6	21.4	30.6	37.7	10.4	1.4	0.81
		1130	0.4	15.8	22.0	44.4	17.7	1.4	0.5
		1270	0.3	14.8	17.8	47.9	19.5	1.2	0.4
		1400	0.3	17.1	14.7	46.6	21.6	0.9	0.3
Matimba	Coal	–	2.0	54.3	24.1	21.7	–	0.4	1.1
	FB Chars	740	1.6	24.4	27.0	35.5	13.13	1.1	0.8
		820	1.3	18.5	22.9	42.8	15.7	1.2	0.5
		900	1.2	20.1	23.1	44.1	12.7	1.2	0.5
		980	0.9	28.8	9.3	41.8	20.2	0.3	0.2
	DTF Chars	1000	0.4	–	33.5	66.5	–	–	0.5
		1130	0.2	–	26.8	73.2	–	–	0.4
		1270	0.2	–	27.3	72.7	–	–	0.4
		1400	0.2	–	26.8	73.2	–	–	0.4

*Nitrogen atoms per 100 carbons

complete absence of pyrrolic and oxidised pyridinic nitrogen in Glisa 1400 °C char and all DTF derived Matimba chars was unequivocally noted.

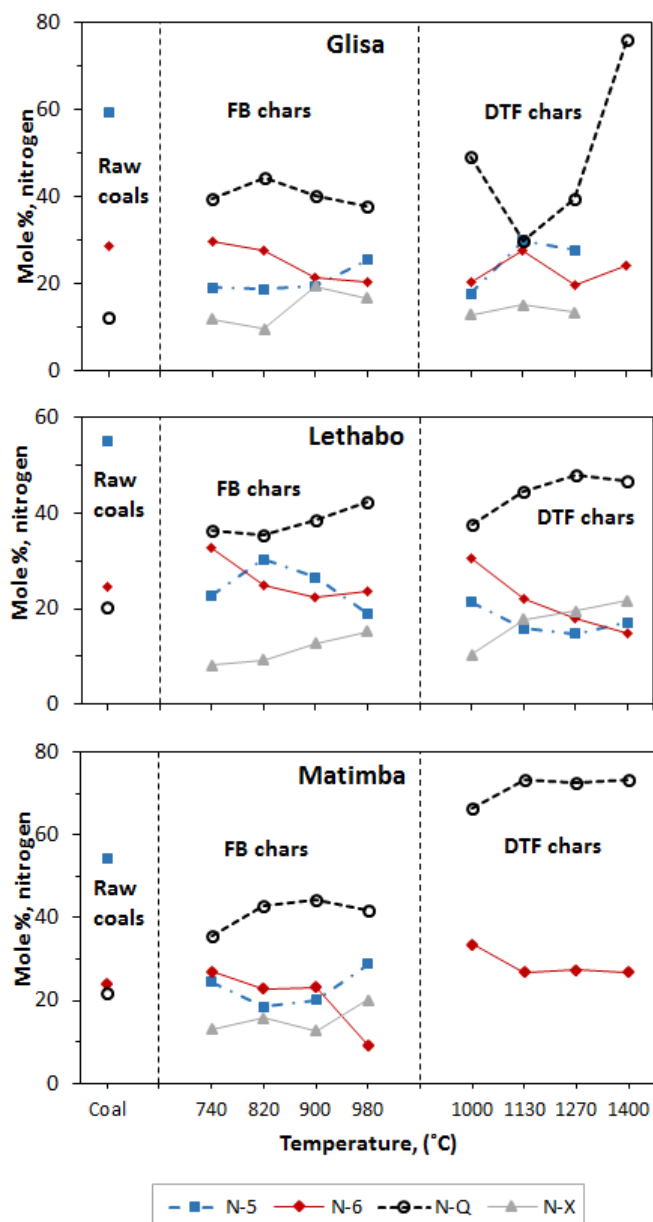


Figure 4.5: Nitrogen functional forms transformation due to pyrolysis in fluidised bed and drop-tube furnace as deduced from the XPS N 1s spectra.

4.3.4 XRD analysis of coals and chars

Structural parameters that were determined from the diffractograms are shown in Table 4.4. The interlayer spacing (d_{002}) and the average number of aromatic layers (N_{ave}) of the chars from the three coals remained fairly constant within the FB and DTF temperature range. The average crystallite height (L_c) remained almost constant at lower temperatures and then displayed an abrupt increase for DTF chars at 1270°C for the inertinite-rich Glisa and Lethabo coals, while the sudden increase was experienced at 1400°C for the vitrinite-rich Matimba coal. The average crystallite di-

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ameter ($L_a(10)$) shows that there is a uniform increasing trend with the temperatures for both FB and DTF chars.

Table 4.4: XRD results for carbon crystallite analysis on demineralised coal and the respective chars

			Coal	FB Chars (°C)				DTF Chars (°C)			
				740	820	900	980	1000	1130	1270	1400
Glisa	d_{002}	(Å)	3.524	3.559	3.563	3.589	3.565	3.599	3.572	3.568	3.539
	L_c	(Å)	13.15	13.49	12.96	13.26	12.97	11.79	12.50	13.50	14.62
	N_{ave}	(-)	4.730	4.791	4.633	4.694	4.638	4.276	4.499	4.785	5.131
	$L_a(10)$	(Å)	17.08	24.23	28.05	31.62	33.43	30.04	35.13	37.79	41.65
	f_a	(-)	0.739	0.856	0.885	0.923	0.938	0.950	0.967	0.982	0.989
	X_A	(-)	0.609	0.316	0.212	0.189	0.139	0.237	0.153	0.142	0.113
	DOI	(-)	0.711	0.415	0.303	0.252	0.192	0.275	0.181	0.158	0.123
Lethabo	d_{002}	(Å)	3.627	3.635	3.621	3.604	3.601	3.642	3.623	3.615	3.630
	L_c	(Å)	12.01	11.76	11.42	11.81	11.88	11.14	11.57	12.25	12.89
	N_{ave}	(-)	4.283	4.236	4.155	4.277	4.299	4.060	4.195	4.389	4.552
	$L_a(10)$	(Å)	17.19	26.42	28.22	32.38	34.06	29.00	30.25	37.62	45.06
	f_a	(-)	0.773	0.884	0.915	0.933	0.945	0.957	0.968	0.980	0.987
	X_A	(-)	0.638	0.227	0.195	0.168	0.142	0.140	0.132	0.106	0.075
	DOI	(-)	0.720	0.317	0.263	0.223	0.181	0.177	0.160	0.124	0.087
Matimba	d_{002}	(Å)	3.553	3.581	3.563	3.557	3.552	3.554	3.538	3.534	3.547
	L_c	(Å)	13.40	12.13	12.06	12.27	13.45	13.88	15.29	14.80	16.37
	N_{ave}	(-)	4.772	4.389	4.384	4.449	4.786	4.904	5.322	5.189	5.616
	$L_a(10)$	(Å)	17.83	22.86	27.34	30.91	34.01	32.91	37.07	38.72	39.53
	f_a	(-)	0.707	0.822	0.867	0.890	0.941	0.955	0.974	0.983	0.988
	X_A	(-)	0.571	0.315	0.221	0.203	0.185	0.239	0.215	0.169	0.117
	DOI	(-)	0.697	0.435	0.328	0.291	0.233	0.273	0.235	0.133	0.128

d_{002} - interlayer spacing; L_c - average crystallite height; f_a - aromaticity

N_{ave} - average number of aromatic layers; $L_a(10)$ - average crystallite diameter

X_A - fraction of amorphous carbon; DOI - disorder index

Among the parent coals, vitrinite-rich Matimba coal possesses a lower f_a compared to Glisa and Lethabo inertinite-rich coals. The growth of the turbostratic carbon structure in the char samples was significant at higher temperatures. There was a marked increase in the level of aromatic carbon upon pyrolysis of the coals. With the exception of 980 °C chars, the chars prepared from inertinite-rich coals, under FB conditions, always maintained higher aromaticity values at the same temperature with the exception of 980 °C. However, at 980 °C the difference in f_a became insignificant. Crossing over to the DTF chars, f_a maintained an increasing trajectory with increasing pyrolysis temperature even though a slight offset was witnessed between 980 and 1000 °C for Glisa and Matimba chars, and from 900 to 1130 °C in Lethabo chars. A slight decrease in aromaticity was experienced in DTF chars prepared at 1000 °C compared to their 980 °C FB predecessors. In Lethabo chars, the f_a of 900 and 980 °C was slightly higher than that of 1000 and 1130 °C chars. As the temperature was increased further under DTF conditions, the difference in f_a among the chars prepared at the same temperature further dwindled until the deviation became insignificant, and subsequently converged at 1130 °C with f_a at 97%. Subsequent

increase of temperature to 1270 and 1400 °C led to the aromaticity of all the chars generated at that particular temperature to increase to 98% and 99% respectively. This was regardless of whether the chars are derived from inertinite- or vitrinite-rich coal, this might give an explanation to the close resemblance of chemical properties of chars generated at high temperatures (Table 4.1). The vitrinite-rich Matimba coal displayed the largest relative f_a increase within the FB range of chars.

Within the chars generated in the fluidised bed reactor, there was no marked variation in L_c and N_{ave} . Lethabo DTF chars also did not display significant change for these two parameters. However, the 1400 °C Glisa char and the entire Matimba chars prepared from DTF displayed a significant increase in both L_c and N_{ave} . In Matimba chars, change began at 1000 °C but a significant increase was experienced from 1130-1400 °C, while 1000-1270 °C Glisa chars were trending along the same level as the FB counterparts. With respect to all the 3 coals, disorder index (DOI) decreased as the pyrolysis intensity increased.

4.3.5 Properties derived from ss ^{13}C NMR of coals

The coal structural parameters from ss ^{13}C NMR which are shown in Table 4.5 were calculated from the integral values according to Solum et al. (1989). Only results from coal are presented, no meaningful results were obtained from the chars. However, the chemistry of chars is very much dependent on parent coal properties (Yu et al., 2007), hence some of the projections on char properties are based on coal attributes extrapolation and postulation.

The results indicate that the inertinite-rich Glisa and Lethabo coals, were more aromatic, 74% and 77% respectively, than the vitrinite-rich Matimba coal whose aromaticity stood at 71%. Similar findings have been reported in other investigations (Roberts et al., 2015a; Van Niekerk et al., 2008). The difference in the fraction of alkylated aromatics, f_a^s , was quite small among the three coals even though f_a^s for Matimba coal was much less. Matimba had more aliphatic structures consisting solely of the $\text{CH}+\text{CH}_2$ group, f_{al}^H , followed by Glisa coal, and the inertinite-rich Lethabo coal had the least. The inertinite-rich coals possessed more bridge head carbons compared to the vitrinite-rich Matimba coal. The results furnished in Table 4.5 include the derived lattice parameters, encompassing the average number of aromatic carbons per cluster which is also referred to as cluster size (C) (Solum et al., 1989). Inertinite-rich coals, Glisa and Lethabo, had larger cluster size with values of 27.4 and 28.5 respectively, as compared to 21.4 for the vitrinite-rich Matimba coal. Roberts et al. (2015a) and Van Niekerk et al. (2008) obtained similar findings.

CHAPTER 4. TRANSFORMATION OF NITROGEN FUNCTIONAL FORMS AND THE ACCOMPANYING CHEMICAL-STRUCTURAL PROPERTIES EMANATING FROM PYROLYSIS OF BITUMINOUS COALS

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

		Coal Samples		
		Glisa	Lethabo	Matimba
<i>Solid state ¹³C NMR structural parameters</i>				
Fraction aromatics C's	<i>f_a</i>	0.75	0.79	0.70
Corrected fraction aromatics (excl CO)	<i>f_a[*]</i>	0.72	0.69	0.66
Fraction aliphatic C's	<i>f_{al}</i>	0.25	0.21	0.30
Fraction aliphatic C's bonded to oxygen	<i>f_{al}^O</i>	0.052	0.056	0.040
Fraction carbonyl/carboxyl and amide C's	<i>f_a^{CO}</i>	0.04	0.10	0.03
Fraction phenolics	<i>f_a^P</i>	0.07	0.10	0.07
Fraction alkylated aromatics	<i>f_a^S</i>	0.16	0.17	0.14
Fraction non-protonated C's in aromatic region	<i>f_a^N</i>	0.61	0.65	0.50
Fraction protonated C's in aromatic region	<i>f_a^H</i>	0.10	0.05	0.16
Fraction bridgehead C's	<i>f_a^B</i>	0.38	0.38	0.29
Fraction non-protonated C's+methyl groups in aliphatic region	<i>f_{al}^{N*}</i>	0.06	0.09	0.09
Aliphatic CH+CH ₂	<i>f_{al}^H</i>	0.19	0.12	0.22
Mole fraction of aromatic bridgehead C's	<i>X_b</i>	0.54	0.55	0.44
<i>Solid state ¹³C NMR derived lattice parameters</i>				
Average number of intact bridges	<i>P₀</i>	0.35	0.41	0.33
Average number of bridges and loop per cluster (cross-links)	<i>B.L</i>	3.05	4.47	2.26
Average number of side chains per cluster	<i>S.C</i>	5.73	6.50	4.52
Average number of aromatic C's per cluster	<i>C</i>	27.4	28.5	21.4
Average number of clusters per 100 C atoms	#clusters/100	2.61	2.43	3.10
Ave. number of attachments (bridges, loops, side chains) per cluster	<i>σ + 1</i>	8.78	10.97	6.78
Fraction of aromatic ring carbons with a directly attached proton	<i>M_G</i>	0.14	0.07	0.24
Average molecular weight of side chain or half of bridge mass	<i>M_δ</i>	25.01	25.49	30.03
Average molecular weight per cluster	<i>MW</i>	552.15	623.66	465.62

4.4 Discussion

The relative nitrogen in FB chars remained comparable to that of parent coals even though a portion of coal-N was released into the volatile stream. The absolute nitrogen ($|\text{N}|$) present in FB chars indicate that a small portion of nitrogen is released into the volatile stream during pyrolysis, implying that nitrogen is preferentially retained in the char, however, it is released in substantial amounts at high temperatures as illustrated in DTF chars (Baxter et al., 1996; Bruinsma et al., 1988; Haussmann and Kruger, 1991; Takagi et al., 1999). The rate of nitrogen release was much slower than the rate of evolution of total volatiles at low FB temperatures (Nelson and Kelly, 1993). Nonetheless, under DTF conditions, an appreciable amount of nitrogen was released as nitrogen containing species into the volatile stream resulting in chars with very low nitrogen content. The portion of nitrogen released during pyrolysis increased considerably with pyrolysis temperature, implying that high temperature treatment led to substantial nitrogen partitioning into the volatile stream, this occurrence is elaborated by the number of nitrogen atoms per 100 carbon atoms as furnished in Table 4.3. It is noteworthy that the FB coal particle size (± 1 mm) was much bigger than that of DTF feed coals of $-75 \mu\text{m}$. However, the solid residence time for FB char formation was quite high relative to that for DTF char production. Elementary results (Table 4.1) highlighted that the vitrinite-rich Matimba coal was more susceptible to

the loss of nitrogen under the given DTF conditions. XPS results exhibited that the loss of nitrogen increased gradually with increasing temperature, although the loss of nitrogen by Matimba chars was quite high at 1130-1400 °C.

Pyrolysis resulted in a substantial increase in levels of N-Q and a decline in N-5. Curve resolving of XPS N 1s spectra of Matimba DTF chars revealed that all the respective chars only had two pronounced sub-peaks that represented the predominant quaternary nitrogen and a bit low pyridinic nitrogen as shown in Table 4.4, nonetheless, 1400 °C Glisa char displayed similar results. Severely pyrolysed chars primarily constituted of N-6 and N-Q (Kelemen et al., 1998; Pels et al., 1995). Elevated temperature pyrolysis of nitrogen attached to amorphous carbon structures essentially drives off edge-located nitrogen atoms (N-5) and the remaining thermally stable nitrogen atoms (N-Q) are preferentially located in the interior of the carbon lattice (Stańczyk et al., 1995; Xiao et al., 2005). The outlined XPS N 1s results indicate that all other chars principally had four peaks denoting N-5, N-6, N-Q and N-X. Chars derived from high temperature pyrolysis of inertinite-rich coals do not lose the edge located N-5 in entirety. These observations of note reveal that inertinite- and vitrinite-rich coal chars behave differently with regard structural attributes of retained and released nitrogen during pyrolysis under DTF conditions. This phenomena is strongly linked to the total reactive macerals of the parent coals. In general, the maceral attributes have influence on the capability to soften, swell, volatiles evolution and reorganization of the main carbonaceous material. When bituminous coals are heated to temperatures exceeding 350 °C, vitrinites, liptinites and some inertinites begin to soften, becoming plastic and expanding. The greater inertinites and the majority of the inherent minerals remain largely unchanged. The extent of expansion is markedly influenced by the heating rate and the final employed temperature. Vesicles may be formed in the reactive coal macerals as the volatiles are released. Bituminous coal components that are rich in reactivities increase in volume on heating to form cellular structures that result in porous chars (Roberts et al., 2015a). The respective chars provide a significantly increased surface areas for subsequent reactions to occur. Nonetheless, most inertinites, particularly fusinites, do not soften, degasify nor become porous structures, but produce quite dense chars which are quite difficult to ignite. They also tend to have lower burn-off rates. The determined distribution of nitrogen functionality in FB chars was almost similar regardless of the maceral attributes of the respective parent coals. Most of the published results in open literature with regard nitrogen functional forms corroborate with the results of Matimba coal and its respective chars, in essence most studied coals are Laurasian and are generally vitrinite-rich (Valentim et al., 2011). However, in as much as Glisa coal is predominantly inertinite, the XPS N 1s spectrum of the respective 1400 °C Glisa

char exhibited similar distribution of nitrogen functional forms as that of Matimba DTF chars which possessed only the thermally stable N-6 and N-Q. This could be attributable to the high total reactivities present in Glisa coal as result of the contribution of reactive semifusinite and reactive inertodetrinite as shown in Table 4.2.

The relative peak intensity of quaternary nitrogen was predominant in all chars. The diminishing N-5 unequivocally displayed a good correlation with DOI as pyrolysis temperature increased, and simultaneously a substantial increase in N-Q seamlessly corresponded with aromaticity as illustrated in Figures 4.6 and 4.7, respectively.

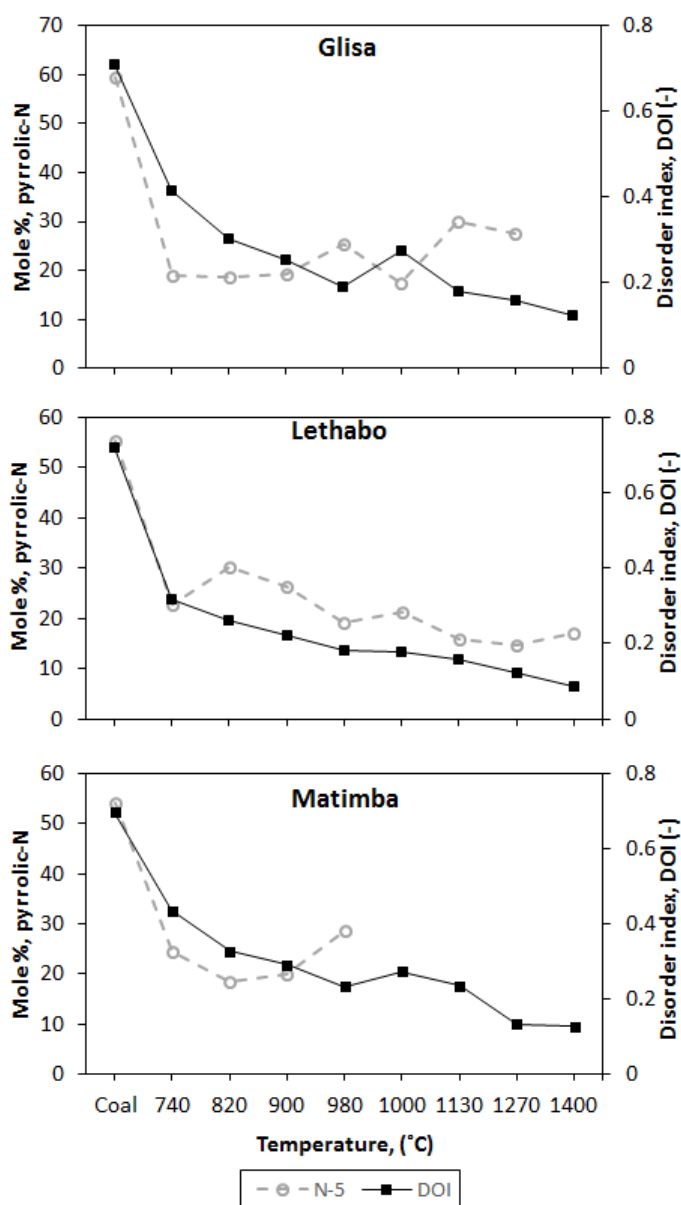


Figure 4.6: Transition of pyrrolic nitrogen and disorder index as a result of pyrolysis.

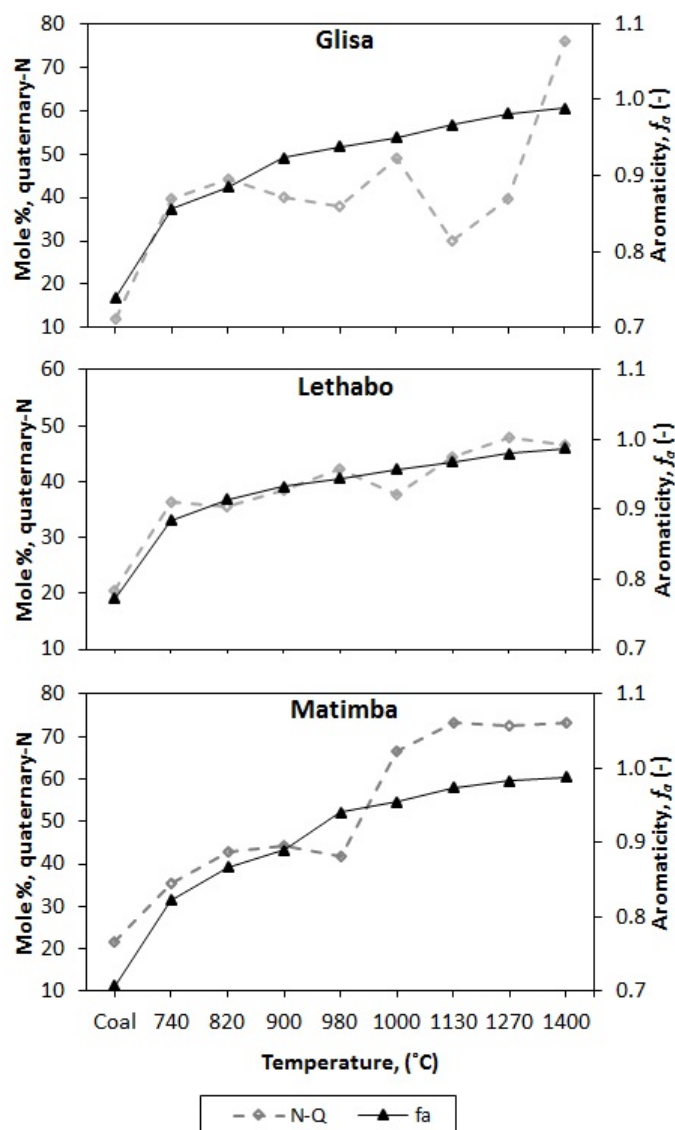


Figure 4.7: Relationship between aromaticity and quaternary nitrogen transformation due to pyrolysis.

The transformation of amorphous carbon in pyrolysed char to crystallised carbon proceeds as the pyrolysis temperature increases (Fermoso et al., 2010). Amorphous carbon fractions are directly related to the edge-located five-membered heterocyclic nitrogen which forms the integral part of N-5, and are not stable under severe pyrolysis conditions (Schmiers et al., 1999). Hence the elimination of edge located heterocyclic nitrogen into the volatile stream during pyrolysis consequentially brought about a decrease, or a complete loss, in pyrrolic nitrogen as witnessed on the entire Matimba DTF chars and Glisa 1400°C char. The transformation of amorphous carbon in pyrolysed char to crystallised carbon proceeds as the pyrolysis temperature increases (Tsubouchi et al., 2003b). During the transformation of char structure,

thermal ordering entails diminishing quantity of amorphous carbon, coupled by an increase in aromaticity (f_a) and crystallite size (L_c) (Lu et al., 2002). Concurrently, formation of polycyclic rings introduce nitrogen atoms into the condensed ring systems. The notable increase in quaternary nitrogen due to pyrolysis is associated with the graphene edge located nitrogen being integrated into the interior of the resultant large polynuclear aromatic carbon structures. The growth of polynuclear aromatic is evident from the XRD results as shown by the increase in average crystallite diameter (L_a) and aromaticity. This implies that the coalescing effect is more prominent during coal pyrolysis compared to stacking mechanisms for the increase of aromaticity. Tsubouchi (2014) suggested that the presence of small amounts of inherent Ca- or Fe-containing minerals in coal enhance the conversion of char-N to N_2 as well as the transition of amorphous carbon to crystallised carbon with turbostratic structures during rapid pyrolysis conditions. Tsubouchi (2014) also illustrated that the yield of N_2 obtained from char-N increases in proportion to the amount of crystallised carbon that is formed.

The reduction in N-5 levels due to pyrolysis may also be caused by the loss of oxygen in pyridones, whose binding energy is approximately 400.6 eV (Pels et al., 1995), and the attenuation of the of amino-type moieties (399.4 eV) (Friebel and Köpsel, 1999). The relative amount of pyridinic nitrogen remained within a moderately narrow range in the all the chars derived from the 3 coals (Figure 4.5). The actual magnitude of the pyridinic sub-peak could be undermined by pyridine oxidation resulting in the emergence of the N-X sub-peak. The N-X sub-peak which inherently stretches from 402 eV to 405 eV may be due to other forms occurring in the proximity (Casanovas et al., 1996; Valentim et al., 2011).

Solid state ^{13}C NMR analysis showed that Matimba coal consisted of more aliphatic structures and the least aromatic carbons as compared to the inertinite-rich Glisa and Lethabo coals. Vitrinite-rich coals possessed more aliphatic carbons and low aromaticity (Sun et al., 2003). On the other hand, inertinite-rich coals comprised of relatively high aromaticity and low aliphatic carbons, and a more orderly carbon structure (Zhang et al., 2008). During high temperature pyrolysis, the aliphatic structures are believed to be released as radicals (Xu et al., 2012), and subsequently form volatile species. Concurrently, the formation of polynuclear aromatic compounds takes place at high temperatures through the condensation process which occurs simultaneously with the elimination of H_2 , resulting in char remnants that have dwindled H/C atomic ratios (Table 4.1) (Cousins et al., 2006; Li and Zhu, 2014; Roberts et al., 2015a; Yu et al., 2007). The substantial increase in fixed carbon with temperature emanates from the direct loss of hydrogen-rich species into the volatile stream. The aromaticity of demineralised parent coals that was determined through ss ^{13}C NMR displayed a

good correlation with aromaticity deduced from XRD analysis. The aromaticity of the coals show an indirect relationship with the total reactivities. Increasing the pyrolysis temperature led to the increase in average crystallite diameter, aromaticity and quaternary nitrogen. There were no conclusive outcomes that emerged from ^{13}C NMR analysis of chars due to the inherent limitations of the analytical technique on high temperature chars. The drawback emanates from high electric conductive properties of high temperature chars which cause line broadening within the aromatic region, the phenomenon hinders the deduction and calculation of structural as well as lattice parameters (Gilman et al., 1998; Roberts et al., 2015a; Solum et al., 2001).

The results from XRD analysis indicate that the average crystallite height (L_c) remained almost constant at the entire FB temperature range and up to 1130 °C for the inertinite-rich Glisa and Lethabo chars, and extending to 1270 °C for the vitrinite-rich Matimba coal within DTF temperatures. Emmerich (1995) reported similar findings in the study of transformation of crystallinity in carbon due to heat treatment, of which L_c did not alter. However, a sudden increase occurred at 1270 °C in Glisa and Lethabo chars, while the abrupt increase happened at 1400 °C. These observations are a result of the growth of L_c which is brought by the coalescence of crystallites along the c -axis during heating, in most cases the coalescence may begin at temperatures exceeding 1000-1200 °C and the phenomenon is applicable to both graphitisable and non-graphitisable carbons Xu et al. (2012). The crystallites formation entails dehydrogenation, polymerisation and condensation reactions. Fermoso et al. (2010) also stated that devolatilisation at low temperatures did not seem to possess any considerable influence on char morphology. Condensation of polynuclear aromatic structures and simultaneous elimination of H_2 start occurring at high temperatures (Cousins et al., 2006; Roberts et al., 2015a; Xu et al., 2012; Yu et al., 2007). The decrease of H from parent coals to the subsequent chars is clearly illustrated in Table 4.1. Zhang et al. (2008) also reported that the d_{002} remained fairly unaltered. A reasonably uniform increase in crystallite diameter (L_a) was experienced among all chars as the pyrolysis temperature. Roberts et al. (2015a) reported similar findings on chars derived from both vitrinite- and inertinite-rich coals. The increase in L_a is brought about by the coalescence of crystallites along the a -axis with a juxtaposition of graphite-like layers. Essentially, the reported data on L_c and L_a implies that the coalescing effect is more prominent during coal pyrolysis compared to stacking mechanisms for the increase of aromaticity. Thomas (1997) explored the influence of heat treatment at short residence times on evolution of char surface area for a set of chars produced from coals of differing rank. It was observed that increasing the temperature between 1000 and 1500 °C caused a sudden decrease in char surface area. The notable structural annealing occurred in parallel to an apparent reduction

in H/C ratio and a marginal decrease in N/C ratio.

Based on XRD analysis, an interpretation can be made that the structure of carbon crystallite of Glisa and Lethabo chars, derived from inertinite-rich-coals, are thermally less susceptible to change than that of Matimba chars. During coal pyrolysis, the transformation of amorphous carbon in the devolatilised char to crystallised carbon proceeds as the temperature increases. Inertinite-rich coals and the respective chars possess a more ordered carbon structure (Roberts et al., 2015a; Zhang et al., 2008). Vitrinite coals are more amorphous and have a less ordered carbon structure. The structural attributes of FB chars generated at 740-980 °C were notably alike with regard to f_a , X_A , DOI , d_{002} , L_c , N_{ave} and L_a values. However, chars derived from the DTF possessed varying extents of structural changes in L_c , L_a and N_{ave} . It is worth noting that L_a for the 980 °C FB chars is clearly higher than the L_a for the 1000 °C DTF chars, more so L_a values for 1000 and 1130 °C Lethabo DTF chars were much less than their 900 and 980 °C FB counterparts. Even though the specified FB chars were generated at a lower temperature, their residence time was much higher compared to that of relatively high temperature DTF chars. It is perceived that this phenomenon was also observed on L_c and N_{ave} for chars derived from predominantly inertinite coals, whereby the 980 °C FB chars possessed higher values of L_c and N_{ave} than the corresponding 1000 °C DTF chars. Notwithstanding the difference in temperature treatment between 980°C FB and 1000 °C DTF chars is quite small, it follows that the much higher FB average residence time was responsible for the increased values of L_c , L_a and N_{ave} in chars prepared from predominantly inertinite coals. In vitrinite-rich Matimba coal, a similar observation at the specified temperatures only occurred to L_a . Therefore, it can be stated that the carbon crystallite still grows even though the interlayer spacing of carbon layers remain unchanged. The similarities of both vitrinite- and inertinite-rich chars is ascribed to close resemblance of char chemical properties emanating from the growth of aromatic fraction (Roberts et al., 2015a). Nonetheless, at high temperatures physical structure characteristics which embodies L_a were substantially different. Carbon structural changes in Matimba chars that were deduced through XRD under the same DTF conditions showed that there was a significant change in L_c and N_{ave} . There were no noteworthy changes from the chars prepared from inertinite-rich coals, with the exception of the 1400 °C Glisa char, and subtle increases in L_c and N_{ave} in the 1400 °C Lethabo char.

The behaviour of char nitrogen is a complex phenomenon, therefore it is important that char preparation experiments are carried out under realistic conditions of solid fuel fired systems in order to acquire meaningful information. The bench scale fluidised bed experiments resemble the bubbling fluidised bed conditions, whereas the drop-tube furnace experiments simulates pulverised fuel combus-

tion (Buhre et al., 2006). The findings from this investigation are significant; there is a strong likelihood that char morphological rearrangements are directly responsible for coal nitrogen release. Char morphological structure influence the reactivity of char, of which the char reactivity is an important factor in determining the coal-N conversion (Carpenter et al., 2006). The employed sequence of analytical methods showed that N moves from crystallite edges into the interiors of larger, condensed polycyclic structures in char, this movement becomes more complete for progressively hotter temperatures. This observation has meaningful practical implications and may ultimately lead to improved kinetic mechanisms for coal-N release in solid fuel fired systems. A substantial portion of coal-N was retained in respective FB chars as compared to DTF chars. In comparison to actual solid fuel fired systems; fluidised bed combustion emits negligible NO_x (NO and NO₂) and a significant amount of N₂O (Glarborg et al., 2003; Wójtowicz et al., 1993), however, the NO_x emissions from pulverised fuel combustion are quite substantial, and in contrast, traces of N₂O are emitted (Carpenter et al., 2006). These well documented observations in literature may further be expounded through factoring the attributes of nitrogen in the condensed heterocyclic aromatic structures in relation to the entire char morphology of the chars prepared from FB and DTF chars.

Coal char properties have an impact on the effectiveness of the primary measures used to control nitrogen oxides emissions. The reactions occurring in low-NO_x burners consisting of pyrolysis occurring in precedence to combustion is dependent on the structural and chemical properties of the coal chars, which requires to be examined to reduce the formation of nitrogen oxides (Carpenter et al., 2006). Low-NO_x burners operate through altering the near-burner aerodynamics, this alteration changes the devolatilisation process, which subsequently influences the amount and type of nitrogenous species that are released (Taniguchi et al., 2011). Rapid devolatilisation and fast nitrogen release rates are regarded as good coal attributes in low-NO_x burners. However, slow release of nitrogen from coal is most likely to result in release of high NO_x levels since a substantial amount of nitrogen retained in the char (Thomas, 1997; Tsubouchi, 2014). Nitrogen remaining in char after devolatilisation is released through heterogeneous oxidation, therefore low-NO_x burners do not have influence on the NO_x produced from char-nitrogen. The char-N and the concomitant carbonaceous char properties depend on the molecular and structural distribution of the condensed heterocyclic nitrogen forms which are determined by advanced analytical techniques such as XPS, XRD and NMR (Almendros et al., 2003; Kelemen et al., 2007; Okolo et al., 2015; Roberts et al., 2015b). The stable pyridinic- and quaternary-nitrogen are the prominent feature of high temperature chars and the respective nitrogen atoms bound in aromatic structures are not easily released into

the volatile stream. Thus extensive knowledge on the functionality and behaviour of char-N, reaction rate equations dependent on the amount of nitrogen in the chars could be developed, which in-turn will contribute to improved designs of low-NO_x burners. The obtained results may also be used as a tool to determine the yardstick for suitability or potential coal feedstock in pulverised fuel combustion systems. Focusing on char absolute nitrogen content and nitrogen functionality, chars derived from coals possessing high reactive macerals, Matimba and Glisa coals, released more nitrogen into the volatile stream under high temperature DTF experiments and are most likely to perform well in NO_x reduction if utilised in low-NO_x burners. The findings may also contribute significantly as input data towards the construction of coal char molecular models, such detailed models that incorporates N structures may in forecast be used to improve efficiencies of coal utilisation processes.

4.5 Conclusions

A battery of analyses for parent coals and the respective chars prepared through pyrolysis of SA bituminous coals in a FB at 740-980 °C and in a DTF at 1000-1400 °C were carried out. The nitrogen content in chars prepared from fluidised bed remained within comparable limits to that of parent coals, however, an appreciable decline took place in DTF chars. The information obtained from XPS and XRD show that the morphological changes during pyrolysis brought about N into condensed aromatic crystallite, this was attested by the increase in aromaticity with temperature as determined by XRD which correlated with increasing quaternary nitrogen as deduced by XPS. A marked increase in average crystallite diameter also symbolised the growth heterocyclic aromatic structures. On the other hand, the decrease of fraction of amorphous and *DOI* corresponded with pyrrolic nitrogen. The distribution of nitrogen functional forms varied with increasing intensity of pyrolysis conditions and maceral composition of the coals. The carbon micro-structure in chars emanating from the vitrinite-rich coals was perceived to be thermally more sensitive than the chars derived from inertinite-rich coals. All DTF chars derived from vitrinite-rich Matimba coal and the 1400 °C only possessed quaternary- and pyridinic-N, the phenomenon was attributed to the high volume of total reactive macerals. The DTF chars from vitrinite-rich coals were also characterised by a substantial increase in average crystallite height and number of aromatic carbon layers, while the chars from inertinite-rich coals had all the four nitrogen functional forms, with the exception of 1400 °C Glisa char. Whether a coal is vitrinite- or inertinite-rich, the significant factor attributing to morphological transformations at elevated temperatures is the amount of total reactives. Glisa coal is inertinite-rich but possess a considerable por-

tion of reactive semifusinite and reactive inertodetrinite, hence the high levels of total reactive macerals, leading to similar morphological behaviour at high temperatures.

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References

Please note that references for this chapter are consolidated in the main references on page 113.

CHAPTER

5

RELEASE OF NITROGENOUS VOLATILE SPECIES FROM SOUTH AFRICAN BITUMINOUS COALS DURING PYROLYSIS

Note: *This chapter has been published as:*

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<https://doi.org/10.1021/acs.energyfuels.7b03356>.

Abstract

The influence of typical South African coal attributes on the release of nitrogen into the volatile stream during pyrolysis was studied by utilizing three bituminous coals. The majority of South African coals are characterized by high mineral matter and are rich in inertinite maceral. Pyrolysis was conducted in a bench-scale fluidized bed (FB) at 740–980 °C, and also in a drop-tube furnace at 1000–1400 °C. Levels of nitrogenous species in the volatile stream in the form of NH₃, HCN, and tar-N were determined. Nitrogen functional forms of tars released at low temperatures were pre-

dominantly distinguished by high levels of pyrrolic nitrogen, followed by pyridinic and quaternary nitrogen, respectively. Tars liberated at 740 °C possessed similar nitrogen functional form attributes as those of parent coals. However, an increase in pyrolysis temperature caused a gradual increase in quaternary nitrogen as well as a concurrent decrease in pyrrolic nitrogen and a concomitant subtle decrease in pyridinic nitrogen. The analysis of nitrogen in tars was only confined to tars extracted from the FB. Vitrinite-rich and/or high mineral matter coal released high yields of nitrogenous species into the volatile stream at low FB temperatures. A large amount of NH₃ was released relative to HCN under FB pyrolysis conditions. However, more HCN was released than NH₃ during DTF pyrolysis. Two coals, one characterized by high mineral matter and being rich in vitrinite, and the other distinguished by relatively low mineral matter and being rich in inertinite, behaved similarly by reaching respective peak amounts of NH₃ yields at 820 °C under FB pyrolysis conditions. On the contrary, an opposite profile displaying a slump at 820 °C was observed for HCN yields from the two respective coals. The third coal, a high mineral matter and inertinite-rich coal, released high NH₃ yields and simultaneously the least HCN yields at 740 °C. Under DTF experimental conditions, both NH₃ and HCN steadily increased with temperature in all coals. The low mineral matter and inertinite-rich coal released high yields of total volatile-N from 1000 to 1270 °C, only to be surpassed by the vitrinite-rich/high mineral matter coal at 1400 °C. The inertinite-rich/high mineral matter coal released the least throughout the entire DTF temperature range. The total mineral matter content of the coals played a significant role toward the nitrogen product distribution. On the other hand, the total reactive macerals also influenced the emission of volatile species at 1130–1400 °C DTF temperature range. The yields and composition of the released nitrogenous species have been attributed to a combination of mineral matter content, petrographic properties of the parent coals, and the utilised conditions. Pyrolysis temperature, coal particle size, and residence time also play a significant role toward the yields and composition of the released nitrogenous species.

5.1 Introduction

Introducing coal into a combustion unit initially gives rise to devolatilization (pyrolysis) causing the partitioning of coal-N into volatile-N and char-N ([Johnsson, 1994](#)). The volatile-N stream constitutes of tar-N, HCN, NH₃, and N₂ ([Tsubouchi and Ohtsuka \(2008\)](#)). HCN and NH₃ have been identified as the main precursors of oxides of nitrogen during coal combustion in several studies ([Chang et al., 2003](#); [Hämäläinen et al., 1994](#); [Kidenä et al., 2000](#); [Ledesma et al., 1998](#); [Leppälahti, 1995](#); [Li and Tan, 2000](#); [Nelson et al., 1991](#); [Tan and Li, 2000a,b](#); [Tian et al., 2005](#); [Xie et al., 2001](#)).

The volatile-N species influence the respective final oxides of nitrogen pollutants produced during the subsequent combustion. Nitric oxide (NO) and nitrogen dioxide (NO₂), often designated as NO_x, are potent pollutants that have been attributed to causing acid rain, ground level ozone, and photochemical smog. Another oxide of nitrogen, nitrous oxide (N₂O), is a potent greenhouse gas and it has been blamed for indirectly depleting the ozone layer (Carpenter et al., 2006). Numerous studies have been conducted with the quest to comprehend the chemistry behind the formation of tar-N, HCN, NH₃ and char-N as precursors of NO_x and N₂O (Bassilakis et al., 1993; Baumann and Möller, 1991; Carpenter et al., 2006; Chen and Niksa, 1992; Genetti and Fletcher, 1999; Kiden et al., 2000; Mori et al., 1996; Phong-Anant et al., 1985; Solomon and Colket, 1978). However, further work is still necessary to comply with the ever increasing stringent legislation on nitrogen oxides emission from coal combustion. South Africa's power generation industry is heavily dependent on coal combustion, hence the need to be more vigilant and heed the call to significantly reduce emissions.

The partitioning and product distribution of coal nitrogen between volatile species and char nitrogen have been perceived to be influenced by coal properties, encompassing parent coal composition, attributes of the respective char residue, and the surface characteristics (Glarborg et al., 2003; Leppälahti and Koljonen, 1995). Nitrogen is preferentially retained in char at low temperature; however, a large fraction is released into the volatile stream at high temperatures (Baxter et al., 1996; Blair et al., 1977; Bruinsma et al., 1988; Haussmann and Kruger, 1991; Kambara et al., 1993; Phiri et al., 2017; Pohl and Sarofim, 1977; Takagi et al., 1999). In addition to pyrolysis temperature, other conditions which include heating rate, residence time, and pressure also influenced the formation and distribution of NH₃ and HCN. Tar is the primary means of nitrogen release from coal (Chen and Niksa, 1992). Essentially, almost all the nitrogen in tars liberated during coal pyrolysis exists in the form of heterocyclic aromatic structures, and the portion of light volatile-N gases is quite negligible during initial phases of pyrolysis (Blair et al., 1977; Chen and Niksa, 1992; Solomon and Colket, 1978; Takagi et al., 1999). Tar may become the significant source of nitrogen production into the volatile stream as the secondary pyrolysis proceeds (Freihaut et al., 1989; Genetti and Fletcher, 1999). Char decomposition during pyrolysis occurs at high temperatures and considerably longer residence times than during the primary devolatilization phase both lead to the liberation of additional nitrogen species into the volatile stream, mostly in the form of HCN (Blair et al., 1977; Carpenter et al., 2006; Li et al., 1996; Phong-Anant et al., 1985; Pohl and Sarofim, 1977). High temperatures may result in the disintegration of remaining heteroatomic aromatic rings of char, which constitutes mostly of comparatively stable

quaternary nitrogen (Phiri et al., 2018b), thereby releasing more nitrogenous species into the volatile stream. The release of HCN has been found to be prevalent during rapid pyrolysis experiments, while NH_3 has been reported to be dominant under low heating rate conditions (Leppälahti, 1995; Leppälahti and Koljonen, 1995; Zhang and Fletcher, 2001). The HCN/ NH_3 ratio has been reported to increase with higher heating rates in both coals and biomass pyrolysis (Bassilakis et al., 1993; Leppälahti, 1995; Solomon et al., 1982). It is widely reported that HCN is the major product of bituminous coals devolatilization, while NH_3 is mainly released from low rank coals and biomass (Aho et al., 1993; Friebe and Köpsel, 1999; Leppälahti, 1995; Niksa and Cho, 1996; Phong-Anant et al., 1985; Rüdiger et al., 1997; Zhang and Fletcher, 2001).

Considerable research has been done on the liberation of nitrogenous species during coal pyrolysis (Chang et al., 2003; Hämäläinen and Aho, 1996; Ledesma et al., 1998; Leppälahti, 1995; Li and Tan, 2000; Li et al., 2015; Mori et al., 1996; Nelson et al., 1991; Tan and Li, 2000a,b; Tian et al., 2002, 2005; Xie et al., 2001). However, some researchers have opted to work with model compounds to avoid the experimental constraints resulting from the complex heterogeneity nature of coal (Deng et al., 2013; Furimsky et al., 1995; Hämäläinen et al., 1994; Hansson et al., 2003; Kidena et al., 2000; Leichtnam et al., 2000; Nielsen et al., 1995; Pels et al., 1995; Schmiere et al., 1999). Model compounds are bound to encounter a drawback due to incorporated solitude species which may fall short or exacerbate the reaction in forecast as compared to the synergistic effect which may arise in coal pyrolysis as a result of the combined effect of N neighbouring heterogeneous components which include minerals, functional groups and free radicals (Tsubouchi and Ohtsuka, 2002a). However, model compounds have shed some light on probable mechanisms of N release during pyrolysis. Numerous mechanisms thought to lead to the formation of NH_3 and HCN have been proposed (Aho et al., 1993; Jones et al., 1999; Kambara et al., 1995, 1993; Li and Nelson, 1996; Li and Tan, 2000; Schäfer and Bonn, 2000, 2002; Stańczyk, 1999; Tan and Li, 2000b). It has been suggested that HCN is initially formed and NH_3 is subsequently generated through direct hydrogenation of HCN and N-sites by hydrogen generated in situ when the solid fuel undergoes pyrolysis (Li and Tan, 2000; Schäfer and Bonn, 2000, 2002). Bassilakis et al. (1993) suggested that NH_3 is principally generated from the heterogeneous reactions between char and HCN. Yuan et al. (2012) proposed that NH_3 is formed directly during the primary stage of rapid pyrolysis through cracking of nitrogen functional forms. The reaction may proceed via $\cdot\text{N}$, $\cdot\text{NH}$, and $\cdot\text{NH}_2$ free radicals being released from the fuel and then merging with $\cdot\text{H}$ or H_2 under the influence of high energy impact to form NH_3 . According to Li and Tan (2000); Tan and Li (2000a,b) the $\cdot\text{H}$ radicals that are liberated during pyrolysis

are adsorbed on the char surface, subsequently attacking the heterocyclic nitrogen bonds leading to the formation of NH_3 . Through molecular modeling, [Espinal et al. \(2007\)](#) used density functional theory to illustrate the dissociation of the C–N bond releasing $\cdot\text{NH}_2$ radicals to the gas phase and the subsequent formation of NH_3 , through either homogeneous or heterogeneous hydrogen abstraction or recombination reactions. However, [Kambara et al. \(1995, 1993\)](#) suggested that the two components are formed simultaneously, and also highlighted that the distribution of nitrogen species during coal pyrolysis and combustion can be quantitatively predicted based on the nitrogen functionality in the substrate coals determined from the XPS N 1s measurements. [Kelemen et al. \(1998\)](#) pointed out that the nature of fuel nitrogen in coal, whether it is infused in aromatic groups or part of the peripheral heterocyclic structures, determines the form of nitrogen species released during devolatilization, implying that the nitrogen species emitted during devolatilization having been correlated to the coal nitrogen functionality. [Hoogendoorn et al. \(1995\)](#) proposed an overview of different paths of fuel nitrogen by suggesting that N-5 and N-6 nitrogen are liberated as HCN in residual chars, while the amino groups in raw coal are evolved as NH_3 . Pyrrolic nitrogen is susceptible to decomposition during heat treatment ([Baxter et al., 1996](#)), the process is perceived to occur through degradation (ring expansion), of which the 5-membered ring embodying pyrrolic nitrogen opens up due to high temperature ([Jacobson et al., 1958](#); [Patterson and Drenchko, 1962](#); [Pels et al., 1995](#)). However, some researchers ([Jones et al., 1999](#); [Nelson et al., 1996](#); [Stańczyk, 1999](#)), have questioned and disputed the correlation of fuel nitrogen functionality with the liberation of nitrogenous species during pyrolysis and/or combustion.

Most coals in Southern Africa are typical of the Gondwana region (southern hemisphere) coals, they are characterised by high levels of mineral matter and inertinite content ([Cadle et al., 1993](#); [Cai and Kandiyoti, 1995](#); [Falcon and Ham, 1988](#)). Southern hemisphere coals vastly differ from the Laurasian region (northern hemisphere) coals that are typically high in vitrinite and low mineral matter. Mineral matter inherently exists in coals in the form of alkali, alkaline earth and transition metal cations ([Hayashi et al., 1995](#); [Ohtsuka et al., 1997](#); [Tsubouchi et al., 2001](#); [Tsubouchi and Ohtsuka, 2002b](#); [Wu et al., 2000, 2003](#)). Coals with high mineral matter content constitute of appreciable quantities of Na, K, Mg, Ca, and Fe cations in ion-exchanged forms ([Hüttinger and Michenfelder, 1987](#)). The presence of some of the mineral species may alter the partitioning of nitrogen into the volatile stream and char during devolatilization ([Mori et al., 1996](#); [Tsubouchi and Ohtsuka, 2002b, 2008](#); [Tyler and Schafer, 1980](#); [Yan et al., 2005](#)). [Yan et al. \(2005\)](#) reported that pyrolysis of demineralized coals tends to suppress the release of nitrogen volatile species. Fe, Ca, K, Si, and Al increase the conversion of coal-N to NH_3 , whereas Na promotes the

formation of HCN (Yan et al., 2005). Mori et al. (1996) pointed out that, at 900 °C, the presence of Fe promotes the formation of N₂; however, it also hinders the conversion of nitrogen to HCN and NH₃. Ohtsuka et al. (1997) demonstrated that the influence of Na, K, and Ca on the composition of HCN, NH₃, and N₂ product species varies to a great extent with temperature from 450 to 950 °C. The particular research group (Mori et al., 1996; Ohtsuka et al., 1994; Ohtsuka et al., 1998; Ohtsuka et al., 1997; Tsubouchi et al., 2001; Tsubouchi and Ohtsuka, 2002a, 2008; Wu and Ohtsuka, 1997), focused on the formation of N₂ during coal pyrolysis, concluded that char-N is the major source of N₂, and also showed that the conversion of char-N to N₂ is catalysed by Fe and Ca cations.

There is limited information in the open literature with regard to the release of nitrogen species from inertinite-rich coals. Inertinite-rich coals generally display higher aromaticity than the vitrinite-rich counterparts (Phiri et al., 2018b; Roberts et al., 2015a). However, vitrinite-rich coals tend to have a higher degree of hydrogen content, H/C atomic ratio, aliphatic moiety as well as aliphatic side chains than coals that are rich in inertinites (Phiri et al., 2018b; Zhao et al., 2011). Zhao et al. (2011) pyrolysed vitrinite and inertinite maceral fractions, and reported that the inertinite produced lower tar and gas yields, as well as possessing higher thermal stability. Given et al. (1984) found that N in maceral concentrates from a number of British coals were as follows; vitrinite (1.6–2.0% N, dmmf) > exinite/liptinite (1.1–1.4%) > inertinite (0.3–1.2%). Rajan and Raghavan (1995) reported that a coal that is rich in liptinite released moderately higher levels of nitrogen as compared to a vitrinite-rich coal, in spite of the vitrinite-rich coal containing slightly higher nitrogen. They ascribed the phenomenon to fuel nitrogen breaking free more easily from the liptinite-rich coal particles than in high-vitrinite-rich coals.

Understanding the chemical and physical processes that determine formation of precursors of nitrogen oxides during devolatilisation remains a challenge even though much research has been conducted in the last four decades. South African (SA) bituminous coals possess the typical attributes of southern hemisphere Gondwana coals, which differ from the northern hemisphere Laurasian coals in being variable between regions and seams. Most SA coals are generally characterised by high mineral matter content, the majority are rich in inertinite and basically have low calorific values (Everson et al., 2008b; Falcon and Ham, 1988). The primary goal of this study was to determine the influence of the typical SA coal attributes on the release of NH₃, HCN, and tar nitrogen speciation. There is relatively limited information reported in the open literature on nitrogen oxides precursors and the distribution of tar nitrogen released from coals with high mineral matter and different petrographic attributes.

5.2 Experimental Section

5.2.1 Coal Samples

The three SA bituminous coals that were utilized in this study were also used by Phiri et al. (2017, 2018b). Prior to the pyrolysis experiments, the parent coals were subjected to the conventional proximate and ultimate analyses, as well as petrographic analysis. The respective chemical properties of the coals are given in Table 5.1. According to ISO 11760 (2005) classification of coals, all three coal samples are classified as bituminous, medium rank C coals. The detailed petrographic analysis of the three coals is outlined elsewhere (Phiri et al., 2018b). The detailed petrographic analysis shows that Matimba coal contains 58% (vol mmb) of total reactive macerals, followed by Glisa and Lethabo coals with 47% and 32% (vol mmb), respectively. Glisa and Lethabo coals are both inertinite-rich, nonetheless Glisa coal possesses substantial reactive semifusinite and reactive inertodetrinite, leading to a much higher portion of total reactive macerals. The mineral composition of the coal samples was analysed by utilising X-ray fluorescence (XRF) spectroscopy analysis according to the ASTM D4326-4 (2004) guidelines. The analysis was carried out on an ARL ADVANTX instrument, of which the X-ray tube was operated at 2500 W (50 kV and 50 mA) to generate Rh $K\alpha$ radiation. The coal samples were heated at 815 °C to obtain ashes based on ISO 1171 (2010). Table 5.2 outline the concentrations of elements that incorporate Al, Ca, Fe, K, Mg, Na, Si, and Ti that are presented in wt % on coal dry basis.

Table 5.1: Properties of the utilised coals.

Coal name	Proximate analysis (wt %, d.b.)			Ultimate analysis (wt %, dmmf) ^d					Maceral analysis (v/v %, mmb) ^e		
	MM % ^a	VM % ^b	FC % ^c	C	H	N	S	O	Vitrinite	Liptinite	Inertinite
Glisa	22.0	21.6	56.4	82.8	4.6	1.9	1.0	9.6	18	3	69
Lethabo	43.3	18.2	38.5	79.5	4.2	1.9	1.1	13.2	15	3	46
Matimba	36.6	23.5	39.9	83.6	5.3	1.8	2.1	7.1	50	3	23

^aMineral matter (MM) analyses conducted according to ISO 1171 (2010) and the Parr formula (Speight, 2012).

^bAnalyses conducted according to ISO 562 (2010).

^cAnalyses conducted by difference.

^dAnalyses conducted according to ISO 29541 (2010).

^ePetrographic analysis carried out using ISO 7404: 2 (1985) guidelines.

Proximate results are reported on dry basis (d.b.), while elemental results are reported on-dry, mineral matter free basis (dmmf). Maceral results are presented on mineral matter basis (mmb)

5.2.2 Pyrolysis Experiments

Pyrolysis experiments were conducted in a bench-scale fluidized bed reactor and drop-tube furnace in ultra-high-purity N₂ (99.995%) obtained from Air Liquide (South

Table 5.2: Metal compositions of utilised coal samples.

Coal	Metal composition (wt %, coal d.b)							
	Al	Ca	Fe	K	Mg	Na	Si	Ti
Glisa	2.68	2.12	0.79	0.15	0.54	0.02	2.60	0.16
Lethabo	5.52	1.60	1.12	0.24	0.30	0.04	8.90	0.33
Matimba	4.50	1.30	2.25	0.25	0.30	0.02	9.50	0.27

Africa) at heating rates exceeding 10^4 °C/s. Both reactors are described in detail by [Phiri et al. \(2017\)](#). In the fluidized bed experimental campaign, ± 1 mm coal particle sizes of the respective coal samples were mixed thoroughly at a ratio of 1:1 with fluidising material comprising of 0.3–0.65 mm silica sand and fed into the reactor at 21 g/min; simultaneously N₂ gas was introduced through the bottom of the reactor at 18.4 Nl/min. Four different temperatures in the range of 740–980 °C inclusive, were utilised in FB experiments. The residence time of the gases in the FB ranged from 1.10 s, recorded at 980 °C, to 1.36 s at 740 °C. However, solid particles experienced a residence time of ± 9.4 min in the reactor. In DTF experiments, fine coal particles of -75 μ m were fed at an ≈ 1 g/min and pyrolysed at 1000, 1130, 1270, and 1400 °C, respectively. The nitrogen gas flow rate ranged from 17.9–23.7 Nl/min so as to achieve a residence time of ≈ 1.8 s at each stipulated temperature throughout the DTF pyrolysis experimental program.

5.2.3 Sampling and Analyses of N Volatile Species

The nitrogenous species reported in this study were sampled at the outlet of each specified reactor. Sampling tar entailed bubbling the flue gas through a multicomponent sampling train containing dichloromethane (DCM). The DCM dissolved the tar constituent of the gas emitted from the FB or DTF. Impingers containing DCM were placed in an ice bath at 4 °C to enhance condensation and trap the condensable organic species in the gas. The DCM in the collected samples was allowed to evaporate under controlled temperature conditions. This technique is usually employed in the analysis of coal tar pitch volatiles (CTPV). The majority of soluble and suspended tar components were left behind after DCM evaporation that was conducted under controlled conditions. The mass of tar was determined by weighing the solids left behind after total evaporation of the DCM sample. The tars were only successfully collected from FB pyrolysis experiments. No quantifiable amount of tar yields was obtained from the DTF operation due to the low coal feed injected into the reactor, and also as a result of tar condensation on the inner surface of the water cooled sample collection probe. Subjecting coal to high heating rates particularly at high temperatures tends to produce low tar yields ([Nelson et al., 1988](#); [Xu and Kumagai, 2002](#); [Yuan et al., 2012](#)).

The speciation of nitrogen functional forms in tars that were collected at 740–980 °C were determined by X-ray photoelectron analysis (XPS). A Kratos Axis Ultra X-ray photoelectron spectrometer situated at The University of Queensland (Australia), operated at a base pressure of 1×10^{-8} Torr and a power of 225 W using monochromatic Al K α radiation, was used to obtain XPS N 1s data. A detailed procedure on XPS N 1s spectra deconvolution and peak allocation is outlined elsewhere (Phiri et al., 2017).

The analyses of HCN and NH₃ absorbed in respective solutions were conducted by Chemtech Laboratory Services (Pretoria, South Africa) using a Dionex DX-100 ion chromatograph equipped with a Dionex CD-20 conductivity detector. A multicomponent sampling train consisting of impingers containing 0.1 N NaOH was used to absorb the released HCN. The HCN that is present in the reactor outlet gas stream reacts with the NaOH to form CN[−] ions, which are retained in the alkaline solution until analysed by ion chromatography in accordance to the US EPA OTM: 29 (2011). The CN[−] ions were separated in a Dionex AS-7 column and subsequently quantified. A similar sampling train setup was utilised for sampling NH₃, however an acidic solution of 0.1 N H₂SO₄ was placed in the impingers to absorb the NH₃. The NH₃ existing in the flue gas was converted to NH₄⁺ ions by the H₂SO₄ solution and subsequently analysed through ion chromatography following the U.S EPA CTM: 27 (1997) guidelines. A Dionex CS-12 column was used for separation prior to the quantification of NH₄⁺ through conductivity detection. It is noteworthy that the NH₃ yields may contain contributions from the hydrolysis of HNCO to form NH₄⁺ ions; however, the yields of HNCO are sparingly low when compared to NH₃ (Ledesma et al., 1998; Li et al., 1998; Li and Tan, 2000; Nelson et al., 1996; Yan et al., 2005). HCN and NH₃ data were evaluated as an average of three analysis results, and the experimental error was determined at 95% confidence interval. The deduced experimental error ranged between 2.034% and 9.155% inclusive.

5.3 Results and Discussion

5.3.1 Nitrogen Distribution

Figure 5.1 illustrates a portion of coal-N that was released as volatile-N during FB and DTF pyrolysis. Volatile-N released from coal pyrolysis could be in the form of NH₃, HCN, tar-N, or N₂. The nitrogenous volatile species released from FB pyrolysis (Figure 5.1(a)) indicate that the conversion of vitrinite-rich Matimba coal-N was quite significant, releasing 47.7% N at 740 °C, and gradually increasing to 63.8% at 980 °C. However, the coal-N that migrated into the volatile stream during pyrolysis of inertinite-rich Glisa and Lethabo coals was constant, just below 20%, throughout

the entire FB temperature range, with the exception of Lethabo coal that released 29.4% of its total nitrogen at 740 °C. Under FB pyrolysis conditions, the fraction of nitrogen released was dependent upon petrographic attributes, with the vitrinite-rich coal releasing a larger fraction of its nitrogen than inertinite-rich coals.

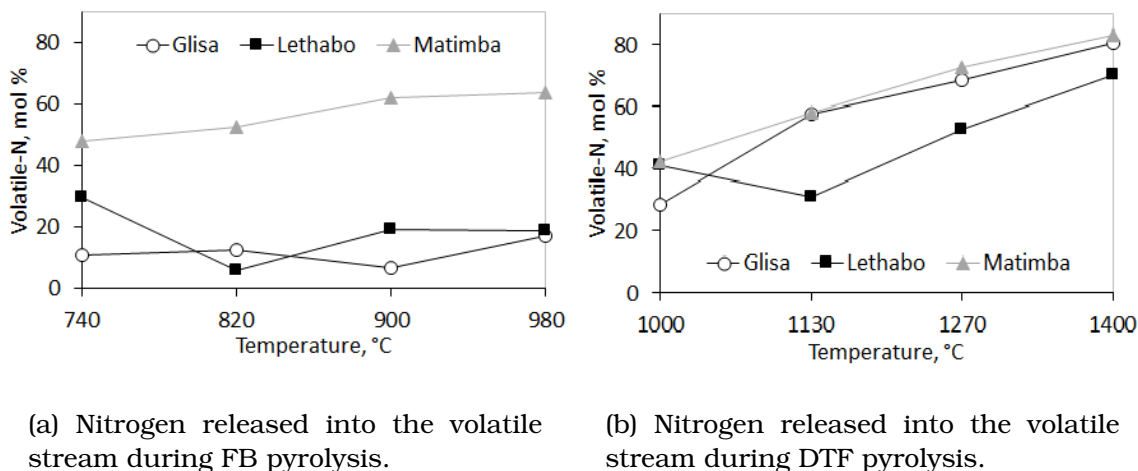
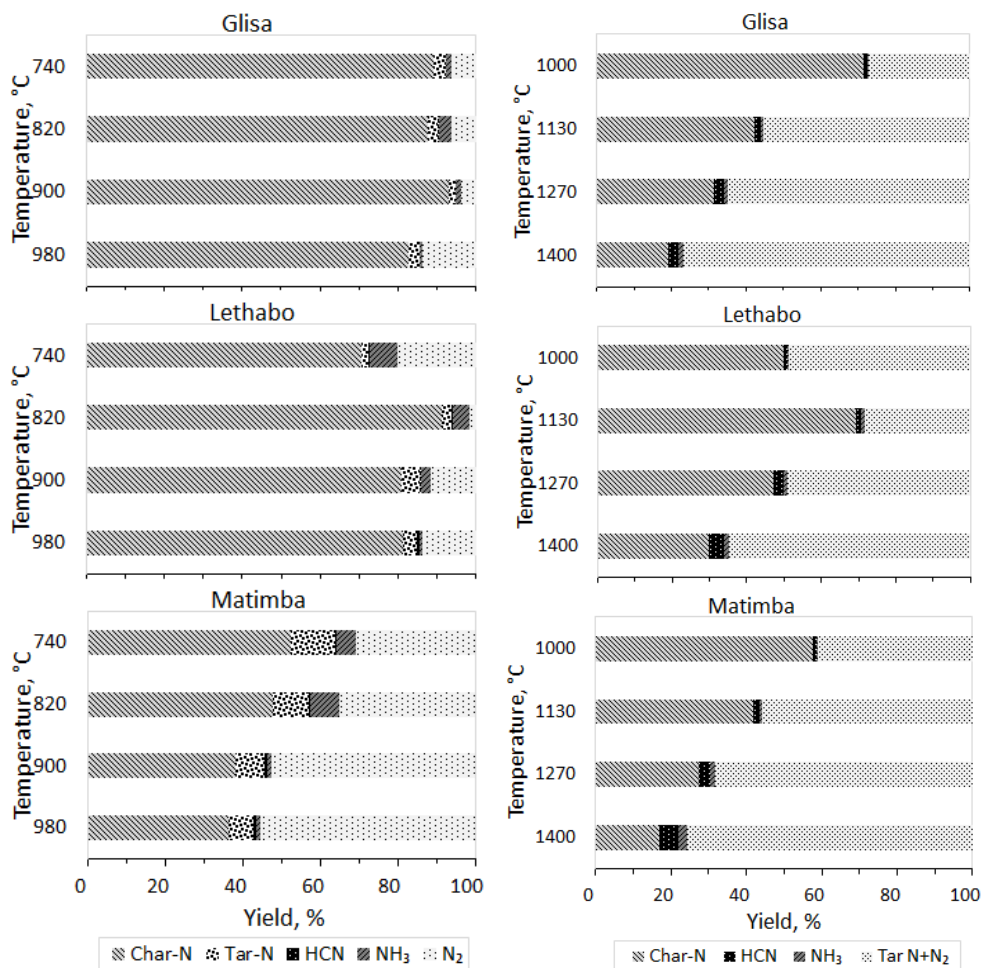


Figure 5.1: Volatile nitrogen released at different temperatures from FB and DTF pyrolysis of three South African coals.

A substantial portion of coal-N was converted into volatile-N during DTF pyrolysis (Figure 5.1(b)) of the three coals. Nitrogen release increased significantly with the pyrolysis temperature; Pohl and Sarofim (1977) reported similar findings. A significant fraction of coal-N being converted into volatile-N was observed as pyrolysis temperature increased. Matimba coal released more nitrogen into the volatile stream under DTF conditions; however, the difference to Glisa coal was quite negligible unlike to FB pyrolysis, implying that the influence of total reactive macerals is more pronounced at high DTF temperatures. Volatile-N from Lethabo coal lagged behind, even though it also displayed an upward trajectory with pyrolysis temperature. The nitrogen in vitrinite-rich coal particles is released more readily than in inertinite-rich coals. Vitrinite macerals are generally richer in hydrogen than inertinite macerals. The increased hydrogen content and high volatile-matter content of the vitrinite-rich Matimba coal are reflected in Table 5.1. The inertinite-rich Glisa and Lethabo coals are more aromatic than the vitrinite-rich Matimba coal (Phiri et al., 2018b), implying that more nitrogen atoms in inertinite-rich coals are within aromatic structures, hence the increased difficulty of release.

The yields of different nitrogenous species acquired from pyrolysis of the three coals in FB and DTF at various temperatures are illustrated in Figure 5.2. The N_2 in FB, and the tar-N+N₂ in DTF were determined by difference (Wu et al., 2003;



(a) Nitrogen product distributions from FB pyrolysis of the three coals.

(b) Nitrogen product distributions from DTF pyrolysis of the three coals.

Figure 5.2: Yields of various forms of nitrogen emanating from FB and DTF pyrolysis of three South African coals at different temperatures.

Yuan et al., 2012). Char-N yields were the most abundant within the N product distribution from FB, with the exception of Matimba 900 and 980 °C, followed by N₂, tar-N, NH₃, and HCN, respectively. The emitted volatile species seem to be influenced by the pyrolysis conditions and the coal type. The inertinite-rich and relatively low mineral matter Glisa coal released less volatile-N species, whereas the high mineral matter and vitrinite-rich Matimba coal converted a substantial portion of coal-N under FB pyrolysis conditions. The char-N yields emanating from pyrolysis of Glisa and Lethabo coals in FB represented the dominant nitrogenous species. In essence, more fuel nitrogen is retained in the chars derived from inertinite-rich coals. The rate at which nitrogen was released was much slower than the rate of release of total volatiles during the relatively low FB temperature range (Nelson and Kelly, 1993). Matimba FB char-N yields ranged from about 40–50%, while N₂ marked the dominant volatile-N component. Besides the N product distribution at 1000 and 1130 °C for Glisa and Lethabo coals, respectively, the determined tar-N+N₂ exhibit prominence across the DTF pyrolysis temperature ranges for the three coals. Significant coal-N for Glisa and Matimba at 1130–1400 °C is partitioned into tar-N+N₂. Coal pyrolysis at elevated temperatures and high heating rates usually release low tar yields (Nelson et al., 1988; Xu and Kumagai, 2002; Yuan et al., 2012), so the tar-N+N₂ portion can be projected to be largely constituting N₂. High temperatures may cause disintegration of the remaining heteroatomic aromatic rings of char-N, which constitutes mostly of comparatively stable quaternary nitrogen (Phiri et al., 2018b), and subsequently releasing more nitrogen species into the volatile stream. Quite a number of researchers (Tsubouchi et al., 2001; Tsubouchi and Ohtsuka, 2002a,b; Wu and Ohtsuka, 1996; Wu and Ohtsuka, 1997) attested that most of the N₂ emanates from char-N and have also indicated that conversion of fuel-N to N₂ increases appreciably with increasing pyrolysis temperature. This is one of the most likely reasons for the apparent decreased yields of char-N, HCN, and NH₃ that are shown in Figure 5.2(b). In addition, several other studies also reported that the presence of metal cations resulted in the reduction of HCN and a concomitant increase in the formation of N₂ during pyrolysis (Mori et al., 1996; Ohtsuka et al., 1994; Ohtsuka et al., 1998; Ohtsuka et al., 1997). Char-N is the major source of N₂ during high temperature pyrolysis, and the phenomenon is perceived to be catalysed by Fe and Ca cations (Mori et al., 1996; Ohtsuka et al., 1994; Ohtsuka et al., 1998; Ohtsuka et al., 1997; Tsubouchi et al., 2001; Tsubouchi and Ohtsuka, 2002a, 2008; Wu and Ohtsuka, 1997).

5.3.1.1 Nitrogen Speciation in Tars

In general, the tar yields from all three coals displayed a gradual decrease as temperature increased. Nelson et al. (1988) reported a similar trend. The vitrinite-rich

Matimba coal released more tar at each temperature across the entire FB temperature range followed by the inertinite-rich Glisa and Lethabo coal, respectively. XPS N 1s analysis revealed that all the 3 parent coals primarily constituted of pyrrolic-N (N-5), followed by pyridinic-N (N-6) and quaternary-N (N-Q), respectively (Phiri et al., 2017), as illustrated in Figure 5.3. The results conform to widely published literature on raw coals (Kelemen et al., 2002, 1998; Pels et al., 1995). The XPS N 1s spectra of coal tars liberated at 740 °C are also shown in Figure 5.3; the composition of nitrogen functional forms is essentially similar to that of the respective parent coals as deduced from the XPS N 1s spectra, implying that the tars released at the specified temperature are also predominantly composed of N-5, followed by N-6 and N-Q, respectively. During the first stage of devolatilisation, a portion of coal-N is emitted rapidly with the tars, but with negligible or no recognisable selectivity with regard nitrogen functionality (Carpenter et al., 2006), implying that, in the absence of secondary reactions, N-5 and N-6 species in coal are released intact as components of aromatic structures in tar. Solomon and Colket (1978) reported that tar possessed similar nitrogenous structural attributes as that of the respective parent coal through the comparison of ^{13}C NMR and infrared spectra of parent coals and the respective coal tars. Utilization of the XPS technique, introduced years later, validated the observation and further elucidated the component functional forms through deconvolution of XPS N 1s spectra.

The effect of temperature on nitrogen speciation of the released coal tars is illustrated in Figure 5.4. It is apparent that increasing pyrolysis temperature resulted in change in the nitrogen functional forms of tars as depicted by the change of sub-peaks on the curve-resolved XPS N 1s spectral shapes. Heat treatment resulted in significant levels of edge located N-5 and N-6 in the parent coals being transposed into the volatile stream mainly as tar; hence the tars were dominated by nitrogen functional forms that resemble parent coals' nitrogen speciation. Almost all the coal tars liberated from the three coals at 740–900 °C were fundamentally composed of N-5; nonetheless, a gradual increase in N-Q and simultaneous appreciable reduction of N-5 occurred as pyrolysis temperature increased, such that the tars liberated at the highest temperature of the FB range were dominated by N-Q. The released coal tars subsequently undergo secondary cracking which generates light gases that constitute additional HCN and NH_3 (Carpenter et al., 2006; Solomon and Colket, 1978). A subtle concomitant reduction of N-6 with increasing temperature was also observed. This is evident of secondary pyrolysis taking place, through the rupture of the heterocyclic aromatic structures that are housing pyrrolic- and pyridinic-N to release light nitrogenous species. However, Li et al. (1998) reported a different pattern that prescribed a relative increase in pyrrolic nitrogen in tars produced at 600–800 °C

with respect to other forms of nitrogen in coal. Tars liberated from Matimba coal at 820–980 °C exhibited a fourth peak on the XPS N 1s spectra which is attributed to protonated and/or oxidised pyridinic nitrogen (N-X). The observation on the increasing proportion of N-Q with temperature in coal tars indicates that some of the N-Q species are sufficiently strong and intact to survive the devolatilisation process or reform from their components. This entails that some of the quaternary nitrogen may be created during rapid heat up pyrolysis. The process proceeds through nitrogen substituting for carbon in condensed polynuclear aromatic structures, partially aromatic/heterocyclic systems giving rise to N being covalently bonded to three C atoms (N-Q). This implies that elevating pyrolysis temperature prompted the N situated on the boundaries of the graphene layers of tar molecules to become positioned on the inner parts of the graphene structures due to condensation and/or polymerisation of polynuclear aromatic structures. [Stańczyk et al. \(1995\)](#) and [Pels et al. \(1995\)](#) suggested that N-5 and N-6 amalgamated concurrently with the ring opening process leading to the formation of stable N-Q. The nitrogen atom in N-Q is shared among two or three aromatic rings; the three bonds connecting to the N atom may break simultaneously when subjected to intense pyrolysis conditions, providing a high energy impact within a short period. This could lead to possible formation of N radicals preceding the formation of N₂, NH₃, and HCN.

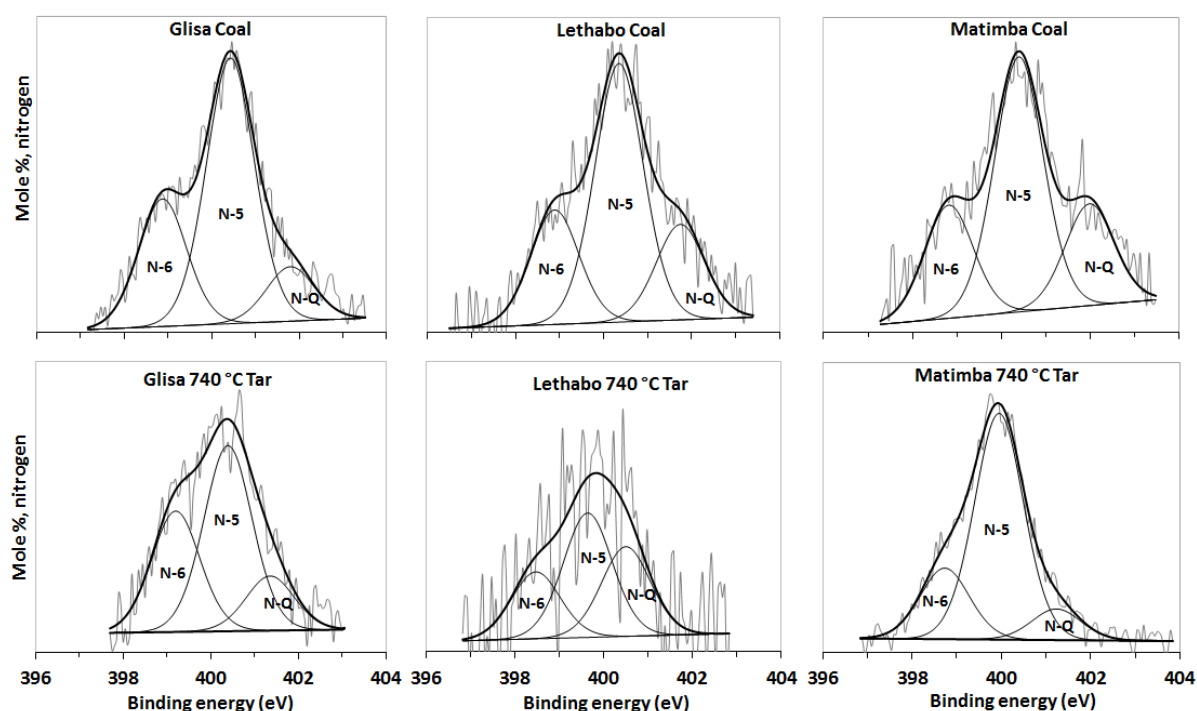


Figure 5.3: XPS N 1s spectra depicting the nitrogen functional forms of the three raw coals and the respective tars released at 740 °C. The N 1s XPS spectrum of each tar is placed beneath that of the corresponding parent coal.

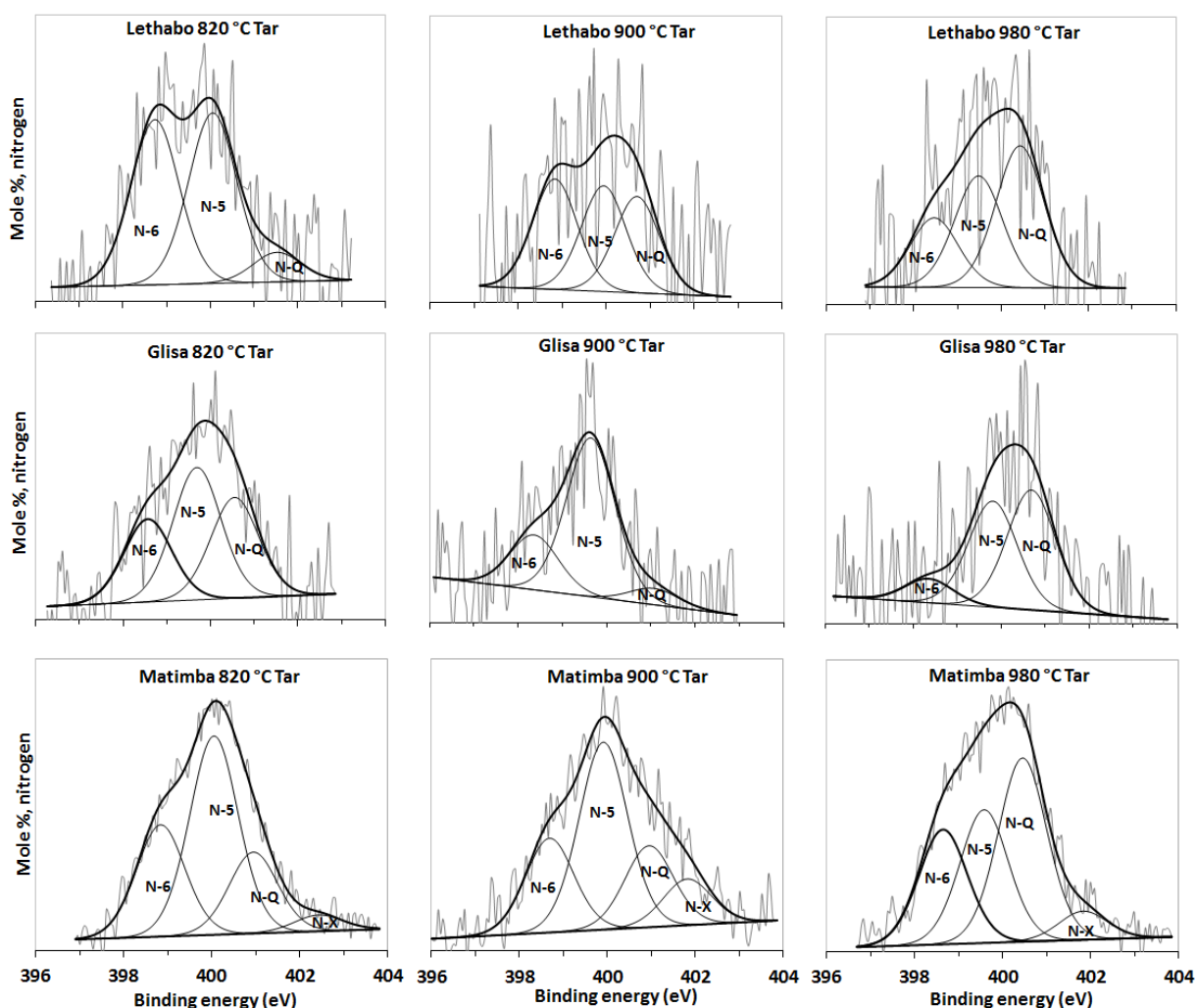
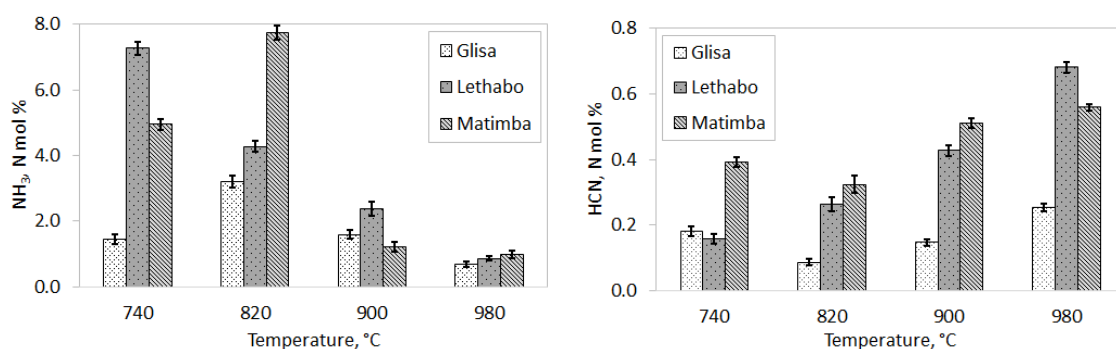


Figure 5.4: XPS N 1s spectra illustrating the transformation of nitrogen functional forms in tars released from the three coals in a fluidized bed from 820–980 °C.

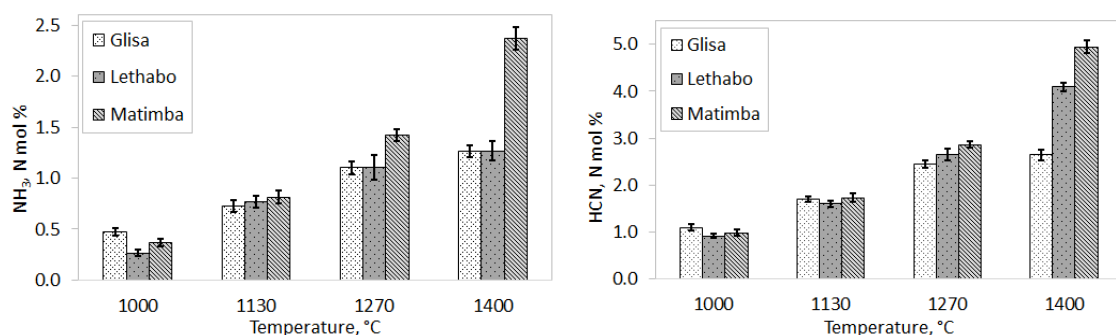
5.3.1.2 NH_3 and HCN Release

Ammonia and hydrogen cyanide released from FB and DTF during pyrolysis of three South African bituminous coals are shown in Figure 5.5. The fraction of coal-N released as NH_3 in FB at temperatures of 740–980 °C is illustrated in Figure 5.5(a). NH_3 emission from Lethabo coal displayed a maximal at 740 °C and a minimal at 980 °C, while Glisa and Matimba displayed their respective maximum NH_3 yields at 820 °C, ranging from about 3.2–7.4%. The effect of temperature on the release of NH_3 shown in Figure 5.5(c) for Glisa and Matimba coals was also observed by Tsubouchi and Ohtsuka (2008) on six Australian coals with a maximum NH_3 release occurring at around 800–850 °C. This trend was also confirmed on coals investigated by Li and Tan (2000). HCN emission principally increased with temperature as shown in Figure



(a) NH_3 released from the fluidized bed.

(b) HCN released from the fluidized bed.



(c) NH_3 released from the drop-tube furnace.

(d) HCN released from the drop-tube furnace

Figure 5.5: NH_3 and HCN expressed as fractional N release of coal-N during FB and DTF pyrolysis of three South African coals.

5.5(b); however, the HCN release from Glisa and Matimba decreased and displayed a minimum value at 820 °C, as opposed to the NH_3 yields at the same temperature. Figure 5.5(c) and 5.5(d) shows the effect of temperature on the respective release of NH_3 and HCN during DTF pyrolysis. In general, HCN was the predominant precursor of nitrogen oxides, while only small portions of coal-N were converted into NH_3 . The release of NH_3 and HCN from Glisa coal was higher than that of the other coals at 1000 °C; however, at 1130–1400 °C the release of NH_3 was higher from Matimba coal. Similar proportional amounts of coal-N were released as NH_3 at 1270 and 1400 °C for Glisa and Lethabo coals.

The results obtained indicate that the release of NH_3 and HCN is influenced by a combination of coal properties and pyrolysis conditions. Under FB pyrolysis conditions, at 740 °C, the high mineral matter and inertinite-rich Lethabo coal released the most NH_3 . Figure 5.5(a) indicates that the release of NH_3 of the three coals at 740 °C were in the order of Lethabo > Matimba > Glisa, which is also the order of

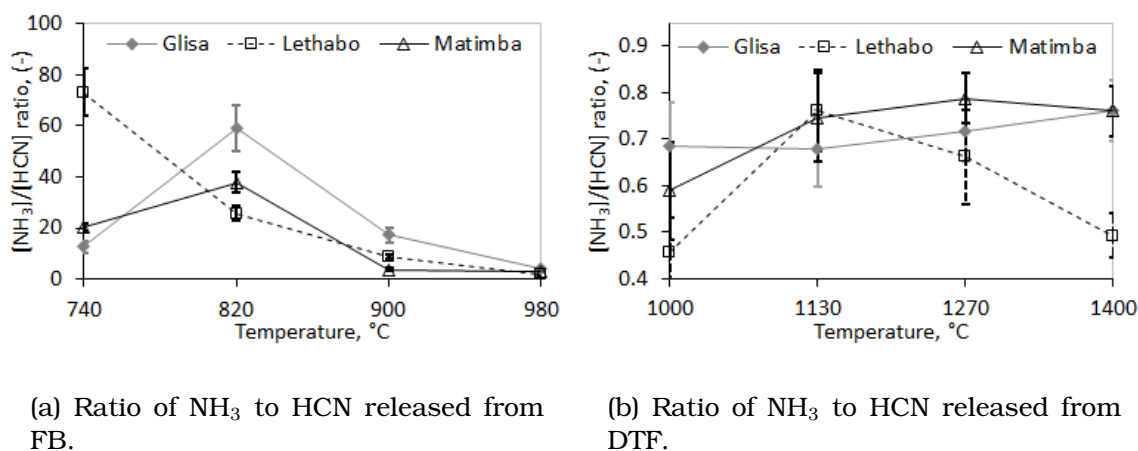


Figure 5.6: Ratio of NH_3 to HCN released during pyrolysis of the three coals in FB and DTF.

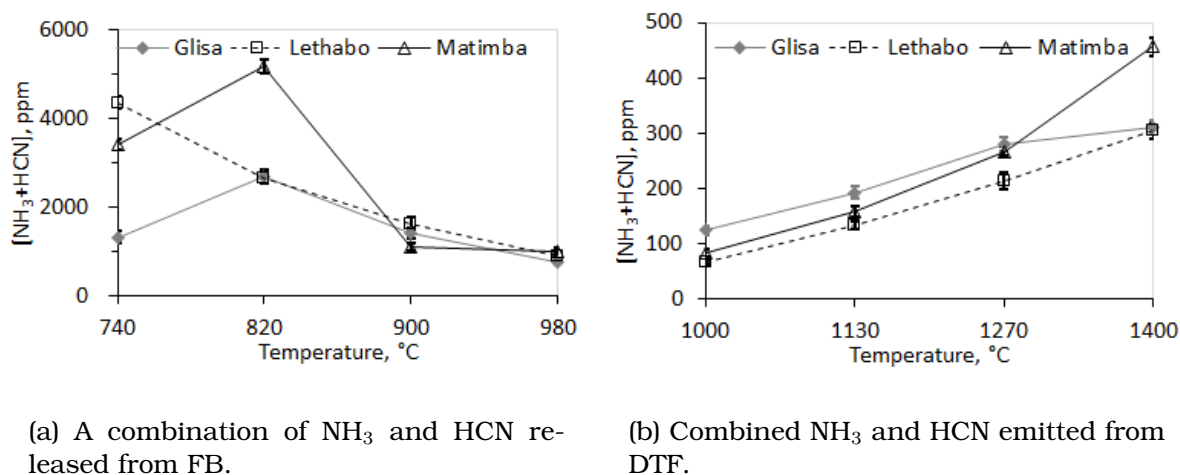


Figure 5.7: Total of NH_3 and HCN liberated during pyrolysis of the three coals in FB and DTF.

mineral matter content of the coals as indicated in Table 5.1. Further, HCN released at 980 °C exhibited a similar order of yields, which is also the order of the mineral matter content of the parent coals. These observations suggest that the catalytic effect of inherent minerals could have had an influence on the release of NH₃ at 740 °C and HCN at 980 °C (Tsubouchi and Ohtsuka, 2002a, 2008). Therefore, the effect of mineral matter on the release of a particular nitrogenous volatile species is also dependent upon the pyrolysis temperature. Yan et al. (2005) pointed out that Fe, Ca, K, Si, and Al heighten the coal-N conversion to NH₃ during pyrolysis, while Na promotes the formation of HCN. Fe and Ca have been reported to increase the decomposition of HCN to N₂ (Johnsson, 1994; Mori et al., 1996), concurrently reduce the conversion of fuel-N to HCN, while simultaneously promoting an increased release of N₂ (Mori et al., 1996; Tsubouchi and Ohtsuka, 2002a,b, 2008). Wu et al. (2003) monitored the influence of Ca and Fe on the release of N₂ during pyrolysis of model coals and determined that more N₂ was released when the additions of Ca and Fe were increased from 0.5 to 3.0 wt %.

The release of NH₃ at 820 °C seemed to be influenced by the maceral composition of the coals. The Matimba coal which has high vitrinite content released the most NH₃ at 820 °C, whereas the other two inertinite-rich coals, Glisa and Lethabo, both released much less amounts of NH₃. Under DTF conditions, at 1000 °C, Glisa coal released the most NH₃ and HCN. The order appeared to be influenced by the reverse of mineral matter content; Glisa coal has the least and Lethabo coal has the most, leading to the sequence: Glisa > Matimba > Lethabo. However, the yields of NH₃ and HCN at 1130–1400 °C gave the impression that they were influenced by the vitrinite maceral; Matimba coal released the most, while the inertinite-rich Glisa and Lethabo coals released approximately equal amounts. Therefore, the catalytic effect of the inherent minerals in parent coals seemed not have a major influence on the release of HCN and NH₃ under the utilized DTF conditions. Tsubouchi (2014) showed that the yields of tar-N, HCN, and NH₃ were almost unchanged when residence time was increased to 120 s regardless of the coal type; however, the N₂ yields increased while the char-N decreased with increasing residence time. Tsubouchi (2014) further highlighted that small quantities of inherent Ca and Fe seem to enhance the formation of N₂ from devolatilised char-N. In their earlier work, Tsubouchi and co-workers (Tsubouchi et al., 2001; Tsubouchi and Ohtsuka, 2002a,b) demonstrated that Ca²⁺ ions doped in low rank coals promoted the formation of N₂ from char-N regardless of the heating rate when coals are pyrolysed at temperatures exceeding 1000 °C. Table 5.2 shows that the three coals possessed substantial amounts of Ca which ranged between 1.30% and 2.12%, as well as 0.79–2.25% Fe. Low mineral matter content seemed to favour the liberation of light volatile-N species under the

given DTF conditions. Tsubouchi and Ohtsuka (2008) reported that slow heating rate pyrolysis of acid demineralized low-rank coals at 1000 °C in a fixed bed reactor increased HCN and decreased NH₃ output. This implies that low mineral matter or absence of mineral matter favours the production of HCN over NH₃. Tsubouchi and co-workers (Tsubouchi et al., 2003a, 2001; Tsubouchi and Ohtsuka, 2002a) also demonstrated that the Fe and Ca cations, which are inherently present in coals or through doping of demineralised coals, alter nitrogen distribution during pyrolysis. An analysis of results presented by Tsubouchi (Tsubouchi, 2014; Tsubouchi et al., 2003a) indicates that coals with high mineral matter content tend to release reduced HCN and increased N₂. This analogy gives the reason behind the obtained low HCN and high N₂ emanating from the three high mineral matter coals utilised in this study as illustrated in Figure 5.2.

Both fluidised bed and drop-tube furnace reactors possessed high temperature zones which provided necessary conditions for the occurrence of secondary reactions. The release of NH₃ from the FB was much greater than HCN under all FB temperature conditions as indicated by the NH₃/HCN ratios illustrated in Figure 5.6(a). However, more HCN than NH₃ was released from the DTF as shown by the NH₃/HCN ratios in Figure 5.6(b). The difference between results from the FB and DTF indicates that formation of NH₃ and HCN are to a great extent dependent upon coal properties and pyrolysis conditions. Leppälahti and Koljonen (1995) as well as Li and Tan (2000) clearly showed that the ratio of HCN/NH₃ released from model compounds varies to a large extent as a result of different pyrolysis conditions used. FB pyrolysis released relatively more NH₃ compared to HCN for all three coals. The FB pyrolysis experiments were characterized by high residence time, large coal particle sizes (± 1 mm) and relatively low temperatures. The high yields of NH₃ may be conceptualized as a result of HCN initially forming during pyrolysis (Bassilakis et al., 1993). The formation of NH₃ occurs by virtue of hydrogenation of HCN which predominantly occurs homogeneously as a result of the inherent H₂ released during pyrolysis. Hydrogenation also takes place heterogeneously on the char surface. Other reactions involving free radical mechanism may also occur on the char surface to convert HCN to NH₃ (Tan and Li, 2000a,b). In addition to hydrogenation, the formation of NH₃ is also perceived to emanate directly from the solid fuel matrix (Bassilakis et al., 1993), however, the conditions favouring the hydrogenation of HCN on the char surface results in high yields of NH₃. Carpenter et al. (2006) stated that despite the observed trends of HCN and NH₃, it remains speculative whether HCN or NH₃ is emitted discretely or whether, and to what extent, NH₃ is an outcome of secondary reactions. Johnsson (1994) reviewed several studies that pointed out that the conversion of coal-N to HCN and NH₃ was dependent on pyrolysis conditions, with a higher proportion of NH₃ to

HCN reported in slow heating-rate pyrolysis compared to rapid heating-rate pyrolysis. The DTF pyrolysis experiments were characterized by high temperatures and small particle sizes. The influence of coal properties on the formation of volatile-N species varies with the heating manner, which is the final temperature in this instance.

The total yields of nitrogen in light volatile nitrogenous species as deduced from the summation of NH_3 and HCN ($\text{NH}_3 + \text{HCN}$) is shown in Figure 5.7. Since the yield of NH_3 in FB was far greater than that of HCN, the trend of total volatile-N species almost resembles the yields pattern of NH_3 . The significant decrease of total volatile N species with temperature (from 740 °C for Lethabo, and from 820 °C for both Glisa and Matimba coals) in the FB is attributed to the increased conversion of tar and char nitrogen into gaseous N_2 . The total volatile-N yields emitted during pyrolysis from the three coals in the DTF (Figure 5.7(b)) increased with temperature. Glisa coal released more volatile-N from 1000 to 1270 °C; however, the yields obtained remained almost unchanged between 1270 and 1400 °C. Nonetheless, the total volatile-N yields from Matimba coal increased significantly at 1400 °C. This observation could be attributed to the low volatile content and the slightly higher aromaticity of the inertinite-rich Lethabo coal. At 1400 °C, all the volatiles had been driven off (Phiri et al., 2017, 2018b), while the moderately high aromaticity suggests that the nitrogen atoms exist in the centre of the clusters in the form of N-Q (Phiri et al., 2017), which is more stable than the N-5 and N-6, hence requiring more energy to break the bonds. The high hydrogen content and relatively low aromaticity of Matimba coal suggest that it has high aliphatic components (Phiri et al., 2018b), of which the energy at 1400 °C caused the driving off of significant quantities of volatiles incorporating nitrogen from the edge located N-5 and N-6. Nitrogen evolution was found to increase significantly with the pyrolysis temperature as illustrated in Figure 5.1. The analysis of respective chars, reported elsewhere (Phiri et al., 2017, 2018b), showed that the char nitrogen content diminished appreciably with temperature. Most of the nitrogen is evolved during the later stages of devolatilisation as HCN, hence the yields of HCN were higher at 1400 °C.

5.4 Conclusion

The influence of SA bituminous coal properties on the release of nitrogenous species during pyrolysis in a bench-scale fluidized bed at 740–980 °C and in a drop-tube furnace at 1000–1400 °C was evaluated. The pyrolysis N product distribution is dependent upon the coal properties and pyrolysis temperature. Char-N yields were predominant from FB pyrolysis, whereas coal-N was mostly converted to N_2 during DTF pyrolysis. Vitrinite-rich Matimba coal released more volatile-N than the inertinite-rich

Glisa and Lethabo coals. The fuel nitrogen in vitrinite-rich coal particles is released more easily than in inertinite-rich coals. However, there is no dominant coal property that can be singled out as being responsible for influencing the formation of a particular volatile-N product across the entire temperature range, but rather a combination or singular mineral matter and/or petrographic properties. Nonetheless, at a distinct point or specified temperature range, a particular coal attribute or combination determines the dominant volatile-N species liberated. Low temperature tars liberated from the three coals possessed similar nitrogen functional form attributes as the respective parent coals. The tars released at low temperatures (740–900 °C) predominantly consisted of pyrrolic nitrogen, followed by pyridinic and quaternary nitrogen, respectively. Relatively minute proportions of protonated and/or oxidized pyridinic nitrogen emerged in high temperature tars emanating from the vitrinite-rich coal. Tars liberated at the highest FB temperature (980 °C) mainly comprised quaternary nitrogen, followed by pyrrolic and pyridinic nitrogen, respectively. Mineral matter has a significant influence on the release of NH_3 at the lowest FB temperature (740 °C). However, the release of NH_3 at 820 °C correlated with the proportion of vitrinite maceral in the respective parent coals. Overall, higher yields of NH_3 than HCN were obtained from the FB pyrolysis experiments; however, the opposite was true for DTF experiments as more HCN than NH_3 was obtained. The formation of NH_3 and HCN during pyrolysis of coal in FB and DTF is perceived to occur through different mechanisms due to different conditions and coal properties. HCN is primarily formed at the inception of pyrolysis. Nonetheless, the FB conditions enabled secondary pyrolysis to prevail, enhancing the hydrogenation of HCN to form NH_3 . FB conditions were characterized by relatively low temperature, long solid residence time, and large coal particle sizes. The conditions employed in DTF (high temperature, low solid residence time, and small coal particle sizes) were favourable for the production of HCN. NH_3 and HCN released from either a vitrinite-rich or an inertinite-rich coal vary with temperature.

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References

Please note that references for this chapter are consolidated in the main references on page 113.

CHAPTER

6

CONCLUDING SUMMARY

Conclusions deduced during the entire course of the study are outlined and linked in this chapter. The practical implications are deliberated, and recommendations are suggested to usher the way forward into future investigations.

6.1 Concluding Remarks

Three South African bituminous coals were pyrolysed at high heating rates under different temperature conditions to generate chars. An extensive series of analytical techniques were utilised on raw coals together with the generated chars to establish morphological transformations. The chars were prepared at temperatures ranging from 740 °C to 980 °C in a FB, as well as at 1000 °C to 1400 °C in a DTF. The influence of systematic chemical treatment (using HCl and HF) on nitrogen functionalities of coals along with the respective chars was investigated. The evaluation of parallel evolution of nitrogen containing species as influenced by the inherent coal attributes in the course of pyrolysis was also performed.

1. The subdivision of coal nitrogen into nitrogenous volatile species and nitrogen retained in char due to pyrolysis is determined by the parent coal attributes and temperature. A significant fraction contained in coal was retained in char in the course of FB pyrolysis. However, appreciable portions of coal-N were discharged as volatiles at elevated DTF temperature ranges. Vitrinite seemed to influence the emission of volatile-N species in the course of FB pyrolysis. However, the

volatile-N evolved from DTF pyrolysis at elevated temperatures (1130–1400 °C) appeared to be regulated by total reactive macerals.

2. All chars obtained from FB pyrolysis possessed N-5, N-6, N-Q and N-X functional forms, of which, N-Q dominated the whole set. However, severe temperature conditions applied in DTF caused chars derived from coals with high total reactive macerals to have only two N functional forms, predominantly N-Q and N-6. On the other hand, chars prepared from the parent coal with the least total reactive macerals contained the four N functional forms like those emanating from FB.
3. The systematic HCl/HF/HCl demineralisation process bore insignificant impact on nitrogen functionalities of the whole set of parent coals. A similar resistivity towards N functionality alteration after chemical treatment was exhibited by the entire char range (FB and DTF) derived from the parent coal possessing high mineral matter content coupled with the least amount of total reactive macerals (inertinite-rich Lethabo coal). Nevertheless, acid treatment of chars containing N-Q and N-6 which were generated from relatively high total reactive macerals caused organic nitrogen structural transformations leading to the formation of N-5 and N-X, resulting in remnants of chemical treatment having four N functional forms.
4. The morphological transformations occurring in the course of pyrolysis caused most of the char retained nitrogen to be included within the heterocyclic aromatic structures. This occurrence was illustrated by the escalation of aromaticity together with N-Q due to temperature. The growth of aromatic ring systems is also depicted by the apparent increment of the crystallite diameter. The marked reduction of N-5, likewise accompanied by X_A and DOI , demonstrates the ease of loss of nitrogen associated with peripheral heterocyclic structures into the volatile stream. This phenomenon sheds clarity on the thermal susceptibility of the reactive macerals, especially the vitrinite. The reactive macerals are linked to N-5 and amorphous carbons, hence the conditions experienced in DTF drove off all the N-5, leaving behind the more stable nitrogen that is infused in aromatic structures in the form of N-Q and N-6. Most of the nitrogen within the inertinite maceral exists in stable aromatic ring systems. The quantity of total reactive macerals plays a major role in determining the morphological transformations as well as the release of volatile compounds at elevated temperatures. Glisa coal is predominantly inertinite. However, it contains a substantial proportion of total reactive macerals contributed by reactive semi-

fusinite and reactive inertodetrinite. This explains its comparable morphological change behaviour to that of vitrinite at high temperatures.

5. The tars that were discharged from the FB at temperatures ranging from 740 °C to 900 °C mostly constituted of N functional form moieties similar to that of raw coals, of which N-5 was dominant, followed by N-6 and N-Q, respectively. Nevertheless, N-Q became the dominant functionality at 980 °C across the board. Minimal proportions of N-X were only experienced in tars derived from the vitrinite-rich coal at 820–980 °C.
6. Mineral matter possessed meaningful impact on the evolution of NH_3 at 740 °C during FB pyrolysis. Nonetheless, the emission of NH_3 at 820 °C appeared to be influenced by the vitrinite maceral. In entirety, NH_3 was emitted in large proportions relative to HCN. However, the DTF liberated appreciable HCN yields in comparison to NH_3 . There is a general consensus that the mechanism of N release initially entails the formation of HCN in the course of pyrolysis. Henceforth, the conditions in the FB were appropriate for hydrogenation of HCN to form NH_3 . On the other hand, the conditions in the DTF did not provide much room for extensive hydrogenation of HCN, hence HCN yields were quite significant.

6.2 Contribution to Coal Science

The following deductions made through the course of this research are deemed to be worthy contributions towards the current status of knowledge within the coal science and technology fraternity:

- (a) The level of total mineral matter and the proportion of total reactive macerals influence the nitrogen product distribution. Coals containing high levels of total reactive macerals tend to be susceptible to pyrolysis severity; high temperature chars only contained N-Q and N-6. The coal with the highest total mineral matter and low total reactive macerals displayed resilience towards rapid N transformation at elevated temperatures.
- (b) The systematic demineralisation procedure utilising HF and HCl, as lixiviants on raw bituminous coals, does not have a meaningful impact on nitrogen functionalities.
- (c) Nitrogen functional forms in chars acquired from coals with low total reactive macerals do not exhibit marked alteration due to de-ashing. On the other hand, the nitrogen functional forms of chars generated at high temperatures from

coals possessing a substantial portion of total reactive macerals tend to be more susceptible to acid treatment.

- (d) Utilising XPS and XRD showed that the transformation of quaternary nitrogen (N-Q), increases correspondingly with aromaticity as a result of pyrolysis. Whereas, heat treatment causes pyrrolic nitrogen to decrease harmoniously with disorder index (DOI), which is directly associated with carbon amorphous fraction (X_A).
- (e) In addition to temperature, the distribution of nitrogen functional forms in chars is determined by the maceral constitution of the respective parent coals. The distribution of nitrogen functional forms in chars obtained from high temperature treatment of predominantly inertinite coals which possess a significant fraction of total reactive macerals is similar to that of high temperature vitrinite-rich derivatives. Thus the proportion of total reactive macerals is the determining property.
- (f) Pyrolysis renders fuel nitrogen in predominantly vitrinite coals to be liberated with ease in comparison to the release from coals with high level of inertinites.

6.3 Implications for Practical Applications

The levels of nitrogen in coals and the respective chars remain almost the same after acid treatment (Phiri et al., 2017). This implies that the pretreatment procedure may not be used as a measure to curb the emission of nitrogen oxides in the course of combustion of the residual carbonaceous material. Nonetheless, the attained results are essential as they provide vital information on unattenuated nitrogen functional forms. Which could be utilised as input data in the development of coal and char molecular model structures. The envisaged comprehensive coal and char model structures that incorporate nitrogen functionalities may be utilised in simulations to enhance effectiveness of coal usage in the foreseeable future.

The results from this study have significant ramifications; there is a high probability that char morphological modifications directly influence the release of nitrogen (Phiri et al., 2018b). The structural properties of char have an impact on char reactivity, that in turn is a significant aspect in establishing the transformation of nitrogen contained in coal. The utilised series of analytical techniques revealed that the nitrogen on the periphery of heterocyclic aromatic structures migrates into the interior of enlarged and condensed polycyclic aromatic structures in char. The prescribed movement of nitrogen turns out to be essentially complete at successive elevated temperatures. The observed phenomenon carries meaningful practical significance

which may eventually contribute towards enhanced nitrogen emission kinetic mechanisms in coal conversion processes.

A significant fraction of nitrogen in coal remained in successive FB chars, in comparison to DTF chars which retained progressively diminishing portions of nitrogen. It is extensively documented in literature that FB combustion systems discharge relatively low NO_x and substantial N₂O emissions (Glarborg et al., 2003; Wójtowicz et al., 1993). On the other hand, the NO_x emitted from pulverised fuel combustion systems is quite high, with traces of N₂O, if any (Carpenter et al., 2006). Therefore, from these findings, NO_x emissions can be linked to volatile-N, while N₂O is associated with char-N.

The observed simultaneous changes of nitrogen functionalities with char crystallite structures are regarded as having influence on the release of nitrogenous species (Phiri et al., 2018a,b). The finding may in future be utilised in designs and applications like low-NO_x burner technologies. Char nitrogen is discharged by virtue of heterogeneous oxidation during combustion, implying that low-NO_x burners possess limited effect on NO_x emanating from nitrogen that is present in char. Char-N as well as the accompanying char crystallite characteristics are dependent on the molecular and structural moieties of condensed heterocyclic aromatic formations. The stable N-6 and N-Q are dominant in high temperature chars, in which the nitrogen does not break away with ease into gaseous components. Therefore, the information on the behaviour of char-N, and levels of nitrogen, could lead to the development of reaction rate equations, which in-turn have the potential of contributing to more developed designs of low-NO_x burner technologies. Thus, the established findings (Phiri et al., 2018a,b) may be utilised to determine potentially suitable input coals to feed combustion units. Fuel-rich conditions promote the formation of N₂, which forms the basis for air-staging techniques and applied in low-NO_x burner designs (Nelson et al., 1996). The low absolute nitrogen reported in chars, especially those generated from high total reactivities, confirm that significant levels of volatile nitrogen were emitted high DTF temperatures. Thus implying that such coals have a high likelihood of releasing reduced NO_x if they are utilised in low-NO_x burners.

6.4 Recommendations for Future Work

Future directions with aspiration to add value and extending the current findings are suggested as follows:

1. Make use of a large sample size that includes coals from different parts of the world, and constituting widely varying mineral matter content and maceral compositions.

2. Utilise a noble gas such as He or Ar as an inert gas during pyrolysis experiments so as to enable the measurement of N_2 released within the nitrogen product distribution.
3. Conduct modifications on the particular DTF equipment so as to facilitate tar collection and measurements.
4. Perform petrographic analysis on chars so as to obtain comprehensive char morphological transformations in conjunction with those deduced from XRD analysis.
5. Carry out subsequent combustion studies using the respective FB and DTF equipments under similar temperature conditions so as to extrapolate and evaluate the release of nitrogen oxides (NO_x and N_2O).
6. Utilise the nitrogen functionalities obtained from XPS in conjunction with HRTEM as an inception for molecular modelling to obtain molecular structures and data concerning kinetics.

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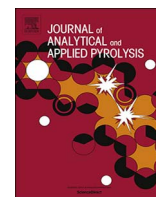
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Appendices

APPENDIX

A

TITLE PAGES OF PUBLISHED
ARTICLES



The effect of acid demineralising bituminous coals and de-ashing the respective chars on nitrogen functional forms



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ABSTRACT

An opportunity presented itself to compare changes in nitrogen functional forms brought by the acid treatment of South African bituminous coals and their respective chars. X-ray photoelectron spectroscopy (XPS) was used to determine functional forms of the raw coals, acid-treated coals, respective chars prepared at 740 and 980 °C in a bench-scale fluidised-bed (FB), and at 1000 and 1400 °C in a drop-tube furnace (DTF), as well as their corresponding de-ashed remnants. The XPS N 1s spectra for the raw coals were typically similar to previous widely reported bituminous coals, of which pyrrolic nitrogen was the predominant form of organically bound nitrogen, followed by pyridinic and quaternary nitrogen. In pyrolysed chars, quaternary nitrogen was the dominant form followed by pyridinic, pyrrolic and protonated-/oxidised heterocyclic nitrogen forms respectively. Nonetheless, XPS N 1s analysis for DTF severely pyrolysed chars (1000 and 1400 °C) prepared from high ash and vitrinite-rich coal, and also a char (1400 °C) from a relatively low ash and inertinite-rich coal, gave a spectra with only two sub-peaks corresponding to quaternary and pyridinic nitrogen. It seems that the HCl/HF/HCl sequential demineralising/de-ashing process had no effect on the nitrogen functional forms of raw coals and the entire chars prepared from the FB. De-ashing of DTF severely pyrolysed chars emanating from high ash and inertinite-rich coal exhibited no marked change to the nitrogen functional forms. However, acid treatment of DTF chars derived from a high ash and vitrinite-rich coal, a char from relatively low ash and inertinite-rich coal, which initially contained pyridinic and quaternary nitrogen resulted in additional nitrogen moieties of pyrrolic and protonated/oxidised nitrogen.

1. Introduction

Nitrogen constitutes a relatively small organic portion in coal in the order of 2% or less, with the bulk organic component comprising of carbon, hydrogen and oxygen atomic components, while sulphur also makes up a very small portion [1,2]. Coal is principally comprised of tiny aromatic structures [3] and almost all the nitrogen in coal exists as heterocyclic nitrogen functional forms [4,5]. The inorganic portion mostly comprises of various minerals whose concentration differ from coal to coal, depending on source. The bulk of the minerals present in coal comprise of kaolinite, quartz, illite, montmorillonite, siderite, calcite, gypsum, pyrite, dolomite and feldspars [6].

The presence of inorganic matter in coal notably influences its chemical attributes and potential utilisation. Prior to certain laboratory analytical techniques or conversion processes, coals and chars are leached by an acid or alkali solution to reduce mineral or ash content significantly. Increasing the efficiency of coal usage and the call to mitigate environmental implications of coal combustion are some of the

major reasons for the need for coal chemical pre-treatment. It is therefore of paramount importance to be equipped with knowledge on whether the leaching procedure modifies the coal or char structure in addition to the intended minerals or ash removal. The demineralisation or de-ashing process is often conducted by utilising one or more of a combination of HCl, HF, NaOH, H₂SiF₆ and HNO₃ [7].

Several other aspects of leaching processes which proved to reduce mineral matter in coals and ash content in chars appreciably have been demonstrated [7–14]. At present, there are no commercially viable technologies for clean coal production. Nevertheless, there is quite a number of pertinent patents in this regard [15–19]. In laboratory analyses, the presence of mineral matter in coal or ash in char causes interference in certain analytical techniques [20–24]. X-ray photoelectron spectroscopy (XPS) can be used on characterising and identifying the chemical forms of nitrogen in both raw and acid-treated samples without limitations. However, a number of coal and/or char analytical techniques such as X-ray diffraction (XRD) to analyse carbon crystallites and amorphous fractions, solid state ¹³C or ¹⁵N nuclear

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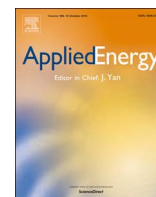
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Transformation of nitrogen functional forms and the accompanying chemical-structural properties emanating from pyrolysis of bituminous coals

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HIGHLIGHTS

- Transformations in N functionalities and carbon crystallite structures were examined.
- Pyrolysis caused the change in aromaticity to correlate with quaternary-N of chars.
- Diminishing pyrrolic-N in chars correlated with the degree of disorder index (DOI).
- Total reactive macerals in coal influence morphological changes at high temperatures.
- Vitrinite- and inertinite-rich coal chars displayed similar and varying N forms.

ARTICLE INFO

Keywords:

Nitrogen forms transformation
Carbon crystallite
Pyrolysis
XPS
XRD
Char morphology

ABSTRACT

Characterisation of simultaneous changes in nitrogen functionalities and condensed aromatic crystallites during pyrolysis of bituminous coals was conducted. X-ray photoelectron spectroscopy (XPS) was utilised to determine nitrogen functional forms in three South African bituminous coals and the subsequent transformation in respective chars. Corresponding structural properties of coal and char were deduced through X-ray diffraction (XRD) analysis. Carbon structural properties in parent coals were also determined by solid state ¹³C nuclear magnetic resonance (ss NMR). The chars were prepared by pyrolysis at 740–980 °C in a bench-scale fluidised-bed (FB) and at 1000–1400 °C in a drop-tube furnace (DTF). The changes in XPS N 1s spectra of the coals through the respective chars were used to determine the nitrogen functionality transformations. Deconvolution of the XPS N 1s spectra revealed that pyrrolic nitrogen decreased with increasing pyrolysis temperature while quaternary nitrogen increased appreciably. Simultaneously, information deduced from XRD spectra showed that aromaticity (f_a) and average crystallite diameter (L_a) increased with severity of pyrolysis temperature in all the chars, while the fraction of amorphous carbon (X_A) and degree of disorder index (DOI) decreased significantly. Chars derived from the vitrinite-rich (also high in total reactive macerals) coal were more susceptible to thermal treatment with regard to nitrogen functional forms and other carbon crystallite transformations; high temperature chars only contained pyridinic and quaternary nitrogen, and exhibited a significant increase in crystallite height (L_c) and the average number of aromatic carbons (N_{ave}). Aromaticity of coals determined from ss ¹³C NMR and XRD corresponded. Comparison of structural changes brought by pyrolysis, as measured by XPS and XRD, showed that a good correlation existed between increasing quaternary nitrogen and f_a . In a marked contrast, the diminishing of pyrrolic nitrogen displayed a good efficacy with DOI and X_A . The reported concomitant transformations of nitrogen functional forms with char morphological changes are considered precursors to nitrogen release. This will inform future detailed studies on the conversion of coal nitrogen in solid fuel fired systems, such as in the applications of low-NOx burner technologies towards the release and reduction of nitrogen oxides in pulverised coal combustion.

1. Introduction

Coal is integral to the economies of several countries and regions

around the world as it provides reliable and affordable power required to meet electricity demand and fuel economic growth. Bituminous coals are mostly used for steam production in the electric power generation

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Release of Nitrogenous Volatile Species from South African Bituminous Coals during Pyrolysis

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ABSTRACT: The influence of typical South African coal attributes on the release of nitrogen into the volatile stream during pyrolysis was studied by utilizing three bituminous coals. The majority of South African coals are characterized by high mineral matter and are rich in inertinite maceral. Pyrolysis was conducted in a bench-scale fluidized bed (FB) at 740–980 °C, and also in a drop-tube furnace (DTF) at 1000–1400 °C. Levels of nitrogenous species in the volatile stream in the form of NH₃, HCN, and tar-N were determined. Nitrogen functional forms of tars released at low temperatures were predominantly distinguished by high levels of pyrrolic nitrogen, followed by pyridinic and quaternary nitrogen, respectively. Tars liberated at 740 °C possessed similar nitrogen functional form attributes as those of parent coals. However, an increase in pyrolysis temperature caused a gradual increase in quaternary nitrogen as well as a concurrent decrease in pyrrolic nitrogen and a concomitant subtle decrease in pyridinic nitrogen. The analysis of nitrogen in tars was only confined to tars extracted from the FB. Vitrinite-rich and/or high mineral matter coal released high yields of nitrogenous species into the volatile stream at low FB temperatures. A large amount of NH₃ was released relative to HCN under FB pyrolysis conditions. However, more HCN was released than NH₃ during DTF pyrolysis. Two coals, one characterized by high mineral matter and being rich in vitrinite, and the other distinguished by relatively low mineral matter and being rich in inertinite, behaved similarly by reaching respective peak amounts of NH₃ yields at 820 °C under FB pyrolysis conditions. On the contrary, an opposite profile displaying a slump at 820 °C was observed for HCN yields from the two respective coals. The third coal, a high mineral matter and inertinite-rich coal, released high NH₃ yields and simultaneously the least HCN yields at 740 °C. Under DTF experimental conditions, both NH₃ and HCN steadily increased with temperature in all coals. The low mineral matter and inertinite-rich coal released high yields of total volatile-N from 1000 to 1270 °C, only to be surpassed by the vitrinite-rich/high mineral matter coal at 1400 °C. The inertinite-rich/high mineral matter coal released the least throughout the entire DTF temperature range. The total mineral matter content of the coals played a significant role toward the nitrogen product distribution. On the other hand, the total reactive macerals also influenced the emission of volatile species at 1130–1400 °C DTF temperature range. The yields and composition of the released nitrogenous species have been attributed to a combination of mineral matter content, petrographic properties of the parent coals, and the utilized conditions. Pyrolysis temperature, coal particle size, and residence time also play a significant role toward the yields and composition of the released nitrogenous species.

INTRODUCTION

Introducing coal into a combustion unit initially gives rise to devolatilization (pyrolysis) causing the partitioning of coal-N into volatile-N and char-N.¹ The volatile-N stream constitutes of tar-N, HCN, NH₃, and N₂.² HCN and NH₃ have been identified as the main precursors of oxides of nitrogen during coal combustion in several studies.^{3–13} The volatile-N species influence the respective final oxides of nitrogen pollutants produced during the subsequent combustion. Nitric oxide (NO) and nitrogen dioxide (NO₂), often designated as NO_x, are potent pollutants that have been attributed to causing acid rain, ground level ozone, and photochemical smog. Another oxide of nitrogen, nitrous oxide (N₂O), is a potent greenhouse gas, and it has been blamed for indirectly depleting the ozone layer.¹⁴ Numerous studies have been conducted with the quest to comprehend the chemistry behind the formation of tar-N, HCN, NH₃, and char-N as precursors of NO_x and N₂O.^{13–21} However, further work is still

necessary to comply with the ever increasing stringent legislation on nitrogen oxides emission from coal combustion. South Africa's power generation industry is heavily dependent on coal combustion, hence the need to be more vigilant and heed the call to significantly reduce emissions.

The partitioning and product distribution of coal nitrogen between volatile species and char nitrogen have been perceived to be influenced by coal properties, encompassing parent coal composition, attributes of the respective char residue, and the surface characteristics.^{22,23} Nitrogen is preferentially retained in char at low temperature; however, a large fraction is released into the volatile stream at high temperatures.^{24–31} In addition to pyrolysis temperature, other conditions which include heating

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