Conversion of coal-N to NO_x under fluidized-bed combustion conditions

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DECLARATION

I declare that this research work submitted for completion of the requirements of master degree at Wits University, Johannesburg is my own original work. It has not been submitted before for any degree or examination in any other institution.

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Abstract

The objective of this project was to assess the conversion of coal-N to nitrogen oxides during combustion in a fluidized bed. Nitrogen oxides are harmful environmental pollutants generated in coal-fired power plants when fossil fuels are burned which contribute to acid rain and photochemical smog. Fluidized-bed combustion technology, with its reduced SO_2 and NO_x emissions, is an attractive option compared to conventional pulverized coal (PC) boilers mainly due to the low operating temperatures employed, usually between (800–900°C).

Four coals namely Secunda, Kuthala, Delmas and New Vaal were characterized using proximate, ultimate, calorific value (CV), ash and petrographic analyses. All tested coals are inertinite rich with Delmas coal having relatively high vitrinite content. All coals were classified as bituminous, with three coal samples falling in the medium rank C (Kuthala, Delmas and Secunda) and one in the medium rank D range (New Vaal).

The effects of coal characteristics on the conversion of coal-N to NO_x for different South African coals tested in BFBR is also examined. The analysis of experimental data on the combustion in FB reactors revealed different trends in the conversion of coal-N to nitrogen oxides. The conversion of coal-N to NO decreased with nitrogen for coals tested. The relationship between the conversion of coal-N and CH/N using a correlation developed by Vermeulen, revealed an almost linear correlation between the two parameters for the tested coals, although the trends were in opposite direction. An even better linear correlation was found between conversion of coal-N and fuel ratio and again two sets of tested coals show excellent linear trends but in opposite direction. The correlation proposed by Vermeulen is therefore not applicable in the case of South African coals as it over predicts the conversion of coal-N to NO. New correlations developed for coals tested at Eskom by Moodley and Papo in the form of the Vermeulen's correlation but with different values of fixed coefficients are: $y = 6.5973x + 0.4649$, $R^2 = 0.9987$ and $y = 4.7911x + 15.297$, $R^2 = 0.9999$ respectively. New correlations for the coal samples tested in this study could not be obtained as NO values could not be measured.

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Abbreviations

AD	Air Dried
AR	As Received
BFB	Bubbling Fluidized Bed
BFBR	Bubbling Fluidized Bed Reactor
CCT	Clean Coal Technology
CFB	Circulating Fluidized Bed
CFBC	Circulating Fluidized Bed Combustion
CFBR	Circulating Fluidized Bed Reactor
CUT	Czestochowa University of Technology
CV	Calorific Value
DAF	Dry Ash Free
DB	Dry Basis
FB	Fluidized Bed
FBC	Fluidized Bed Combustion
FC	Fixed carbon
FGD	Flue Gas Desulphurization
FR	Fuel Ratio
FTIR	Fourier-Transform Infrared Spectroscopy
HHV	Higher Heating Value
ID	Internal Diameter
MS	Mass Spectroscopy
PC	Pulverized Coal
R	Correlation coefficient
R&D	Research and Development
SCR	Selective Catalytic Reduction
SNCR	Selective Noncatalytic Reduction
TGA	Thermogravimetric Analysis
VM	Volatile matter
XRF	X-ray Fluorescent

Chapter 1. Introduction

1.1 Combustion of coal as a source of nitrogen oxide emissions

Coal is one of the most abundant fossil fuels. In the South African economy, it plays an important role in the energy sector and in the chemical and steel industries. Whilst contributing more than 90% in electricity generation, coal also supplies approximately 30% of the country's liquid fuels. In total, approximately 70% of the country's total energy needs are derived from coal, making it primary energy source [1]. Different technologies are used in South Africa for generating power using coal. The most popular one is combustion in pulverised coal boilers [2] .

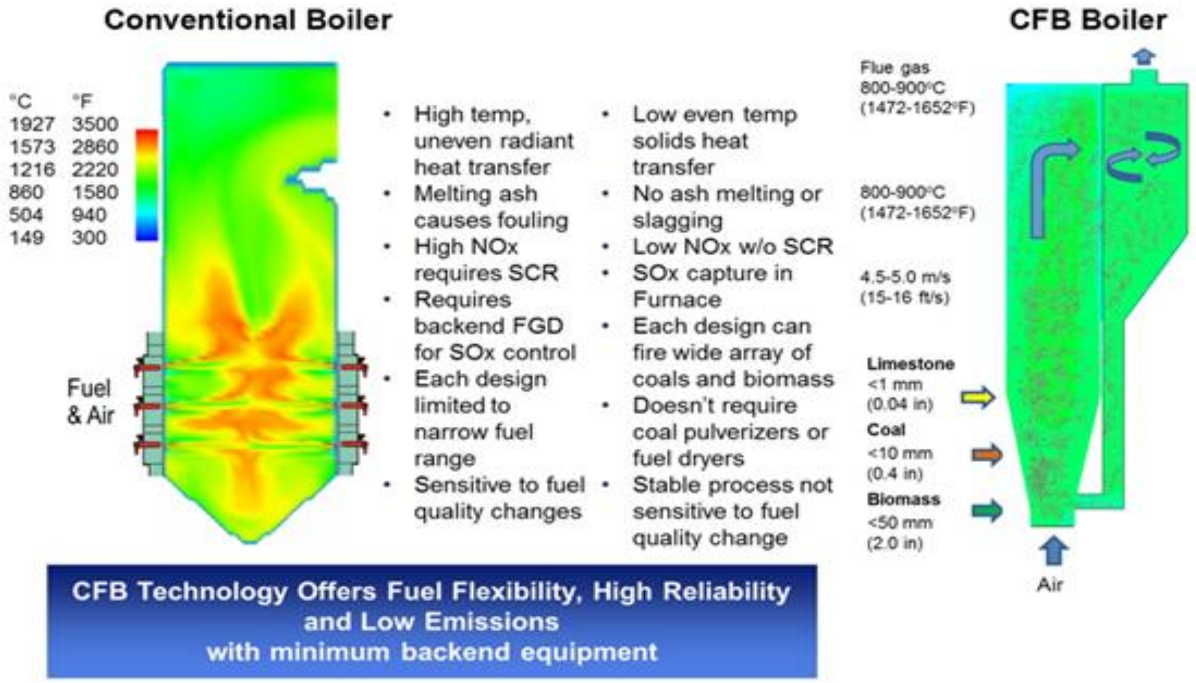
Despite coal's economic value, several harmful pollutants result from power generation as the carbonaceous fossil fuel is combusted to generate electricity. Coal combustion emits greenhouse gases, mainly CO_2, which contributes to global warming and climate change [2]. Other known environmentally harmful emissions in coal-fired power generation include nitrogen oxides such as NO and NO_2 commonly referred to as NO_x. These oxides contribute to acid rain and photochemical smog [3], [4], [5]. Nitrous oxide, N_2O, is also known to be involved in both the greenhouse gas effect and in ozone layer depletion [5], [6]. Coal burning in South Africa accounts for approximately two-thirds of SO_2, one-third of CO_2 and a quarter of nitrogen oxides total emissions [2] . Apart from Kusile power station, South African coal-fired power plant have no flue-gas desulphurisation (FGD) equipment fitted (This a post combustion flue-gas desulphurisation). These plants, therefore, contribute heavily to the emissions of SO_2 in the country [2].

As a result of the above mentioned problems, stringent environmental regulations have been introduced that prompted the need to revisit coal combustion technologies in order to curb environmental destruction.

Besides the above-mentioned environmental impact challenges, to which the country's primary power supplier, Eskom, is failing to comply, South Africa has also endured electricity shortages and steep electricity price hikes since 2008 [2], [62] .

In order to address these challenges, the quality of the remaining South African coal reserves has to be looked at. Most good quality coals have been mined, leaving lower grade, high ash-content discard coals in abundance [2]. Estimates are that 1.5 billion tons of historically discarded coals are in stock in the country[2], [62]. The current conventional South African pulverised coal boilers require a certain quality of coal. Unfortunately, discarded coals cannot be used as a fuel in pulverised coal boilers [2].

The Fluidised bed combustion (FBC) technology proves to be an attractive option for power generation because it can utilize low-quality coals, discards and rejects that are available at lower prices. A great advantage of FBC is its fuel flexibility. Fluidized-bed boilers can burn low-grade fuels with low calorific value, high ash content and high moisture content [2]. Conventional PC boilers will have problems accepting these low-grade coals due to their low calorific values. Figure 1.1 shows the main differences between PC and FBC combustion technology. South Africa has abundant resources of low quality coals which could be burned in FB boilers [2].



- High temp, uneven radiant heat transfer
- Melting ash causes fouling
- High NOx requires SCR
- Requires backend FGD for SOx control
- Each design limited to narrow fuel range
- Sensitive to fuel quality changes

- Low even temp solids heat transfer
- No ash melting or slagging
- Low NOx w/o SCR
- SOx capture in Furnace
- Each design can fire wide array of coals and biomass
- Doesn't require coal pulverizers or fuel dryers
- Stable process not sensitive to fuel quality change

CFB Technology Offers Fuel Flexibility, High Reliability and Low Emissions with minimum backend equipment

Figure 1. 1: Comparison of conventional versus CFB technology [7]

Fluidized-bed combustion is an alternative technology to the PC combustion because it produces lower SO_2 and NO_x emissions. It is among the combustion technologies that have been identified as a viable clean coal technology option [7], [9], [10], [12], [13]. Fluidized-bed combustion technology offers significant reduction of SO_x and NO_x emissions without expensive flue gas emission control systems such as Selective Catalytic Reduction (SCR), Selective Non Catalytic Reduction (SNCR) and Flue Gas Desulphurisation (FGD). This reduction is due to significantly lower combustion temperatures (800–900°C) compared to those prevailing in PC boilers (1300–1700°C) [5],[8],[10] . The low combustion temperature however enhances the formation of N_2O that is ranging from 20 to 300 ppm and is higher than that observed in PC boilers (approximately 10 ppm) [8].When sorbents, such as limestone or dolomite, are introduced into the combustion chamber approximately 90–95% of SO_2 emission reduction can be achieved [9]. Reduced corrosion of heat transfer surfaces and limited ash-fouling is also a result of lower combustion temperature allowing circulating fluidised bed boilers (CFB) to handle fuels that are difficult to burn in a PC boiler [9]. Efficient heat transfer to water walls is achieved even at low temperatures due to the circulation of hot particles which allows a longer residence time for combustion and reaction with sorbent [9], [10].

Circulating fluidized-bed combustion has more advantages than its counterpart, the PC combustion technology, however research and development in matching CFBC technology to local coals and sorbents is currently lacking in South Africa. As such, an establishment of a CFBC test facility to conduct this much needed R&D is required to allow for skills development in this new technology when it is deployed in the country.

1.2 Problem statement

The emissions of NO_x from coal combustion processes have attracted considerable attention due to their serious impacts on the environment. Nitrogen oxides are acid rain precursor and contribute to photochemical smog [5], [6], [11], [12]. As a consequence, stringent limits on these emissions have been introduced in an effort to improve the air quality and to lower the emissions from coal-fired plants. This has led to large amounts of work being done on the kinetics and mechanisms of NO_x reduction [11]. Fluidized-bed combustion is rapidly emerging as the most suitable and highly efficient power generation technology which allows combustion of coal with the reduced emissions of NO_x and SO_2 [13].

Moreover, with its wide fuel-quality intake range, FBC is particularly suited for considerably diverse rank and grade for South African coals [2]. Nowadays, CFB boilers with supercritical or ultra-supercritical steam parameters belong to “clean coal technologies” [9].

1.3 Hypothesis

It is expected that a significant reduction of NO_x emissions can be achieved using fluidised-bed combustion technology as an alternative for pulverized coal boilers currently used by the South African power industry.

1.4 The main and general objectives of the Research

1.4.1 The following were the main objectives:

- To provide an insight into the conversion of coal-N to NO_x based on the literature data and own data.
- To determine the influence of coal characteristics on the conversion of coal-N to NO_x. The main coal properties of interest are: nitrogen content, fuel ratio and ash composition.

1.4.2 General objective:

The general objective was to develop correlations that can predict the conversion of coal-N to NO as a function of coal properties.

1.5 The structure of the report

The present report contains four chapters. Chapter 1: provides a brief background of the investigation, problem statement and the aim of the project. Chapter 2: summarises coal formation process and discusses the main differences between coals of the Northern Hemisphere (Laurasian region) and those found in Southern Hemisphere (Gondwana region) in terms of the conditions at the time the coal was formed. This is followed by a discussion on coal combustion process highlighting the mechanisms and chemical reactions involved in each process. Finally, the chapter concludes with a section on formation of nitrogen oxides which identifies sources from which NO_x is formed. Chapter 3: covers the methodology and experiment techniques carried out during this investigation. Chapter 4: details experimental findings and discussion surrounding them.

Chapter 2. Literature review

2.1 Introduction

This chapter provides a brief overview of coal formation process and discusses the main differences between coals of the Northern Hemisphere (Laurasian region) and those found in Southern Hemisphere (Gondwana region) in terms of the conditions at the time the coal was formed. A detailed discussion on coal combustion process follows highlighting the mechanisms and chemical reactions involved in each process (i.e. drying, devolatilization, VM combustion and char burn out). Finally, the chapter concludes with a section on formation of nitrogen oxides which identifies sources from which NO_x is formed.

2.2 Coal formation process

For South Africa and many other developing countries worldwide, coal is and, for the foreseeable future, will be a relatively cheap major energy source due to its abundance over other energy sources [9].

Coal is a heterogeneous, combustible, carbon-rich rock containing over 50% of carbonaceous material derived from plants that lived hundreds of millions of years ago [15]. This is due to climatic and plant conditions during its formation period, as well as to subsequent geophysical actions. Organically, it is composed of oxygen, carbon, sulphur, hydrogen and nitrogen in small quantities. Inorganically it consists of ash forming compounds (minerals) distributed throughout the coal matrix [14].

The formation of coal resulted from the actions of pressure, heat and moisture being exerted on vegetation over millions of years [9]. Coal can be classified into different types depending on the extent of pressure and the time it was exposed to. As the pressure increases, this lowers volatile matter, oxygen percentage and increases carbon content leading to a glossier and less porous form. Coal's geological transformation path is from vegetation matter to peat, lignite, subbituminous coal, bituminous coal then anthracite [9]. The degree of maturation during the coalification process and the degree of chemical change in the coal determine the rank of the coal [11]. The type of vegetation at the peat formation time as well as changes taking place during the metamorphosis of the coal, determine the type of coal. [11]. The formation of coal in terms of rank, type and grade is shown in Figure 2.1

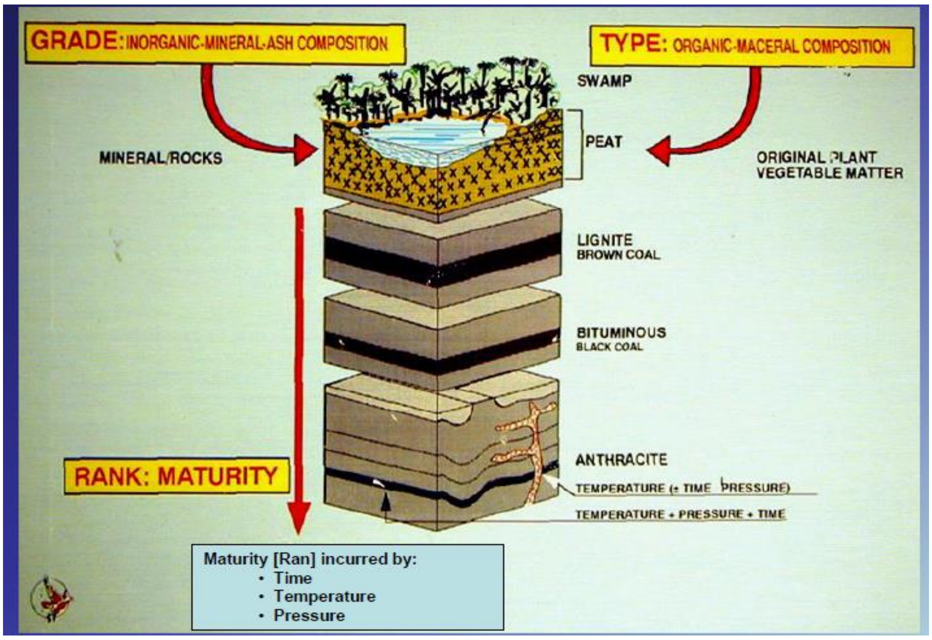


Figure 2. 1: The formation of coal in terms of rank (maturity), type (organic composition) and grade (mineral composition) [15]

2.2.1 Macroscopic constituents of coal

Coal can be described at two levels of resolution: macroscopically and microscopically. Macroscopically coal is subdivided into non-banded/sapropelic coal and banded/humic coal. Macroscopic constituents of coal are shown in Figure 2.2 [17]. The non-banded coal is dull and can be recognized by an even granular surface. This type of coal is believed to have originated from non-woody materials such as algae or water-borne detrital organic matter (spores, pollen) that have accumulated. The non-banded coal usually also comprise of mineral matter that is finely distributed. In banded coal, alternating fine layers of varying brightness is observed [16]. Banded coals are produced from the accumulation of abundant humic matter within the original peat swamp [16].

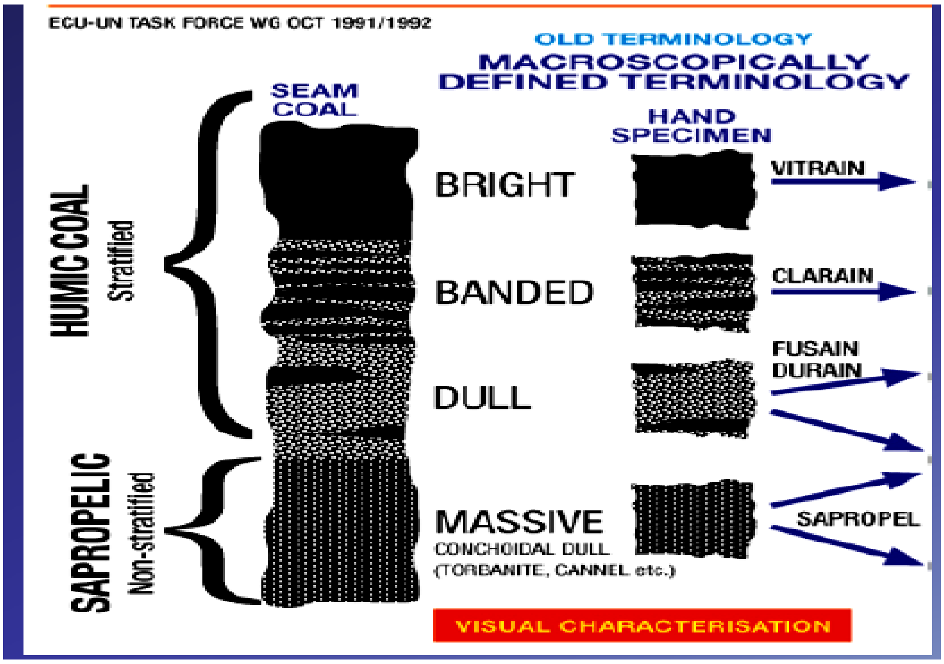


Figure 2. 2 Macroscopic components of coal [17]

2.2.2 Microscopic constituents of coal

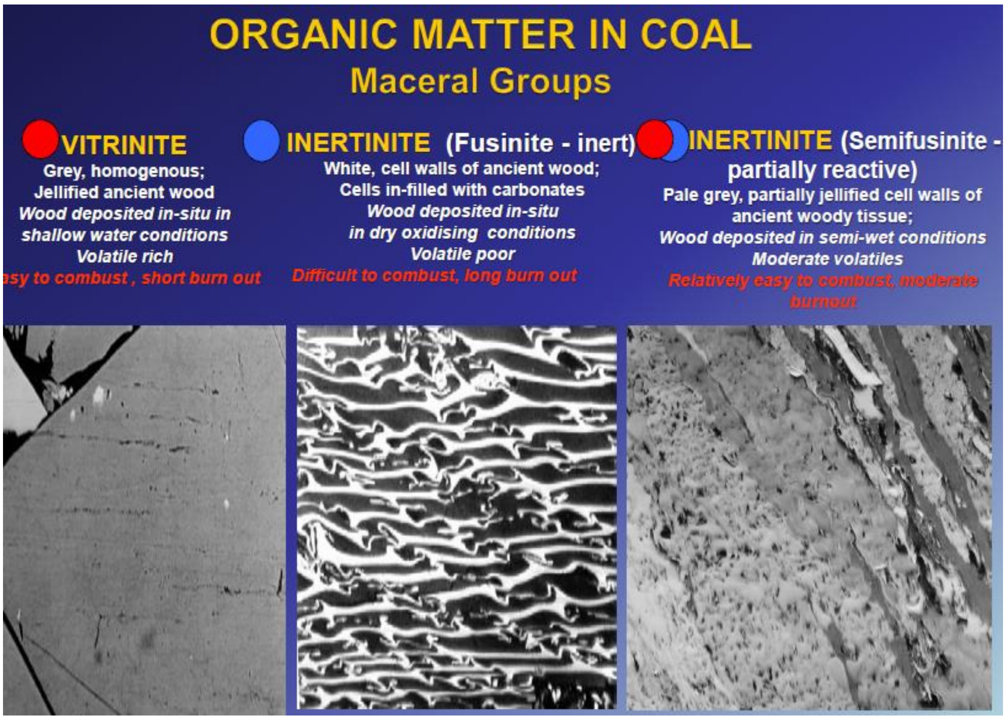
On a microscopic level the constituents of coal can be divided into three components namely: macerals, mineral matter and microlithotypes.

Macerals

Microscopically the type of coal is determined by the partially decomposed organic remains and fragmented units of the organic matter which are known as macerals. Macerals can further be divided into chemically reactive and chemically inert macerals. Although appearing in a wide-ranging variety, macerals can be grouped into three classes: vitrinite, liptinite (exinite) and inertinite. The maceral groups are shown in Figure 2.3 [15].

Vitrinite is the darker part of coal that shows low reflectance and a high hydrogen content and moderate volatile matter compared to liptinite and inertinite. Vitrinite is largely responsible for imparting coking properties to the coal as it devolatilizes fairly rapidly, becomes plastic and swells on heating [15].

Liptinite contains a high volatile and hydrogen content compared to other macerals and is the primary producer of heavy tars, bitumens and hydrocarbon products [16]. Liptinite is a maceral group defined by chemically distinct parts of plants (spores and cuticles), plants (algae) and products of plants (waxes and resins) [18]. Compared to other maceral groups, it is hydrogen-rich and aliphatic, it exhibits lower reflectance, appears predominantly in low to medium-ranked coals, and has a black to dark-grey or rusty-brown appearance in white light.



ORGANIC MATTER IN COAL
Maceral Groups

● **VITRINITE**
Grey, homogenous;
Jellified ancient wood
Wood deposited in-situ in
shallow water conditions
Volatile rich
asy to combust , short burn out

● **INERTINITE** (Fusinite - inert)
White, cell walls of ancient wood;
Cells in-filled with carbonates
Wood deposited in-situ
in dry oxidising conditions
Volatile poor
Difficult to combust, long burn out

● **INERTINITE** (Semifusinite - partially reactive)
Pale grey, partially jellified cell walls of ancient woody tissue;
Wood deposited in semi-wet conditions
Moderate volatiles
Relatively easy to combust, moderate burnout

Figure 2. 3: Organic components of coal [17]

Inertinite is the shiny part of the coal. It is a maceral group derived from plant material that was extensively oxidized during the formation of peat stage [16]. Although sharing the same woody and cellular material as vitrinite, inertinite was exposed to a high degree of carbon-enrichment. Compared to macerals of the same rank, it has a higher carbon content, higher reflectance and lower volatile and hydrogen content [16].

Mineral matter

In addition to a coal's organic constituents, coal also contains inorganic (mineral) components in varying amounts. Mineral matter is inert, naturally-occurring heterogeneous solid that would be left behind after coal combustion [16]. Being highly variable in physical appearance and chemical composition it occurs in several forms in coal. Depending on the chemical and mineralogical composition the mineral matter mainly includes clays, shales, pyrites quartz, calcite and lesser amounts of other material. The mineral matter can be divided into inherent mineral matter which is the inorganic matter that existed in the original plant vegetation and the extrinsic mineral matter which was introduced into the cavities within the coal seam by percolating water long after the formation of original peat [16]. The extrinsic mineral matter is readily removed during beneficiation as opposed to inherent mineral matter [16].

Microlithotypes

The association of organic matter (macerals) and inorganic matter (minerals) in varying ratios into microscopic layers of coal greater than 50 µm is called microlithotypes. Microlithotypes can be composed of pure maceral groups or a mixture in varying proportions of the different maceral groups. An association of microlithotypes consisting of more than 20% minerals by volume is termed carbominerite [16].

2.2.3 Images of peat, lignite, bituminous coal and anthracite

As already mentioned, as a result of different plant material which were buried over time and the length of time the coal was forming, several types were formed [15]. This is shown in Figure 2.4.

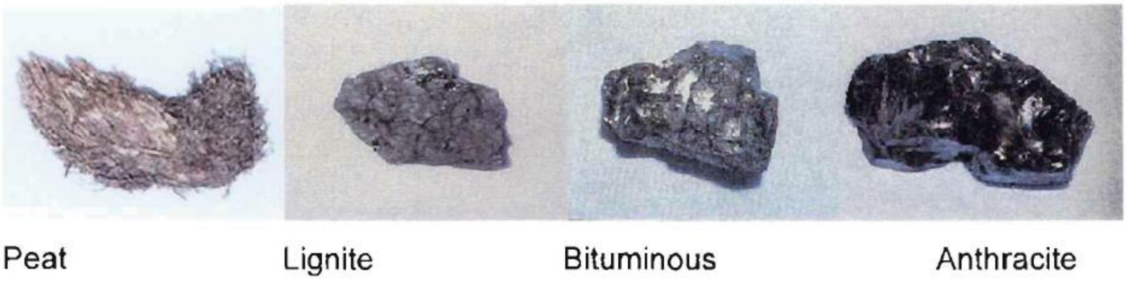


Figure 2. 4: Images of peat, lignite, bituminous coal and anthracite [16]

Depending on the composition, each type of coal burns differently and releases emissions in varying quantities. Four types of coal are mined today namely: lignite, subbituminous coal, bituminous coal and anthracite [16].

Lignite: is a soft, brownish-black coal. It is at the lowest level of the coal family with even texture of the wood being visible on the surface.

Subbituminous coal: is a dull black coal. Slightly higher in rank than lignite, has lower moisture content and yields more energy when burnt.

Bituminous coal: Its ranking can be subdivided into: low, medium and high ranks. It is of higher quality than lignite but poorer quality than anthracite.

Anthracite: is a coal characterized by low moisture content and more energy yield. This coal is top ranked, generally harder and more often gives off a black vitreous lustre.

2.3 Characteristics of South African coals

Important conditions that determined the composition of South African coals include temperature, sedimentation and the type of vegetation. In comparison of coal with Laurasian coals, South African coals (and those from other Gondwana regions such as India, Australia and South America) have been found to be rich in mineral matter, relatively difficult to beneficiate and highly variable in rank and in organic matter composition. South African coals are generally less mature as a result of the time, temperature and pressure the organic material has been exposed to, and generally range from sub-bituminous to mid-bituminous coals with the exception of locally heat-affected deposits [15].

The South African conditions involved lower temperatures associated with the waning of a massive iceberg, whilst conditions associated with coal formation in the Northern Hemisphere were hot and humid. The Gondwana region was characterised by vegetation ranging from sub-arctic through cold weather deciduous (hardwood) forest to warm savanna-like with reed-infested swamps. This is contrasted with the Laurasian's water-loving subtropical equatorial lycopod horse tails and fleshy-barked trees with abundant fern [15].

With time, temperature and pressure comes coal maturity. In Gondwana, the coal-bearing strata was at generally shallow depth and exposed to frequent intrusion by hot igneous (volcanic) lavas in the vertical and horizontal streams through strata. This varying type and sizes of intrusion resulted in highly uneven maturation. The Laurasian region by contrast, experienced rapid subsidence and deep burial of coal-bearing strata together with elevated geothermal temperatures at depth for considerable lengths of geological time. The results were relatively consistent in rank on a regional basis [15].

The existence of igneous activity in some regions resulted in rapid heating effects on coal in areas in the proximity of sill and dyke. These effects contributed to the formation of anthracite, and in some instances where heating was moderate, bituminous coal was formed [15].

As a result, South African coals show a considerable diversity of types (organic composition), grade (mineral matter composition), and rank (maturity). Differences in deposits can be of considerable qualitative, quantitative, technological and economical significance. The coal of carboniferous age (Northern Hemisphere) is much less diverse and more mature than that in South Africa [15].

2.4 Fluidized-bed combustion (FBC)

In FBC coal, air and sorbent (e.g. limestone) are mixed during combustion. Combustion occurs at temperatures typically between 800˚C and 900˚C. The mixing enhances mass and heat transfer. A continuous stream of combustion air is used to suspend the mixture of fuel, sorbent and fuel ash particles to create turbulence in the combustor chamber. A liquid-like characteristic of the mixture is thereby maintained by the gas flow [9].

Fluidized-bed combustion technology was introduced in the 1970s as a waste disposal solution in petrochemical industry. Over time it evolved to be 'clean energy for the future' technology [19]. Its development was mainly driven by countries with abundant low-grade, high-sulphur coal. These countries included, among others, China, Germany, India and the United Kingdom. Fluidized-bed combustion was also used for the burning of low-grade fuels e.g. peat, municipal solid waste, sewage sludge and biomass as in the case of Finland where biomass-based fuels are by-products of large pulp and paper industry. The acceptance of FBC as a solution in various industrial applications is for two reasons: 1) high energy demand makes the production of energy from cheaper fuels favourable, 2) combustion of waste reduces the cost of its disposal and waste-based fuels can replace more expensive fuels for energy production[19].

With CFBC having been established as a better combustion technology, it is important to control the nitrogen emissions and the conversion of nitrogen chemically bonded in coal.

Nitrogen oxides and N_2O control in FBC systems has been an important issue for some time, and it is still a work in progress item. Various parameters that have been tested in attempt to reduce NO_x and N_2O emissions include temperature, operating pressure, excess air, staged combustion, re-burning, sorbent type, coal and char characteristics, coal particle size distribution, and co-combustion of coal with other fuels e.g. biomass [5], [6] [20], [21], [22], [23], [35]. The influence of operating parameters of the CFB boiler on the N_2O emission was studied by Kambara and co-authors [20]. They found that the effect of the temperature on the N_2O and NO_x emissions are negatively correlated, i.e. the N_2O decreases and the NO_x increases with the increase in temperature. This is consistent with most other studies e.g. [20], [21] ,[22], [23]. Kinetic studies have indicated that higher temperatures favour direct conversion of nitrogen radicals, such as NCO and NH to either NO or N_2 than to N_2O [21].

The effect of fuel characteristics and operating conditions was studied by Zhou et al. [8]. According to their findings, at high temperature vitrinite-rich coal that produces high porous char controls NO_x and N_2O better compared to inertinite rich coal [8].

Studies involving the relationship between temperature, NO_x, N_2O, char morphology and coal type showed that at high temperatures the nitrogen in coal is released with volatile matter in greater quantities during devolatilization [4]. This ties up with other works regarding nitrogen release during pyrolysis by various techniques [5], [6], [7], [8].

Gavin et al. [21] showed the fraction of fuel-N released during devolatilization to increase with temperature, where 15% was recorded below 800°C and 40–50% above 900°C. The important influencing parameter in the fuel-N release during devolatilization was found to be the temperature of the bed. Temperature increase from 730°C to 900°C was found to increase fuel-N release by 80–90% on average [21]. Other combustion parameters found to influence fuel-N release were higher heating rates and reduced particle size.

Tables 2.1–2.4 show selected literature data on the conversion of fuel-N to NO_x, split of coal-N between char and volatiles, the conversion of fuel-N to NO for various coals (as %wt. of fuel-N) at different temperatures and emissions for five high-VM bituminous coals.

Table 2.1 shows the emission of NO_x of eight types of coals at different temperatures [23]. It was observed that the amount of NO_x emitted increases with increasing temperature in a laboratory-scale combustor. The nitrogen in char seems to be the contributing factor to the amount of NO_x produced. Similar observations were obtained for coals tested in TGA instrument.

Table 2. 1: Conversion of fuel-N to NO_x [23]

			%wt. of fuel-N as NO_x			
Coal	N in VM, %	N in char, %	700°C	800°C	900°C	1000°C
A	4.5	95.5	22.5	37	45	55
B	5.3	94.7	10	23	42	55
C	37.9	62.1	18	24	27	34
D	40.4	59.6	18	24	27	34
E	55.5	46.5	26	36	36	35
F	48.8	51.2	26	32	34	33
G	0.0	100.0	25	42	53	58
H	21.6	78.4	15	27	34	47

Table 2.2 shows the split of fuel-N between VM and char for Cimpor coal and a South African coal [24]. In this study, combustion of VM released was investigated in an electrically-heated fluidized combustor. It was observed that VM was released at a faster rate from Cimpor coal

compared to South African coal. The conversion of fuel-N to NO is also higher in Cimpor coal than that of South African coals.

Table 2.2: Split of coal-N, %wt., between char and VM [24]

Temp. °C	Cimpor char	Cimpor VM	S.A. char	S.A. VM	Cimpor coal fuel-N to NO	S.A. coal fuel-N to NO
700	91.4	8.6	95.1	4.9	11–20 % (over the temperature range used)	7.5–15% (over the temperature range used)
800	85.6	14.4	87.1	13.0		
900	77.1	22.9	80.5	19.5		
1000	72.7	27.3	75.3	24.7		

Table 2.3 shows the conversion of coal-N to NO and N_2O during the combustion of four bituminous coal at temperatures of 700–950˚C [21]. The main findings from these experiments were that the conversions of coal-N to NO and N_2O varied with temperature. Nitrogen oxide concentration increased as the temperature increased and N_2O concentration decreased with temperature.

Table 2.3: Conversion of fuel-N to NO and N_2O, %wt. [21]

	Coal	**700˚C**	**750˚C**	**800˚C**	**850˚C**	**900˚C**	**950˚C**
Conversion to NO_x	Bagworth	12	18	25	29	32	34
	Littleton	15	18	24	27	32	36
	Point of Ayr	14	20	26	30	34	36
	Tilmanstone	14	22	27	32	34	34
Conversion to N_2O	Bagworth	27	27	25	21	16	13
	Littleton	32	31	28	25	19	16
	Point of Ayr	24	25	23	23	17	14
	Tilmanstone	17	21	18	17	14	12

Table 2.4 shows the NO concentrations during combustion of five high-volatile bituminous coals which included vitrinite-rich Colombian coal, a vitrinite-rich U.S coal and three inertinite-rich South African coals [10]. The results show that the NO emission from

Colombian and U.S coals are generally lower than those from South African coals. Furthermore, there seems to be a general tendency for NO emission to decrease with combustion temperature in the case of vitrinite-rich coals and to increase in the case of inertinite-rich coals.

Table 2.4: NO emissions at different temperatures [10]

	NO, ppm			
Coal	**700°C**	**800°C**	**900°C**	**1000°C**
SA1	225	231	285	275
SA2	185	517	488	514
SA3	219	328	320	357
Colombian	186	210	133	63
U. S	112	145	132	133

2.5 Coal combustion process

Combustion is a rapid chemical reaction between fuel and oxygen. In the case of the coal, combustion process includes the oxidation of VM followed by oxidation of char. A coal particle injected into the combustion chamber undergoes several physical and chemical transformations [25], [27]. These transformations include:

- drying,
- devolatilization (release of volatiles upon heating),
- VM combustion, (oxidation of the released VM),
- char combustion (oxidation of the remaining solid).

The coal combustion process is shown in Figure 2.5 [25]. It should be noted that combustion conditions can determine whether VM combustion and char combustion take place simultaneously, sequentially or with some overlap [16].

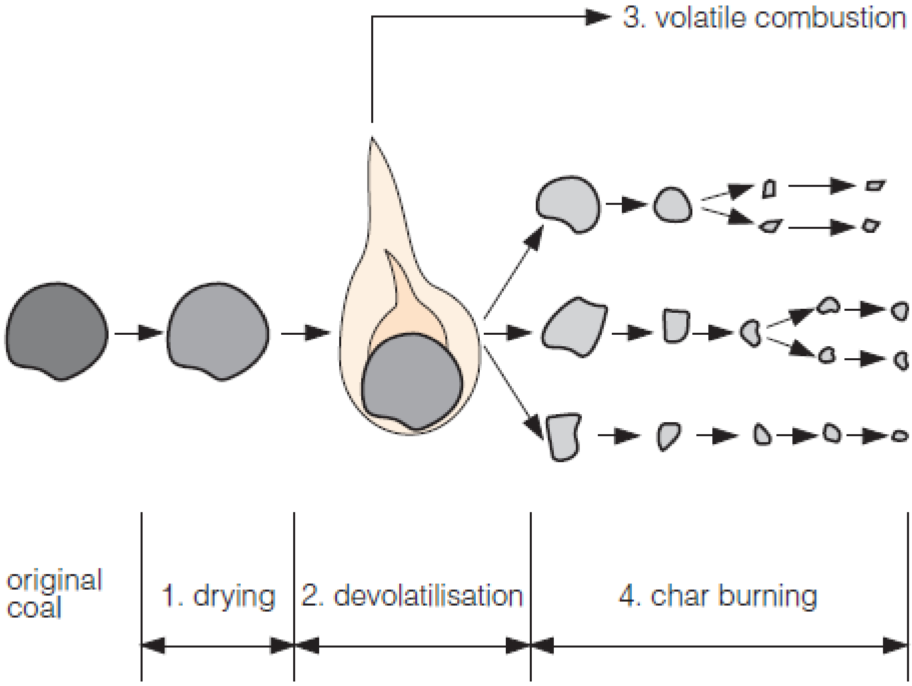


Figure 2. 5: Coal combustion process [25]

2.5.1 Drying

The drying of a coal particle occurs once it enters a FB combustor. This process removes moisture that typically is in the range of 2–20%. However extremes of up to 70% have been experienced [25]. Drying can be divided into two stages, the evaporation of surface moisture and loss of inherent moisture. The evaporation of surface moisture has not been found to affect the combustion process, but in the case of slurried fuels it may lead to particle agglomeration [25]. High content of inherent moisture delays the devolatilization process and ignition of evolved VM. Morphological changes in low rank coals can be significant as up to 40% volume reduction was reported for an Australian brown coal during drying in FBC [26]. Low rank coals can contain above 40% of inherent moisture.

2.5.2 Devolatilization

Heating of a coal particle causes the release of volatile matter. This process is called devolatilization. Typically devolatilization of coal begins around 300˚C [25]. It is a pyrolytic process, where the organic part of coal breaks up to produce light and heavy molecules. A variety of products are released during coal devolatilization. At lower temperatures, the weaker carboxyl, hydroxyl and aliphatic bonds break up whilst at high temperatures, above 600˚C, coal decomposes into more stable heterocyclic components [25]. Various gases including hydrocarbons, hydrogen, carbon monoxide, carbon dioxide, methane and also tars are released. Finally, char which contains approximately 98% carbon remains as a solid residue [25].

Significant changes in coal structure occur during the devolatilization process. These changes include particle softening, resolidification and contraction [25]. Structural changes have been attributed to the transformation of hydrocarbons from solid to gaseous phase [25]. Such a transition causes a pressure build-up inside a coal particle as the volume of gases increases approximately three folds. The coal structure changes include increase in porosity and the appearance of bubbles in the particle [25]. Depending on the particle size, coal type and temperature, devolatilization takes a few milliseconds or several minutes to complete [27].

Devolatilization degree

As already mentioned, when a coal particle is heated, volatiles are driven out of the particle and a solid residue, known as char, remains. It appears that the quantity of VM released increases with the devolatilization temperature but decreases with coal rank. This is apparent from the graph in Figure 2.6(a) which shows the correlation between VM released and coal rank at temperature of 1000°C [25]. The release of VM decreases with increasing carbon content from 37% to 26%. Figure 2.6(b) shows the correlation between the VM released and temperature for an anthracite. The release of VM increases with increasing temperature. The same trend is observed for all types of coals [25].

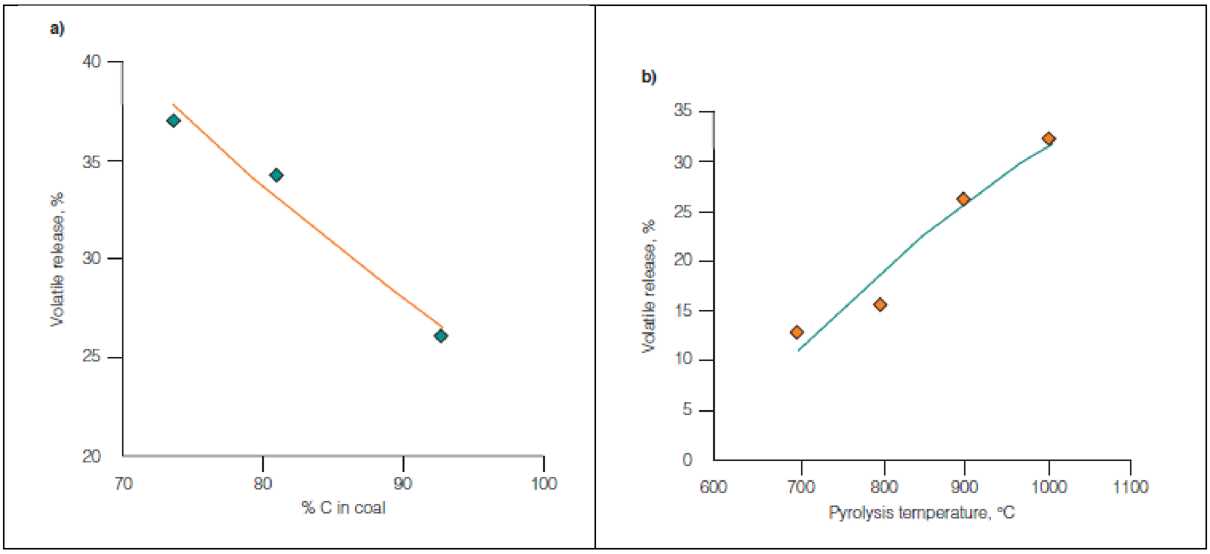


Figure 2. 6: Effects of coal rank and temperature on the release of VM [25]

Devolatilization rate

Devolatilization process is usually completed within seconds to minutes depending on fuel particle size. It is generally accepted that the rate of devolatilization, which is expressed as devolatilization time, may be controlled by three mechanisms: chemical reaction kinetics, heat transfer to and within the particle, and mass transfer of the volatiles within the particle [29], [26]. Rate controlling models, it is suggested by [26], and [29] that three different regimes exist:

- For small particles, smaller than 0.1mm, devolatilization time is independent on particle size and therefore chemical reaction kinetics is the rate controlling step. This has also been confirmed for particles smaller than 0.6 mm [30] .
- As the particle size increases, reaction kinetics and heat transfer control devolatilization rate. The extent of mixed regime depends on the coal type and operating conditions, e.g. bed temperature [30].
- For particle sizes larger than 1.0 mm, heat transfer controls the devolatilization rate. The devolatilization time in this case is proportional to the square of particle diameter [30].

Physical behaviour of coal during devolatilization

Coal is a mixture of several maceral components. The maceral composition of coal controls the physical behaviour of a coal particle upon heating [31]. Depending on the composition of coal, different behaviour of coal particle may be seen.

Some coal particle become soft, swell and become liquid as VM produced within the particle break out from the surface through bubbles which are passing through the particles as shown in Figure 2.7. The process of forming bubbles and their passage through the liquid particle can be rate controlling for the gas evolution and may also determine the species evolved [31].

Some other coals can only develop the cracks as a result of the escape of gases. Such particles, even though loosing mass, do not visually change their size. They form porous residue known as char [31].

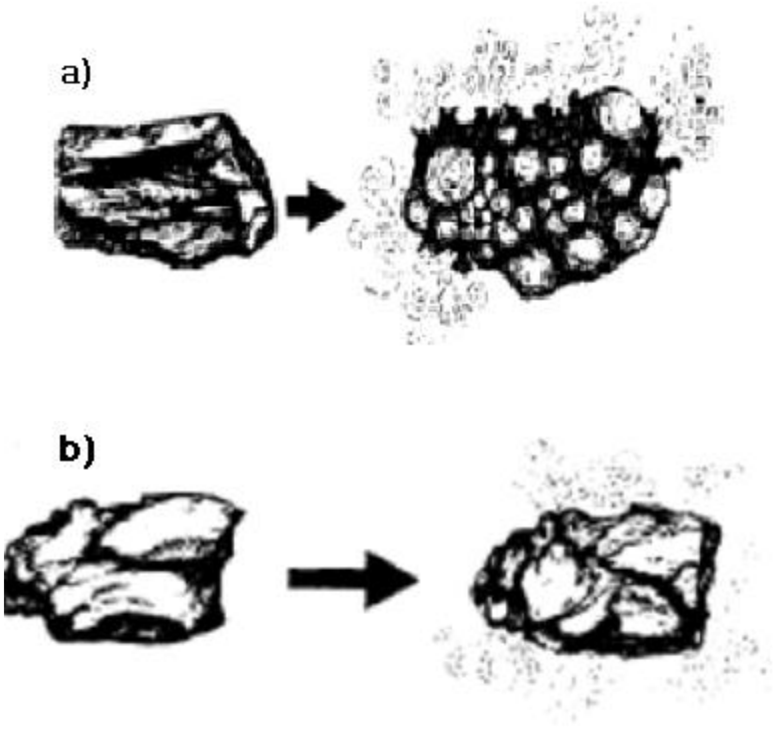


Figure 2. 7: (a) Melting coal: Escape of volatiles through bubbles – shape of particle is not maintained, (b) Non – melting coal : Escape of volatiles through fissures and pores – shape of particle is maintained [31].

2.5.3 Combustion of volatiles

The combustion of evolved VM progresses in the presence of oxygen. This process is rapid. Fluidizing air is the main source of O_2 taking part in the reactions. This oxygen comes from the coal and also contributes.

Chemical reactions

In a FB boiler, the combustion of volatiles is a homogeneous process. Oxidation of CO, H_2, CH_4, C_2H_6 and C_3H_8 is a homogeneous process whilst the oxidation of HCN and NH_3 can be a homo- or heterogeneous process. The oxidation of CH_4 and H_2 is particularly fast with that of CO being comparatively slow. The main chemical reactions occurring during combustion of volatile matter are [25]:

Oxidation of carbon monoxide:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \tag{1}$$

Oxidation of hydrogen:

$$2H_2 \ + O_2 \ \rightarrow 2H_2O \tag{2}$$

Oxidation of methane:

$$CH_4 \ + \ \frac{3}{2}O_2 \ \rightarrow CO + 2H_2O \tag{3}$$

Oxidation of HCN:

$$HCN \ + \ \frac{5}{4}O_2 \ \rightarrow NO \ + CO \ + \frac{1}{2}H_2O \tag{4}$$

$$HCN \ + \ \frac{3}{2} \ O_2 \ + NO \rightarrow \ N_2O \ + CO \ + \ \frac{1}{2} \ H_2O \tag{5}$$

$$HCN \ + \frac{5}{4}O_2 \ \rightarrow \ \frac{1}{2}N_2 \ + CO_2 \ + \ \frac{1}{2} \ H_2O \tag{6}$$

Oxidation of NH_3:

$$NH_3 \ + \ \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O \tag{7}$$

$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \tag{8}$$

2.5.4 Combustion of char

Char is the residue of the devolatilization process. It is mainly carbon, nitrogen, sulphur and ash. It is usually porous and have many cracks which result from the escape of gaseous products [27]. Char oxidises to gases such as CO, CO_2, NO, NO_2, N_2O and SO_2 above 750°C leaving ash as a residue. The reaction between char and oxygen is a gas-solid heterogeneous reaction. The gaseous O_2 diffuses to, and into, the char particle, where it reacts with carbon [25]. There are three possible mechanism of char oxidation in a fluidized-bed combustor (see Figure 2.8). The mechanisms are described by reactions (9)–(11).

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{9}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{10}$$

$$C + CO_2 \rightarrow 2CO_2 \tag{11}$$

Mechanism 1: Oxygen diffuses to the surface of char particle and oxidises carbon to CO. Carbon monoxide oxidises further to form CO_2 in a gas phase reaction. Due to CO oxidation occurring close to the surface, CO_2 is considered to be the primary combustion product. This mechanism is predominant for particles greater than 1mm and bed temperature in the range of 900−1300°C [25].

Mechanism 2: As O_2 diffuses to the surface of the char CO and CO_2 are produced. Carbon monoxide and CO_2 then diffuse away from the surface. Carbon monoxide further reacts in the gas phase with arriving O_2 from the bulk gas forming CO_2. Low temperature or small particle size may cause CO to escape unburnt into the gas stream. Carbon monoxide and CO_2 are primarily the combustion products, with CO/CO_2 ratio dependant on the type of char and particle temperature [28] . Under fluidized-bed combustion conditions this ratio is about 10.

Mechanism 3: Oxygen cannot reach the char surface. It reacts with CO in the gas phase away from the char surface. Part of the formed CO_2 diffuses to the char surface and is reduced to CO through the Boudouard reaction which is relatively slow [25].

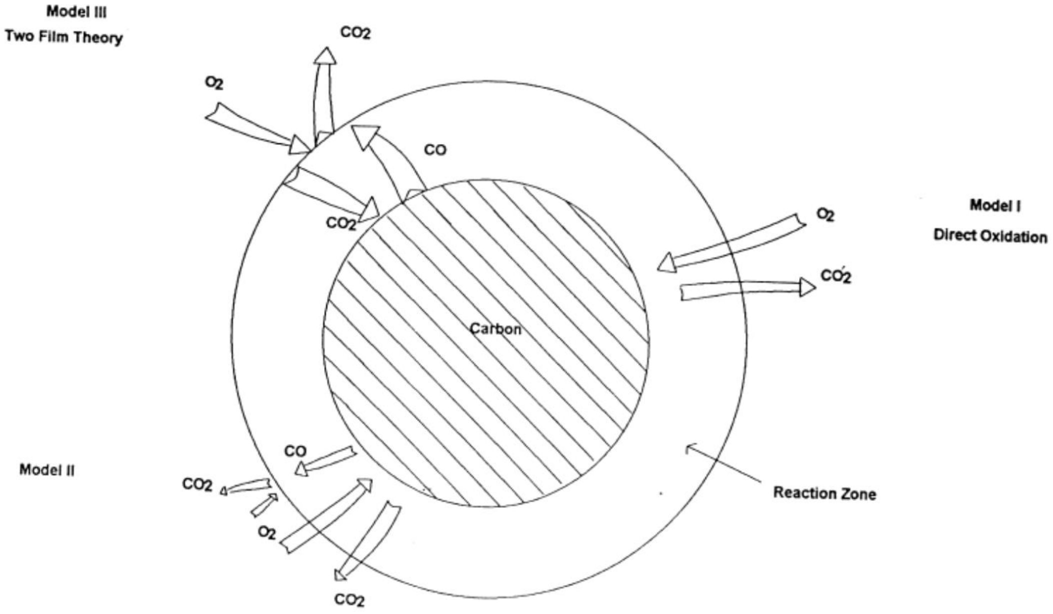


Figure 2. 8: Mechanisms of combustions for non – porous carbon particles [28]

2.6 Formation of nitrogen oxides in coal-fired boilers

During coal combustion nitrogen is oxidised to nitrogen oxides, NO and NO_2, commonly referred to as NO_x. In fluidized-bed combustion, about 90% of NO formed originates from coal-N oxidation. The remainder comes from thermal-NO_x mechanism (oxidation of N_2 present in the combustion air) [12].

2.6.1 Thermal NO formation

The thermal NO process involves the oxidation of nitrogen in air to NO via the following reactions [32]:

$$O + N_2 \rightleftharpoons NO + N \qquad (13)$$

$$N + O_2 \longrightarrow NO + O \qquad (14)$$

$$N + OH \longrightarrow NO + H \qquad (15)$$

This process is important at high temperatures (above 1400°C) prevailing in flames of PC boilers and is not considered important in much cooler FB boilers operating at temperatures below 1000°C [20].

2.6.2 Prompt NO

Hydrocarbon radicals, produced in coal flames, react with N_2 to produce HCN or CN which are subsequently oxidised to NO. Under fluidized-bed combustion conditions, the contribution of prompt NO to total NO formation is negligible because the FBC is flameless [8], [31] .

2.6.3 Fuel NO formation

As has already been mentioned, the principal source of NO emission in combustion systems is the nitrogen that is chemically bound in the fuel [33], [34]. Coal comprises of a complex mixture of aromatic hydrocarbons and heterocyclic aromatic compounds with nitrogen ranging between 0.5 to 2.5%wt. [35]. The chemically bound nitrogen in coal and coal-derived fuels occurs predominantly in the form of heterocyclic compounds with pyrrolic and pyridinic structures [22]. Furthermore, the presence of quaternary nitrogen, whose nature is not clear, has been observed. The pyrrolic, pyridinic and quaternary nitrogen, account for 50–80%, 20–40% and 0–20% of the total nitrogen content of coal respectively [22]. The effect of nitrogen functionalities on the formation of NO is believed to be small [32].

2.6.4 Formation and reduction mechanisms

Nitrogen oxides and N_2O formation from coal-N involves oxidation of volatile matter, oxidation of char and finally partial reduction of NO and N_2O to N_2. During devolatilization, the organically-bound nitrogen in fuel is partitioned into (a) volatile-nitrogen and (b) char-nitrogen [8]. These two forms of nitrogen contribute to the formation of NO and N_2O and their subsequent emission in the flue gas from the boiler.

The volatile nitrogen is mostly released as simple amino- and cyano species such as NH_3 and HCN [8]. The volatile-N compounds subsequently oxidise through homogeneous gas phase reactions or heterogeneous catalytic reactions over char and other bed solids such as limestone, ash and silica sand [8]. Hydrogen cyanide gives NO, N_2O or N_2 while NH_3 is predominantly oxidised to NO or to N_2 [8]. The reaction products depend on the bed temperature and the catalytic activity of the bed material [8]. At high temperatures both amino- and cyano species will partly oxidise to NO, however at lower temperatures N_2O may also be formed (HCN → N_2O → NH_3) [35]. Dulce et al. [24] studied the oxidation of NH_3 and HCN at temperatures between 627°C and 1077°C in a plug flow reactor. The results indicated that the oxidation of HCN produces approximately one order of magnitude more N_2O than NH_3 at similar conditions [24]. The mechanism of formation and destruction of N_2O in FBC is complex because it involves several homogeneous and heterogeneous reactions. These reactions can be catalysed by minerals in the char and even by bed material [24].

In the char, the nitrogen is bound in the aromatic structures. Char burning is the final stage of the coal combustion process. It is much slower than the combustion of volatile matter. During char oxidation, nitrogen is oxidised mainly to NO, N_2O, and N_2 leaving ash as a residual product, however, small amounts of HCN and NH_3 may also be formed [25]. Char-N is believed to oxidise directly to NO, it is also believed that it contributes more to NO and N_2O formation than volatiles. Also worthy to note is that the nitrogen bound in char is important for the determination of the total NO_x [32]. The heterogeneous char-oxygen reaction, the complex char structure and the surrounding gas species are among factors which makes it very difficult to explain the conversion of char-N to NO [32]. A summary of the conversion of char-N in different reactors including FB, PC, TGA and FBR is given in Table 2.6. It can be seen that the percentage of fuel-N converted to NO, N_2O and HCN varies between 3–90.7%, 0.2–5.7% and 0.5–10% depending on coal type, char preparation, residual VM content, temperature, reactor type, stoichiometry and particle size. The NO is the major product of fuel-N converted and the ratio of fuel-N conversion to NO is remarkably different for different researchers [32]. The simplified formation and reduction pathways for NO and N_2O is schematically represented in Figure 2.9.

During the char-N oxidation the main reactions are as follows [25]:

$$Char - N + \frac{1}{2}O_2 \rightarrow -CNO \tag{16}$$

$$-CNO + \frac{1}{2}O_2 \rightarrow NO + CO_2 \tag{17}$$

$$-CNO + NO \rightarrow N_2O + CO_2 \tag{18}$$

The NO and N_2O formed are then further partially reduced to N_2. They both can be reduced directly by char or through homogeneous reactions with CO and NH_3 catalysed by char and bed solids. The reduction reactions are given below [25].

NO reduction:

$$NO + char \rightarrow \frac{1}{2}N_2 + CO \qquad (19)$$

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2 \qquad \text{char, bed solids} \qquad (20)$$

$$NO + NH_3 + \frac{1}{4}O_2 \rightarrow N_2 + \frac{3}{2}H_2O \qquad \text{homogeneous} \qquad (21)$$

$$NO + \frac{2}{3}NH_3 \rightarrow \frac{5}{6}N_2 + H_2O \qquad \text{char, bed solids} \qquad (22)$$

N_2O reduction:

$$N_2O + char \rightarrow N_2 + CO \qquad \text{char} \qquad (23)$$

$$N_2O + CO \rightarrow N_2 + CO_2 \qquad \text{char, bed solids} \qquad (24)$$

$$N_2O \rightarrow N_2 + \frac{1}{2}O_2 \qquad \text{homogeneous} \qquad (25)$$

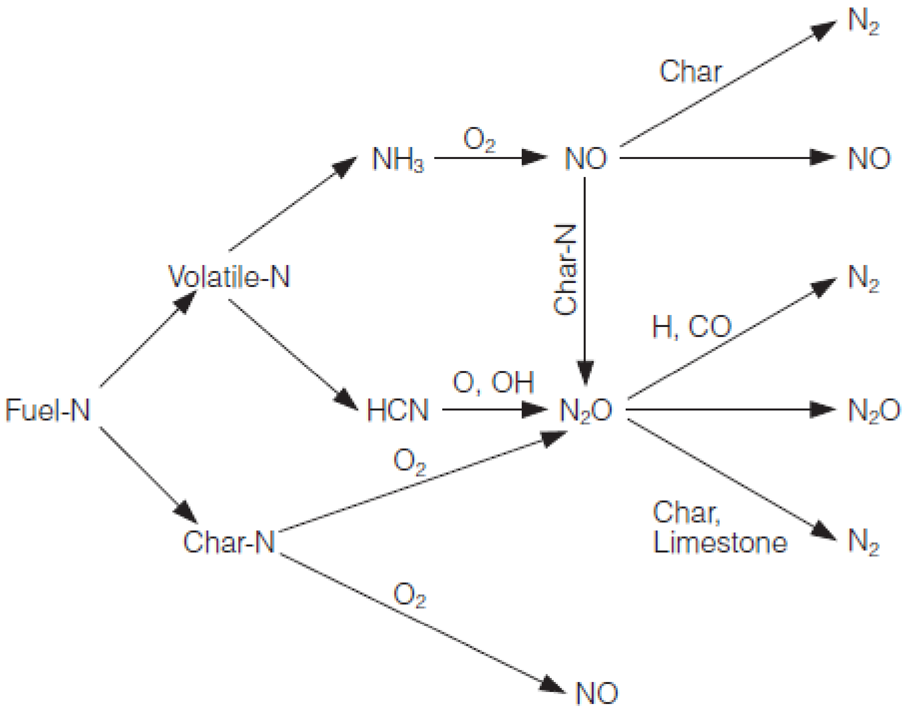


Figure 2.9: Pathways for the formation and reduction of NO and N_2O [25].

Table 2.5: A summary of experimental char-N to NO_x conversion studies (adapted from [32]).

Reactor	Parent coal	Char preparation	Nitrogen (N/C, mass ratio)	Fraction of char-N to NO_x, N_2O, and HCN	Operation conditions	Reference
FB	9 coals	Fixed and fluidized bed at 900°C	0.00758-0.02275	f_{NO} = 0.24–0.5	500–590 μm, 5–10 mg, 890°C, 3.15 O_2/Ar, particle level	[36]
FBC	Kentucky No. 9 bituminous coal	FBC at 950°C	0.021	f_{NO} = 0.18–0.58	1.02–4.48 mm, 0.2–1.2 g, 10% O_2, 480–730°C	[37]
FB	2 subbituminous coal 1 lignite	FB up to 950°C	0.0144-0.0188	f_{NO} = 0.03–0.3 f_{N2O} = 0.009–0.036	90–106 μm, 0.2 MPa, 6–20% O_2, 0–50% CO_2	[38]
FBC	3 coals – Tilmanstone, Holditch, and Baddesley	FBC	Not available	f_{NO} = 0.06–0.33 f_{N2O} = 0.002–0.025	1.0/2.5 g (1–2 cm), particle level and 1-g batches of particles (1.4–1.7 or 2.0–2.4 mm) 800/900°C	[20]
FBC	Bituminous and sub-bituminous coal	FBC	0,0126-0.018	f_{NO} = 0.16–0.18 f_{HCN} = 0.014–0.005 f_{N2O} = 0.015–0.035	5, 10, 15 mm, 327–900°C, 5–21% O_2/N_2, at particle level	[53]
FB (TGA)	20 coals from anthracite to bituminous coal	Entrained flow reactor at 1000°C	0.0124-0.031	f_{NO} = 0.04–0.03	37–75 μm, 5 mg, 20% O_2/Ar, 600–1050°C	[39]
FBC	Newland coal	Fluidized bed at 850°C	Not available	f_{NO} = 0.31–0.035 f_{N2O} = 0.04	200 mg (4–5 particles), 8019°C, 8% O_2/He	[40]
FBC	Anthracite and bituminous coals	Rapid pyrolysis at 850°C	0.0157-0.017	f_{NO} = 0.25–0.54 f_{N2O} = 0.04	0.25–1.5 mm, 850°C, 2.5–21% O_2/N_2, single or a few particles	[54]
FB (TGA)	Bituminous coals	Quartz reactor up to 850°C	0.0145–0.022	f_{NO} = 0.05–0.063	25 mg, 20% O_2/Ar, 500–1200°C	[41]
FB	Blair Athol and bituminous coals	Fluidized bed at 1000°C	0.018	f_{NO} = 0.11–0.22	70–150 μm, 50–250 mg, 0.55–2.0 % O_2/He, up to 1000°C	[42]
FB (TGA)	Bituminous coal	Entrained flow reactor	0.0109–0.0244	f_{NO} = 0.22 f_{HNCO} = 0.12 f_{HCN} = 0.06 f_{N2O} = 0.01	45–75 μm, 60 mg, 2% O_2/He, 600°C	[55]
FB	bituminous and anthracite coals	Fixed bed at 850–1150°C	0.09–0.016	f_{NO} = 0.06–0.90	10–20 μm, 0.1–20 mg, 10% O_2/N_2, 850, 1050, 1150°C, experiments performed at particle level	[43]
FB	bituminous and lignite coals	Fluidized bed at 1000°C	0.0067–0.0075	f_{NO} = 0.06–0.68	0.25–0.5 mm, 25 mg, 5% O_2/N_2	[56]
FB	Australian bituminous coal	Entrained flow reactor	0.021	f_{NO} = 0.2 f_{HCN} = 0.1	0.1–1.0 MPa, 45–75 μm, 60 mg, 600°C, 2% O_2	[57]
				f_{NO} →1 when loading is close to zero	0.1 MPa, 1–120 mg	

2.7 Summary

In summary, when coal particles enter a fluidized bed, they under go a sequence of events including drying, devolatilization, combustion of volatiles and combustion of residual char. The drying process removes both the surface and inherent moisture of a fuel. Further heating releases the volatiles matter of the coal particle. The volatiles released then burn rapidly in the air. Char burning is the final stage of coal combustion. It produces CO and/ or CO_2 as the primary product. Reactions can occur both at the particle surface and internally. The burning rate depends on the coal type and other factors such as fluidization regime and char diameter. At relatively low temperatures of FBC, nitrogen in the combustion air does not oxidize to a significant extent, thus virtually all NO_x and N_2O are generated from fuel-nitrogen. The formation of NO and N_2O is a complex process. During devolatilization, nitrogen in the fuel is partitioned into volatile-N (mainly as HCN and NH_3) and char-N. Both the volatile-N and char-N are subsequently oxidized to NO and N_2O. HCN is an important precursor for N_2O formation while NH_3 is mainly formed to NO and N_2. Char-N oxidation generally gives much higher levels of NO compared to N_2O. The NO and N_2O formed are then partially reduced to N_2 through homogeneous reactions or heterogeneous reactions over char and other bed solids.

Chapter 3. Analytical techniques

3.1 Introduction

The need for understanding the implications of the fundamental properties of coal upon its utilization as a fuel has led to the development of advanced techniques for characterising its heterogeneity. The purpose of this chapter is to outline the experimental equipment, operating conditions and general analytical procedure used for characterisation of coals tested.

3.2 Preparation of coal samples

Four South African coals were used in this project. The samples were milled to –0.25 mm size and then air dried in a furnace at a temperature of 105 °C for an hour. Air dried samples were used for proximate, ultimate and calorific value analyses. Char was then obtained from each sample by devolatizing the coal in nitrogen atmosphere in a tube furnace. The devolatilization conditions under which the chars were obtained are shown in Table 3.1. Two furnaces for charring coals were used. Two coals were charred a at shorter time but at higher heating rate and other two coals at longer time but lower heating rate. The difference was related to the equipment used for charring.

Table 3.1: Char preparation conditions

Charring conditions	Delmas	Secunda	Kuthala	New Vaal
Heating rate, °C/min	10	10	5	5
Holding time, h	1	1	2	2
Final temperature, °C	850	850	850	850
Cooling rate °C/min	6	6	6	6

3.3 General characterization of coal

Coal is naturally highly heterogeneous, as a result various analytical techniques are required to characterize it in order to accurately predict its behaviour during conversion processes such as combustion, gasification or liquefaction [44].

The characterization of coal can be divided into three categories, namely chemical analysis, mineralogical analysis and petrographic analysis. In this study a general characterization of the coal was conducted that involved chemical analysis, petrographic analysis, mineral analysis (ash analysis) and calorific value (high heating value). Results of proximate and ultimate analyses were used to determine the split of coal-N between char and volatile matter. Two additional analyses namely: ash analysis (using the XRF technique) and petrographic analysis were performed to complete coal sample characterization.

3.3.1 Proximate analysis

Proximate analysis determines contents of moisture, volatile matter, ash and fixed carbon (by difference). It is the simplest and most common form of coal evaluation and it constitutes the basis of many coal purchasing and performance prediction used by operators. In this study proximate analyses were conducted using a modern instrumental technique commonly known as thermogravimetric analysis (TGA). Calcium Oxalate and a LECO 502-683 certified reference standard was used to verify the data. The proximate analysis was conducted in sequence starting with inherent moisture, volatile matter and finally ash, fixed carbon content was calculated by difference. Only 1 gram of the prepared sample was used. The analyses were conducted once for each coal. Inherent moisture was determined at a temperature between 105 and 110°C using nitrogen (99.5% purity) and argon (99.5% purity), volatile matter was determined at 900°C for 7 minutes using nitrogen (99.5% purity) and argon (99.5% purity) and ash at 815°C for 3 hours using oxygen (99.5% purity).

Inherent moisture

Inherent moisture refers to water held within the coal. Its presence causes delayed combustion and results in a decrease in calorific value. The typical range of moisture in South African coals is 2–6% [45].

Ash content

Ash yield refers to the post-combustion coal residue and is derived from inorganic complexes present in the original coal substance and associated mineral matter. It is commonly used as an indication of the grade or quality of coal since it provides a measure of the incombustible material. For South African coals the ash yield is typically in the range 25–35% [45].

Volatile matter

Volatile matter stems from two sources: organic matter and mineral matter. At high temperature, the organic matter of coal releases gases such as CH_4, C_2H_6, H_2, CO and tar. The decomposition of inorganic matter (minerals) releases incombustible gases such as CO_2 from carbonate minerals and SO_2 from pyrite minerals. Volatile matter is used to determine the rank of coal and its burning characteristics such as combustibility (reactivity), the ease of ignition and flame stability. The release of VM starts at temperatures 200–300°C [16].

Fixed carbon

Fixed carbon refers to a combustible solid residue remaining after moisture, ash, and volatile matter from coal have been eliminated. It is used as a measure of combustion reactivity and burn out. It is a calculated figure and is estimated by subtracting ash, moisture and the VM from a 100%. Generally the FC is in the range 50–60% [16].

3.3.2 Ultimate analysis

Ultimate analysis refers to the elemental composition of organic matter. It determines contents of carbon, hydrogen, nitrogen and sulphur. The content of oxygen is then calculated by difference to 100%. The ultimate analysis was conducted at the School of Chemistry using Leco-932 CHNS analyser after calibration with sulfamethazine as standard. The data processing was simply performed by the software incorporated in the instrument and the results are given in percentage of carbon, hydrogen, nitrogen and sulphur in the sample. The results are presented in Table 4.2.

3.3.3 Calorific value

In addition to conducting the proximate and ultimate analyses of great importance is the calorific value. A bomb calorimeter was used to determine the calorific value of the coals and their corresponding chars. Benzoic acid was used as a certified reference standard. Mass of the sample used for the experiment was 10mg.The analysis was done in replicate and the average values were taken into consideration. The calorific value determined in a bomb calorimeter, refers to the higher heating value (HHV) of the coal [15] . A sample of coal was ignited in a vessel filled with oxygen at a predetermined pressure of 3.0 Mpa. This vessel is then placed in a water jacket whose temperature can be accurately determined before, during and after combustion. The temperature rise of water surrounding the pressure vessel is accurately measured and used to calculate the calorific value. This is a fundamental test in determining the quality of coal and coke.

3.3.4 Ash analysis

When coal is burned, the mineral constituents form an ash residue that is mainly composed of the oxides of silicon, aluminium, iron, calcium, magnesium, sodium and potassium. Ash analysis is useful in the description of the quality of the coal. Understanding the makeup of ash and its direct contribution to slagging and fouling in boilers can lead to massive savings.

Slagging and fouling can also reduce the thermal efficiency and cause damage to many parts in a boiler.

XRF analysis – Methodology for analytical procedure

Major elements were determined using the Norrish Fusion technique using in-house correction procedures and using an Analytical PW2404 X-ray fluorescence spectrometer (XRF). A particle size of -0.25mm was used. The XRF technique employed provides the following ash elemental analysis: silicon (as SiO_2), aluminium (as Al_2O_3), iron (as Fe_2O_3 and FeO), manganese (MnO), magnesium (MgO), calsium (as CaO), sodium (as Na_2O), potassium as (K_2O), titanium (TiO_2), phosphorus (as P_2O_5), chromium (as Cr_2O_3) and nickel (as NiO). Major elements were fused using Johnson Matthey Spectro flux 105 at 1100°C and raw data corrected using in-house software. Standard calibrations were made up using synthetic oxide mixtures and international standard rocks as well as in-house controls. Calibration standards were primary international reference materials USGS (U.S Geological Survey mafic rocks) series (USA) and NIM (National Institute of Metallurgy) (South Africa).

3.3.5 Petrographic analysis

Petrographic analyses – methodology

The polished blocks were analysed using a Zeiss Axio Imager M2m reflected light petrographic microscope fitted with a Hilgers Fossil system for vitrinite reflectance and maceral determination at a magnification of ×500 under reflected white light, with oil immersion. The analyses were conducted following the SANS ISO 7404-5 standard for vitrinite reflectance. A detailed maceral point count was conducted. According to SANS ISO 7404-3 standard results are reported on a volume percentage (%vol.) basis.

3.3.6 Thermogravimetric analysis

Thermogravimetry and differential thermal analysis have been widely applied for studying of the pyrolysis and combustion behaviour of fossil fuels such as peat, lignite, bituminous coal, anthracite, oil shales, crude oils, light oils mixtures etc. Thermogravimetric analysis has the ability to monitor one or more physical properties of substance that is undergoing a temperature programmed heating as a function of temperature or time. Other analytical techniques like gas chromatography, Fourier-transform infrared spectroscopy and mass spectroscopy and sometimes a combination of more than one of the above can be used for interfacing with TGA to detect specific components of released gases and their evolution profiles [58].

In this study coal and char samples were tested to determine their combustion behaviour using a TGA analyser (Pyris 1 Perkin Elmer) coupled to Fourier-transform infrared spectroscopy (FTIR-NIR spectrometer- Frontier, PerkinElmer). About 20mg of coal and char samples were tested respectively. Non-isothermal tests were carried out in air with a gas flow rate of

20ml/min, at a heating rate of 20˚C/min and maximum temperature of 850°C (This is presented in Table 3.1). This is the typical temperature prevailing in FBC systems. A limitation in this apparatus is that TGA is not a fluidised-bed reactor but a fixed-bed reactor. It does not simulate real conditions in terms of hydrodynamic, mass transfer. TGA is a lab instrument that provides an initial indication on the nitrogen conversion to NOx. How good is this indication can only be assessed when TGA data are compared with data from a FB combustor. However, because the combustion temperature is the main factor affecting coal-N conversion to NOx, we can expect that data collected from a TGA will follow the same trend in an FB combustor, operating at the same temperature, with accuracy sufficient for our study.

Chapter 4. Results and discussion

4.1 Introduction

This chapter discusses the data and the results of the test work conducted on the coals under investigation. Comparison is made to work conducted by other researchers.

4.2 Proximate, ultimate and CV analyses

Proximate analysis

The proximate analysis of four coals and their chars was conducted to determine contents of moisture, VM, FC and ash. The results on the air-dry basis are presented in Table 4.1.

Table 4.1: Proximate analysis, %wt. (AD)

	Coal				**Char**			
	Moisture	**VM**	**Ash**	**FC**	**Moisture**	**VM**	**Ash**	**FC**
Secunda	2.37	25.89	27.58	44.16	1.16	5.38	34.55	58.91
Kuthala	3.18	20.66	25.55	50.61	1.11	6.21	33.17	59.51
New Vaal	3.29	21.98	34.72	40.01	1.29	4.75	47.57	46.39
Delmas	2.26	21.90	27.18	48.66	0.95	16.05	31.52	51.48

The FC contents in Secunda, Kuthala and Delmas coals and chars are comparable (This was also observed to be comparable to the results of six different coals from Highveld mines). The New Vaal coal and char have the lowest FC contents. This is attributed to the high ash content of this coal. Similar findings were observed in coals tested by Papo in the Eskom bubbling fluidised bed (BFB) combustion test faculty.

The level of inherent moisture in the tested coals is comparable. The inherent moisture ranges from 2.26 to 3.29 wt. % and 0.95 to 1.29 wt. % in coals and in chars respectively.

With regards to ash, New Vaal coal has the highest content of ash; more than 30 wt.% in the coal and more than 40 wt.% in the char. Ash is an impurity that does not burn. It affects the stability of the flame in the PC boilers and reduces thermal efficiency. Differences in volatile matter contents of Kuthala, New Vaal and Delmas coals are not significant; these contents are in the range of 20.66–21.98 wt.%. The Secunda has the highest VM content of 25.90 wt.%. In the case of char, the highest VM is produced in Delmas char with VM of 16.05 wt.%. For other chars VM contents are similar and they are in the range 4.75–6.21 wt.%.

Ultimate analysis

The analysis of major elements in coals and their chars was conducted using a CHNS analyser. The results of ultimate analysis are shown in Table 4.2.

Table 4.2: Ultimate analysis, % wt. (AD)

	Coal					**Char**				
	C	**H**	**N**	**S**	**O**	**C**	**H**	**N**	**S**	**O**
Secunda	50.15	2.91	1.3	0.73	14.97	57.74	1.04	1.27	0.79	3.45
Kuthala	49.49	2.87	1.18	0.63	17.10	52.47	2.82	1.28	0.63	8.11
New Vaal	39.69	2.69	0.94	0.62	18.05	41.44	2.55	1.02	0.74	12.40
Delmas	48.28	2.96	1.19	1.57	16.56	50.08	2.93	1.25	1.83	10.82

The oxygen content in coal and char was calculated by difference to 100% using Equation (27):

$$O = 100 - (A + M + S + C + H + N) \tag{27}$$

Where O, S, C, H and N denotes contents of oxygen, sulphur, carbon, hydrogen and nitrogen in %wt. and A and M denote ash yield and moisture content (from proximate analysis). The content of carbon in the New Vaal coal is significantly lower than in other coals. In the case of Secunda, Kuthala and Delmas coals carbon content is similar, from 48.28–50.15%. The nitrogen content of all the samples did not differ that much. The sulphur content of all coals also did not differ that much. The ultimate analysis provides values for total C, H, N and S, and O is calculated as a difference to 100%. All these elements occur in both organic and inorganic matter in coal. An additional analysis is required to distinguish between organic and inorganic carbon, sulphur etc. The sulphur content in Delmas coal and char is relatively high. With respect to oxygen, the values are relatively close to each other for Kuthala, New Vaal and Delmas coals. The oxygen content is much lower in the Secunda coal when compared to other coals.

Calorific value (HHV)

Table 4.3 shows HHVs of the coals, their respective chars and VM. Assuming that the devolatilization process is energy neutral, i.e. it is not endothermic nor exothermic, the HHV of volatiles evolved can be calculated from the energy balance described by Equation (28):

$$m_{\mathrm{coal}}HHV_{\mathrm{coal}} = m_{\mathrm{char}}HHV_{\mathrm{char}} + m_{\mathrm{volatiles}}HHV_{\mathrm{volatiles}} \tag{28}$$

where m_{coal} is the mass of coal before charring, HHV_{coal} is the higher heating value of coal, m_{char} is mass of coal after charring, HHV_{char} is the higher heating value of char, $m_{\mathrm{volatiles}}$ is the mass of volatiles and $\mathrm{HHV}_{\mathrm{volatiles}}$ is the higher heating value of volatiles. The HHV of Secunda, Delmas and Kuthala coals are comparable whereas HHV of New Vaal coal is significantly lower. This is backed by its high ash content and high moisture content as indicated in Table 4.1. This coal also have low VM content of 20.00%. The low HHV can also be attributed to the decomposition of minerals which might produce species with zero CV such as CO_2 and SO_2.

Table 4.3: Higher heating values of coals, their chars and VM, MJ/kg (AD)

	Coal	**Char**	**VM**
Secunda	19.90	19.23	24.29
New Vaal	15.23	15.04	20.00
Delmas	19.46	18.91	26.00
Kuthala	19.29	18.03	24.29

4.3 Composition of coal, char and volatiles

Table 4.4 indicates the split of coal nitrogen, carbon, hydrogen and sulphur between char and volatiles. The figures were calculated using Equation 29 that describes the elemental mass balance:

$$m_{\mathrm{coal}}w_{\mathrm{x,coal}} = m_{\mathrm{char}}w_{\mathrm{x,char}} + m_{\mathrm{volatiles}}w_{\mathrm{x,volatiles}} \tag{29}$$

where m_{coal} is the mass of coal before charring, $w_{\mathrm{x,coal}}$ is mass fraction of N, C, H and S in coal, m_{char} is mass of coal after charring, $w_{\mathrm{x,char}}$ is mass fraction of N, C, H and S in char, $m_{\mathrm{volatiles}}$ is mass of volatiles and $w_{\mathrm{x,volatiles}}$ is weight fraction of N,C,H and S in volatiles. For all coals the quantity of nitrogen retained in the char is much higher than that retained in volatile matter. Most of the nitrogen bound to the char is seen in Delmas and New Vaal coals.

Table 4.4: The split of coal-N, -C, -H and -S between char and volatiles

	Delmas		**Secunda**		**Kuthala**		**New Vaal**	
	g	%	g	%	g	%	g	%
N in coal	0.056	100	0.056	100	0.034	100	0.028	100
N in char	0.051	91.07	0.049	87.50	0.027	79.40	0.026	92.86
N in VM	0.005	8.93	0.007	12.50	0.007	20.60	0.002	7.14
C in coal	2.270	100	2.48	100	1.42	100	1.17	100
C in char	1.830	80.62	1.95	78.63	1.10	77.46	1.05	89.74
C in VM	0.440	19.38	0.53	21.37	0.32	22.54	0.12	10.26
H in coal	0.140	100	0.09	100	0.08	100	0.08	100
H in char	0.110	78.57	0.03	33.33	0.06	75	0.06	75
H in VM	0.030	21.43	0.06	66.67	0.02	25	0.02	25
S in coal	0.070	100	0.03	100	0.02	100	0.02	100
S in char	0.070	100.00	0.03	100	0.01	50	0.02	100
S in VM	0.000	0.00	0.00	0	0.01	50	0.00	0

4.4 Ash analysis

The results of ash analysis are shown in Table 4.5. The chemical composition of ash is dominated by SiO_2 and Al_2O_3 for all tested coals. (For bituminous coals, an ash with a high combined alumina and silica content can be troublesome. The ash tends to be glassy and therefore not wettable) [53]. This is followed by the sum of F_2O_3 and FeO and lastly CaO. The low contents of Fe_2O_3, MgO and CaO indicate the low slagging and fouling propensity [58]. XRF ash values do not have to be 100% and, usually, is not 100%. Reason for it, not all elements that occur in coal are analyzed.

Table 4.5: XRF analysis of ash samples, %wt.

	Delmas	**Kuthala**	**New Vaal**	**Secunda**
SiO_2	46.54	50.58	54.46	56.53
Al_2O_3	25.97	29.82	31.23	22.44
F_2O_3	0.82	0.24	0.32	0.46
FeO	6.64	1.93	2.55	3.68
MnO	0.06	0.03	0.04	0.05
MgO	1.88	2.14	1.00	1.89
CaO	7.53	7.44	4.15	7.19
Na_2O	0.28	0.54	0.14	0.14
K_2O	0.63	0.80	0.60	1.05
TiO_2	1.50	1.60	1.50	1.28
P_2O_5	0.52	0.74	0.35	0.73
Cr_2O_3	0.05	0.01	0.05	0.09
NiO	0.02	0.01	0.02	0.03
LOI	1.03	0.87	0.90	0.80
Total	**93.57**	**96.75**	**97.31**	**96.61**

4.5 Petrographic analysis

The analysis of maceral groups is shown in Table 4.6. All tested coals are rich in inertinite. The Delmas coal has the highest vitrinite content (36%vol., mmf), but all coals are classified as low vitrinite coals (less than 40%vol. vitrinite, ISO 11760:2018 (E)). The Delmas coal has the highest proportion of reactive macerals (vitrinite being more reactive). Clays dominate the mineral matter, although the Secunda sample has a higher proportion of liberated quartz particles. The New Vaal coal has the highest proportion of mineral matter. All coals appear fresh although some fissuring was evident in particles from New Vaal coal (see Figures 4.1–4.4).

Table 4.6: Maceral group analysis (%vol.)

		Kuthala		**New Vaal**		**Delmas**		**Secunda**	
		inc. mm	mmf	inc. mm	mmf	inc. mm	mmf	inc. mm	mmf
Maceral	Vitrinite	17.7	21.5	23.0	23.8	31.7	36.4	22.0	26.5
	Inertinite	62.5	76.1	40.0	72.2	52.2	60.0	58.9	70.9
	Liptinite	2.0	2.4	1.0	3.9	3.1	3.6	2.2	2.6
Mineral matter	Clay	7.9		8.3		5.9		5.9	
	Quartz	6.7		6.3		3.9		9.2	
	Pyrite	0.2		1.2		0.6		0.8	
	Carbonate	2.4		1.2		2.0		1.0	
	Other	0.8		0.2		0.6		0.0	
	Total mm	**17.9**		**36.0**		**13.0**		**16.9**	

inc. mm – including mineral matter, mmf – mineral matter free, mm – mineral matter

Petrographic results - rank determination

The mean random vitrinite reflectance values ranged from 0.56 to 0.70 RoV%. All coals are low rank bituminous, with three coal samples falling in the medium rank C range, and New Vaal coal in the medium rank D range. The standard deviation values are low, indicating a single population and no evidence of heat effect.

Table 4.7: Vitrinite reflectance analysis (RoV %)

Coal	**Kuthala**	**New Vaal**	**Delmas**	**Secunda**
Random vitrinite reflectance	0.70	0.56	0.61	0.64
Standard deviation	0.089	0.075	0.078	0.057
Number of points	102	99	104	101
Range	0.5–0.93	0.44–0.76	0.42–0.82	0.52–0.82
Rank category	Med. rank C bituminous	Med. rank D bituminous	Med. rank C bituminous	Med. rank C bituminous

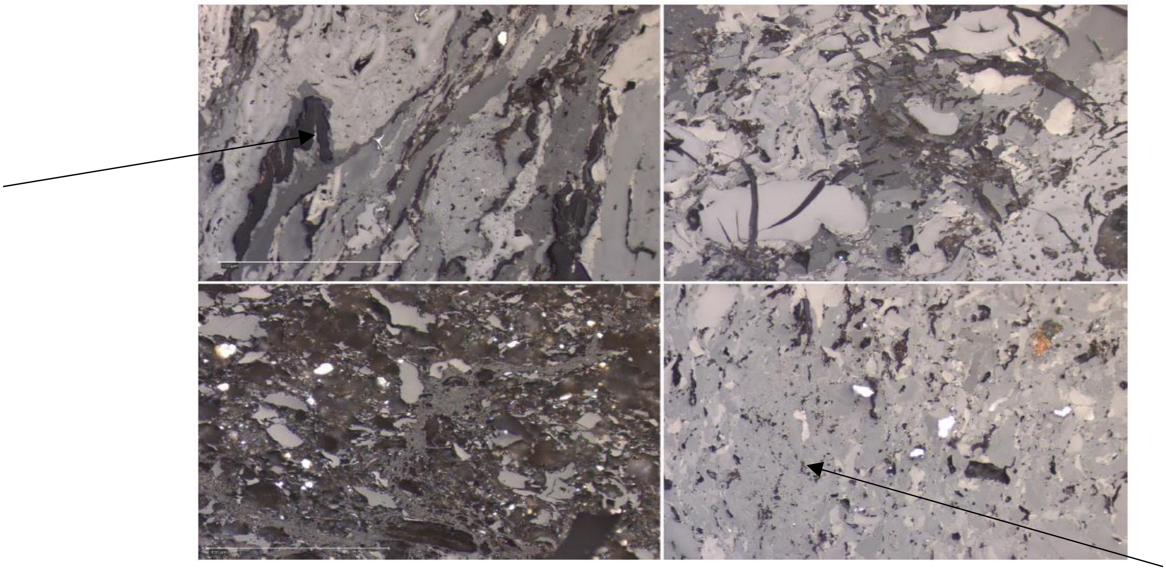


Figure 4.1: Kuthala coal: Banded inertinite and liptinite (black), various macerals cut by carbonate minerals, small quartz particles associated with vitrinite (grey) inertinite.

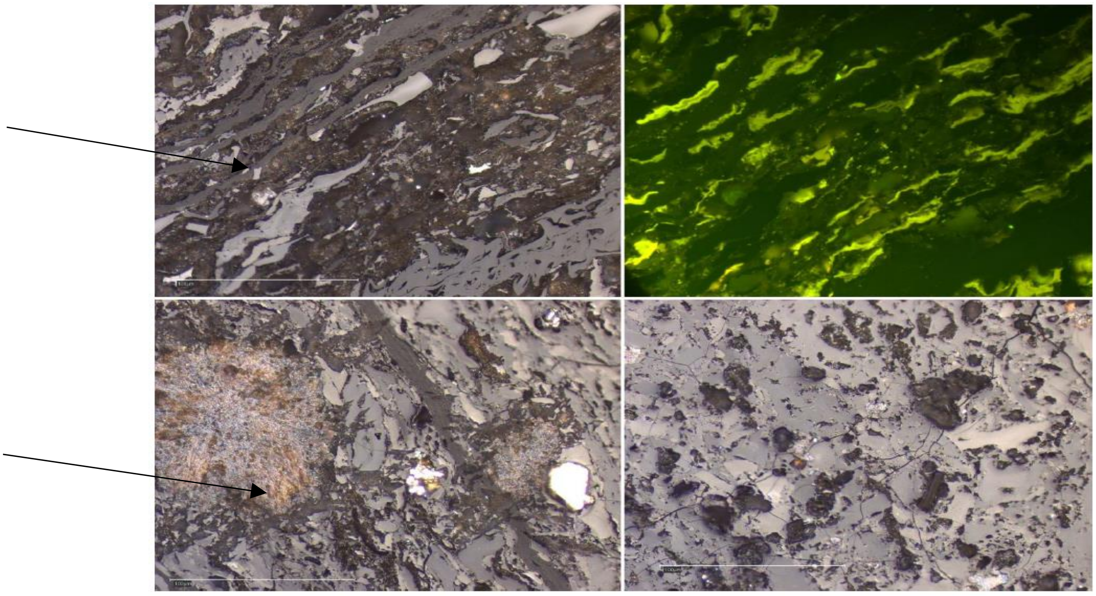


Figure 4.2: New Vaal coal: Clays associated with liptinite (top row), top right picture is a fluorescent image of top left, various carbonate minerals and pyrite in organic particle (bottom left), inertodetrinite with fissures (bottom right).

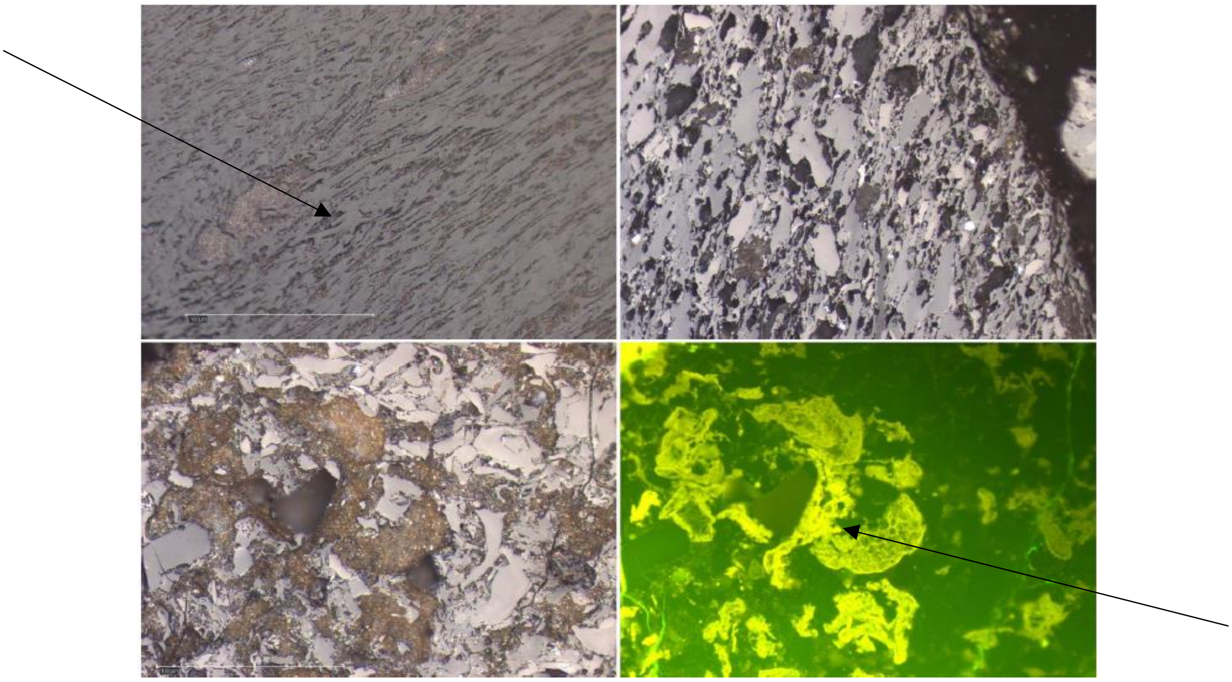


Figure 4.3: Delmas coal: Vitrinite with clays (granular) (top left), inertinite, specifically, inertodetrinite (top right), liptinite associated with inertinite and clays (bottom row, right image in fluorescent mode).

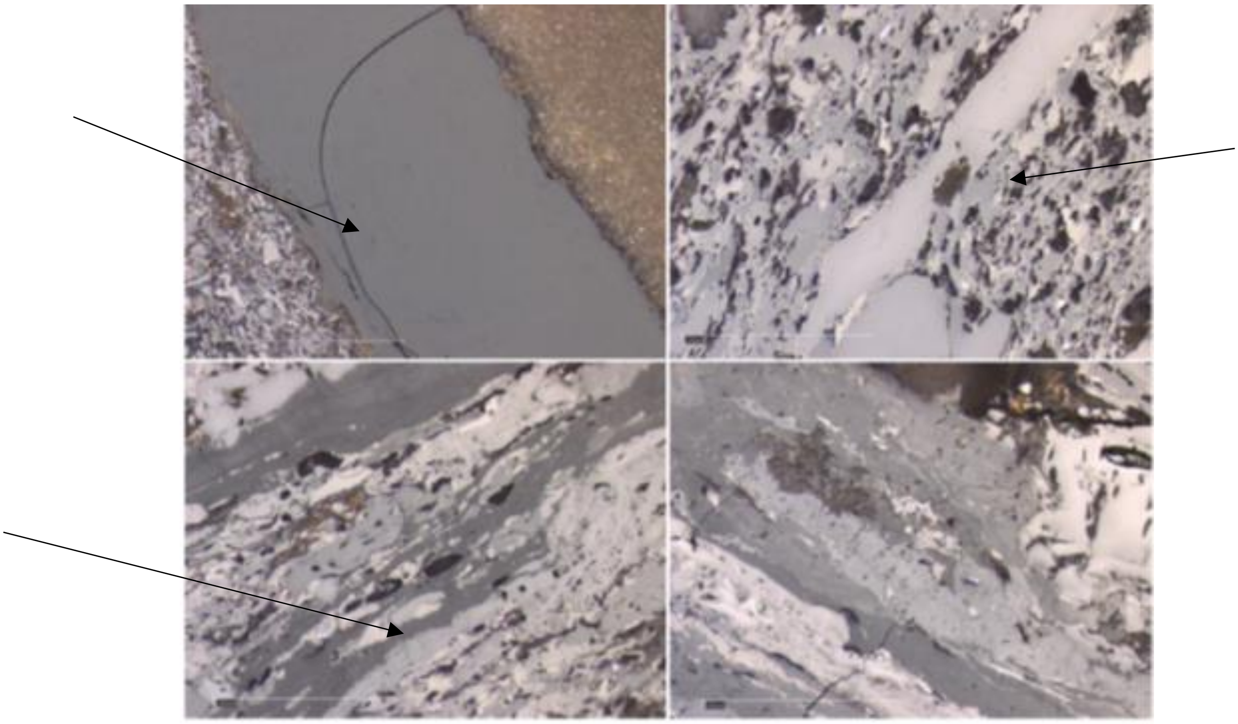


Figure 4.4: Secunda coal: Vitrinite band (top left), inertodetrinite with fusinite band (top right), thin vitrinite bands in inertinite–rich particle (bottom left), banded semifusinite.

4.6 Thermogravimetric analysis

The TG/DTG for combustion of coals and their chars are shown in Figures 4.5–4.8. It was noted that Secunda, Kuthala and Delmas coals exhibited almost similar trends with respect to loss of moisture and VM during the devolatilization and combustion stages.

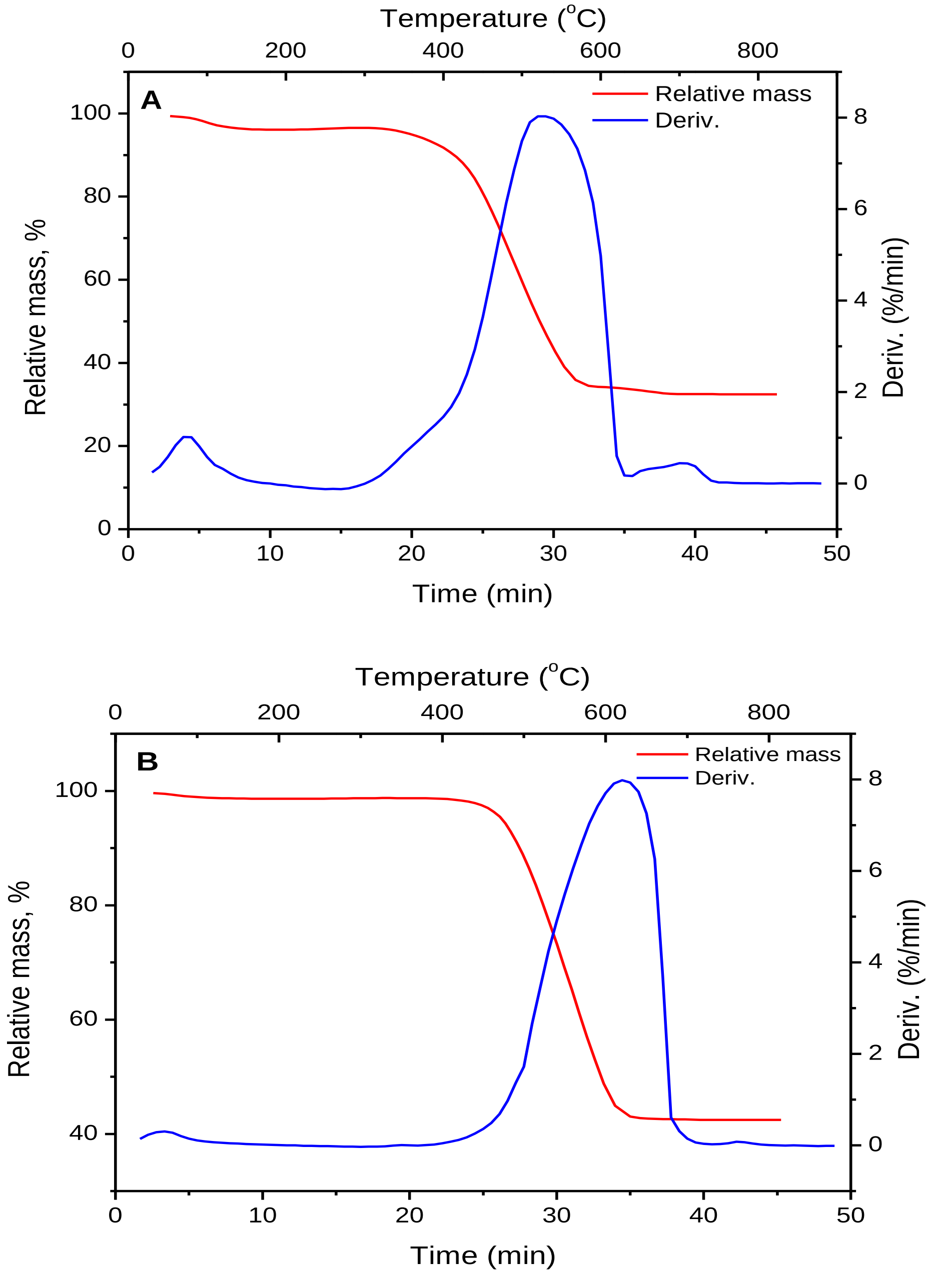


Figure 4.5**:** TG/DTG profiles of (A) Secunda coal and (B) Secunda char

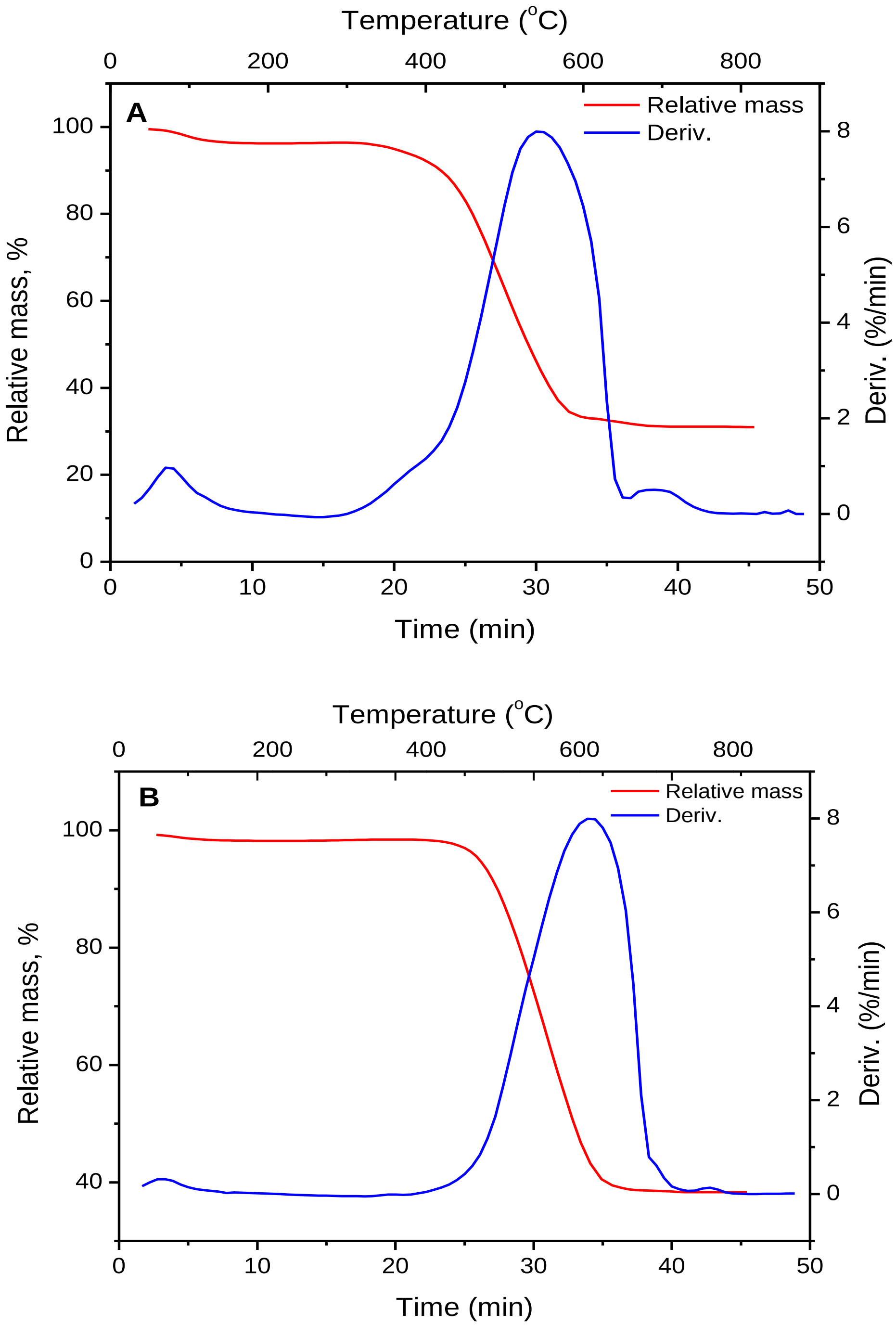


Figure 4.6: TG/DTG profile of (A) Kuthala coal and (B) Kuthala char

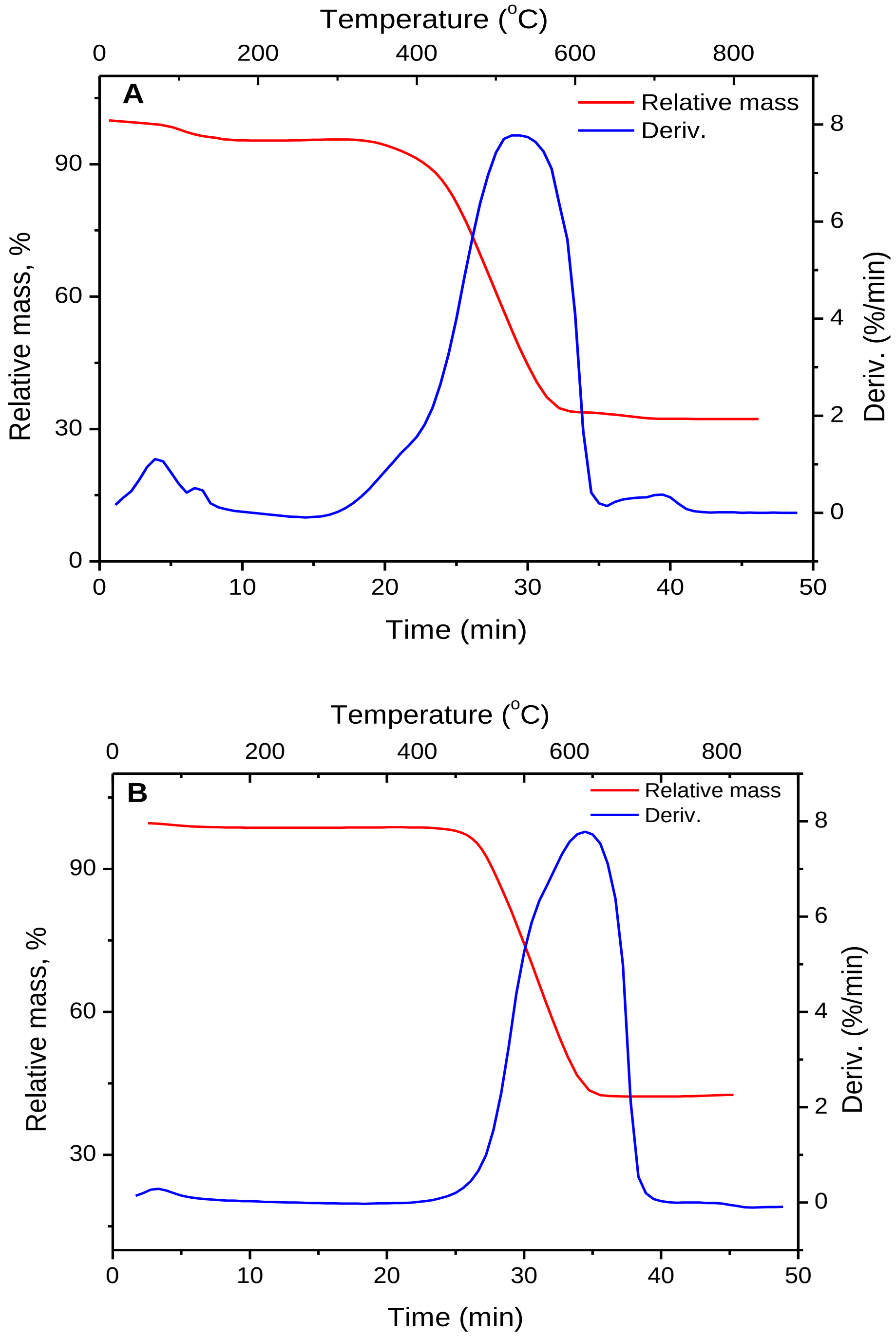
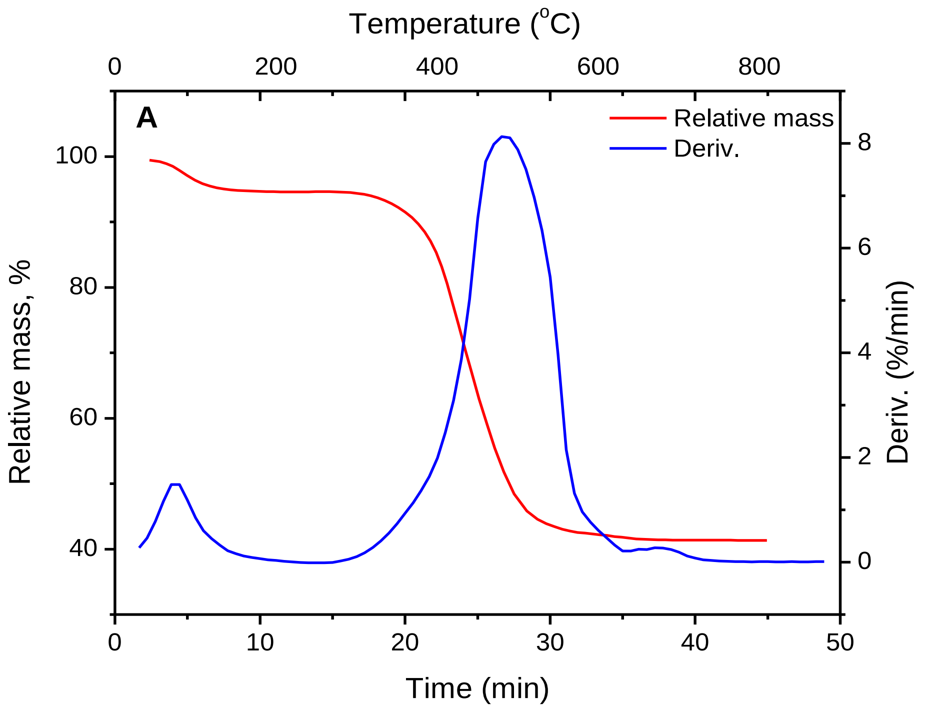


Figure 4.7: TG/DTG profile of (A) Delmas coal and (B) Delmas char



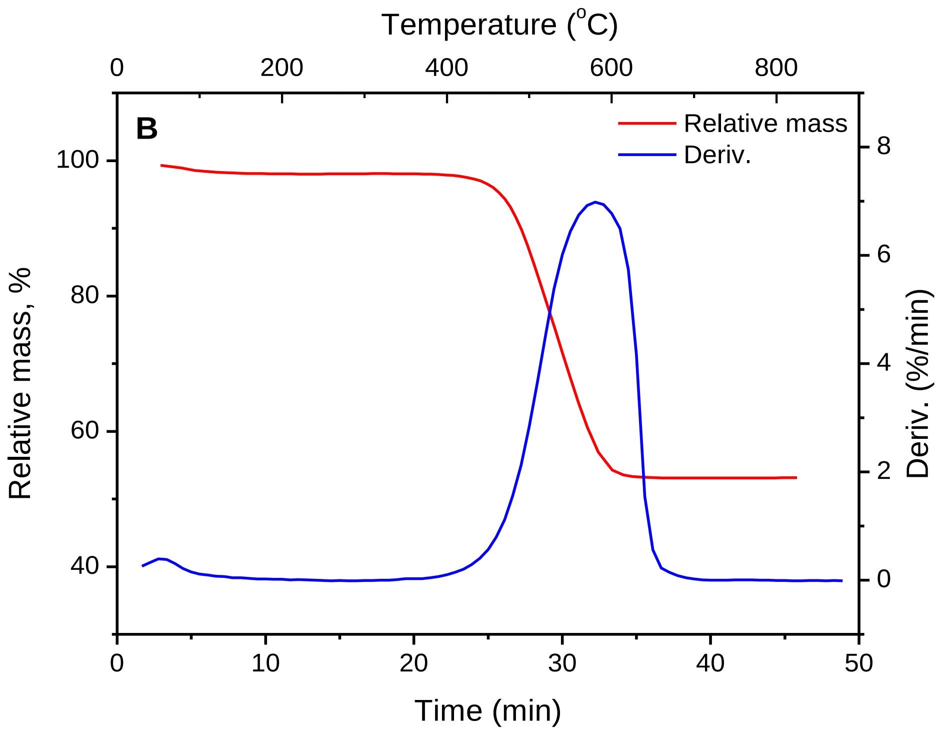


Figure 4.8: TG/DTG profile of (A) New Vaal coal and (B) New Vaal char

Moisture and VM loss occurred in two temperature regions around 105–180˚C and 260−405˚C respectively. After these periods, char oxidation was initiated. The oxidation of char occurred in two successive temperature regions 420–550˚C and 590–650˚C. It can also be noted that in the TG curves the final maximum mass loss of Secunda, Kuthala and Delmas coals are 67.54wt.%, 67.73wt.% and 69.03wt.% respectively.

In the DTG curves three peaks are observed in three temperature regions. The first mass loss appears at approximately 105˚C. This is attributed to the evaporation of water. The second highest peak is around 580˚C. According to [53] at this temperature various gases consisting of low molecular mass hydrocarbons, H_2, CO, as well as tars are evolved [25]. The third peak is seen at temperature above 750˚C. This temperature corresponds to oxidation of char to gases such as CO, CO_2, NO, NO_2, N_2O and SO_2 [25]. It is also worthy to note that in the DTG curves of all four coals, the rate of mass loss in the second region is much higher compared to the mass loss in the first and third region. This indicates that oxidation reactions are much faster than other processes responsible for mass loss during heating. The height of the peaks is more or less the same and the maximum oxidation rate is the same for coals and their chars.

TG/DTG curves of New Vaal coal are shown in Figure 4.8. This coal depicts a significant difference during the devolatilization stage compared to the three other coals. Devolatilization also occurs in two successive regions but at higher temperatures i.e. 135–188 ˚C and 305–470˚C which means later in time than in the case of the other three coals. The oxidation phase starts at 480˚C and lasts until 570˚C. Also, important to note is that New Vaal coal has the lowest mass loss among the four tested coals with the final mass loss of 41.33% and 53.14% for coal and char respectively. This can be attributed to high content of incombustible material (ash).

4.7 TG-MS/TG-FTIR analysis

Challenges faced during the implementation of the project.

Though the aim of this research was to assess the conversion of coal-N to nitrogen oxides on four coals (Secunda, Kuthala, Delmas and New-Vaal) during oxidation under conditions prevailing in fluidized-bed combustion, the experimental equipment (TG-MS or a TG-FTIR) required to get the quantitative/qualitative information on these coals with regards to emitted oxides of nitrogen, was difficult to obtain. Different institutions were consulted and most didn't have this equipment. For those that had it in their possession, it turned out to be faulty. There was an FTIR equipment at our school (School of Chemical and Metallurgical Engineering) but its adaption to our purpose was very costly. The coals were then tested in a hyphenated TG-

MS instrument at School of Chemistry. Some qualitative data was obtained but was not valuable to use. The aim was to detect NO, NO_2 and N_2O that were formed during coal and char combustion tests. Unfortunately the instrument was unable to detect these species. This is depicted in Figure 4.9 and Figure 4.10 respectively below. The tests were then repeated in the TG-FTIR instrument at the Nelson Mandela University. The interpretation of data generated there was, however, impossible due to measurement errors and mechanical problems with the instrument. Similar situation was encountered at the University of Johannesburg; both in Auckland Park and Doornfontein the instrument available there was also faulty. Other universities such as Unisa and NWU and research centers such as Mintek and NECSA were also contacted. Mintek does not have the required instrument and NECSA's and NWU instruments were not operational. Other companies like Delmas, Eskom and Sasol were also approached and the response was the same.

Finally, the samples were sent to CSIR, National Centre for Nano Structured Materials. A qualitative TG-FTIR analysis was performed there. Unfortunately the operator pyrolized our samples in nitrogen despite clear instructions for the samples to undergo combustion in air. As a result, the oxidation of char-N and volatile-N could not take place. Clearly, these results were inadequate for our purpose (CSIR is a big company, we had trusted that the instructions would be followed and that the test work would be conducted properly by a trained and experienced operator. We therefore couldn't override their procedures and supervise their employers as it could have not been envisioned that the testwork would be jeopardised). The TG results indicated a low mass loss for all coals even at high temperature. The non-isothermal TG method enables the observation of the weight loss of a sample as a function of temperature and time through a predetermined temperature regime and/ period of time. For instance, looking at the performance of the New Vaal coal, the TG curve showed a mass loss of 31–33% at 900°C which would be typical for pyrolysis conditions. The TG test with the same coal was then repeated in air at the School of Chemical and Metallurgical Engineering under the same temperature conditions. The recorded mass loss was 58% which is more or less what was anticipated. These results are indicated below in Figure 4.11 and Figure 4.12 respectively. The FTIR at CSIR could not detect nitrogen oxides because an inert, non-oxidizing atmosphere was used (as a result influence of various factors such as temperature, macerals, nitrogen content etc. on production of NO_x could not be evaluated). The instructions were not followed although sample information sheet stating the sample's details on testing environment, temperature profile, heating rate, instrument to be used and concentrations required was provided. The only functional groups identified in our samples were O–H, C–O and C=O (The aim was to compare qualitatively/quantitatively the combustion behaviour of these coals and determine various gases evolved at varying temperature regions. Most fossil fuels possesses different common phases such as loss of moisture and volatiles, oxidation of fixed carbon and evolution of heat. This difference dictate the nature and efficiency of combustion reaction. The temperature ranges, the effect on the overall combustion period, the whole reaction series rely on the composition, origin, mineral matrix etc.). This information was however, meaningless to evaluate the conversion of coal-N to nitrogen oxides and, therefore, the significance of the CSIR results could not be assessed. The data was inadequate to argue the findings. Although the literature that is presented in the report was adequate to can draw from, it couldn't however be used to support the results that were obtained, and this led to this part of the project to be omitted.

Because funds were no more available for this project, the TG-FTIR tests in air could not be repeated at CSIR. This was the main reason the scope of the project had to change. The initial intention was to provide insight into the conversion of coal-N to NOx and to compare this to what is available in literature. We did all we could to get the right information, unfortunately the challenge to find suitable instrument was too big and we started running out of time.

Because of the problems described above, eventually as the last resort, the data from fluidized-bed combustion tests performed at Eskom was analyzed. This data was more than adequate, and were able to quantify the conversion of fuel nitrogen to NO_x and to assess the influence of some of the factors like CH/N mass ratio, fuel ratio, nitrogen content and ash content on the conversion of coal-N to NO and N_2O. Some of the factors (like CH/N) is related to the coals which formed part of the investigation and the project was still related to the conversion of fuel nitrogen to NO_x in fluidized-bed combustion. As a result the tittle of the project was retained.

None the less, a lot was achieved under described circumstances. The proximate analyses, ultimate analyses, CV analyses, ash analyses and petrographic analyses were performed and assessed. These enable to calculate the split of coal-N and CV between the char and volatiles and to compare the combustion behaviour of the four coals through a qualitative TG analysis. The only part that could not be done for this research project is the quantitative/qualitative analysis of nitrogen oxides emitted during the TG-MS tests at CSIR and although the test was not under combustion conditions, the mention of effort that went into the project, albeit unsuccessful towards achieving the desired outcome, may seem irrelevant, but, such steps taken should serve the purposes of exposing the level of understanding of the topic by the researcher and more importantly, exposes the readiness of institutions in supporting some topics with the relevant supporting equipment and competency (e.g. CSIR work ethics).

TG-MS analysis

Figure 4.9 shows TGA and DTG curves for Delmas coal tested in the hyphenated TG-MS instrument at School of Chemistry at University of the Witwatersrand. The MS spectrum is depicted in Figure 4.10 (Heating of this coal sample resulted in approximately 50% mass loss at 800˚C).

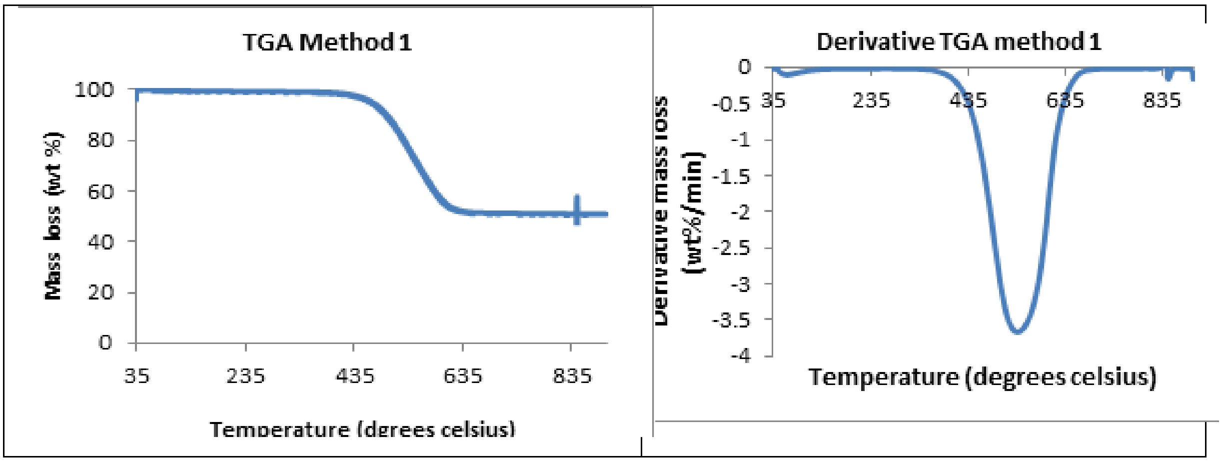


Figure 4.9: TGA curve (left) and DTG curve (right) for Delmas coal

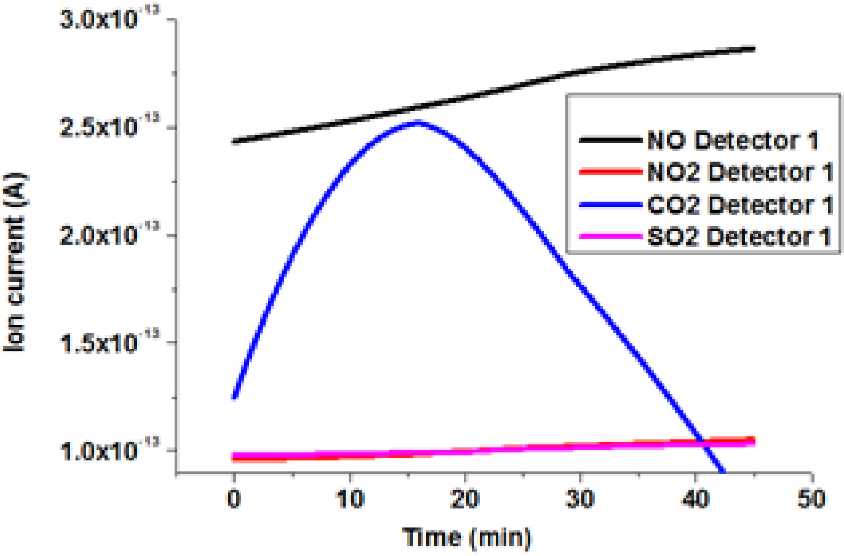


Figure 4.10: MS spectrum for Delmas coal

The purpose of using a TGA-MS instrument was to determine the fraction of coal-N and char-N that were converted to NO, NO_2 and N_2O. Unfortunately, the instrument was unable to detect these species. The machine could not read the nitrogen content from the coal sample. As depicted in figure 4.10 only the graph for carbon is observed.

TG-FTIR analyses

Figure 4.11 shows TGA and DTG curves for the coals and their chars which were tested at CSIR, Centre for Nano Structured Material using the hyphenated TG-FTIR instrument [47]. The FTIR spectrum for tested coals is shown in Figure 4.12.

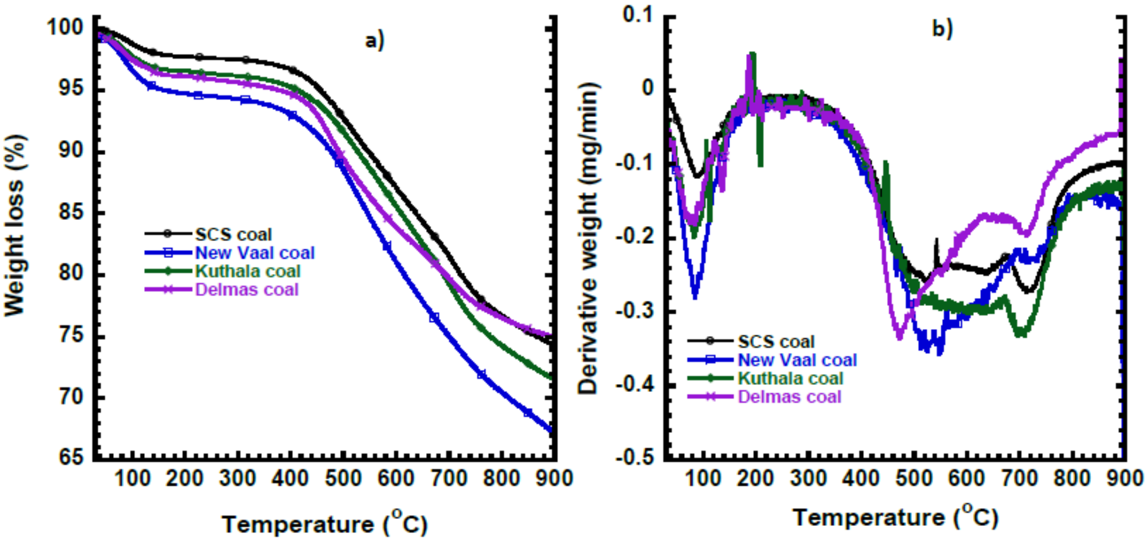


Figure 4.11: a) TGA and b) DTG thermograms for tested coal samples [47]

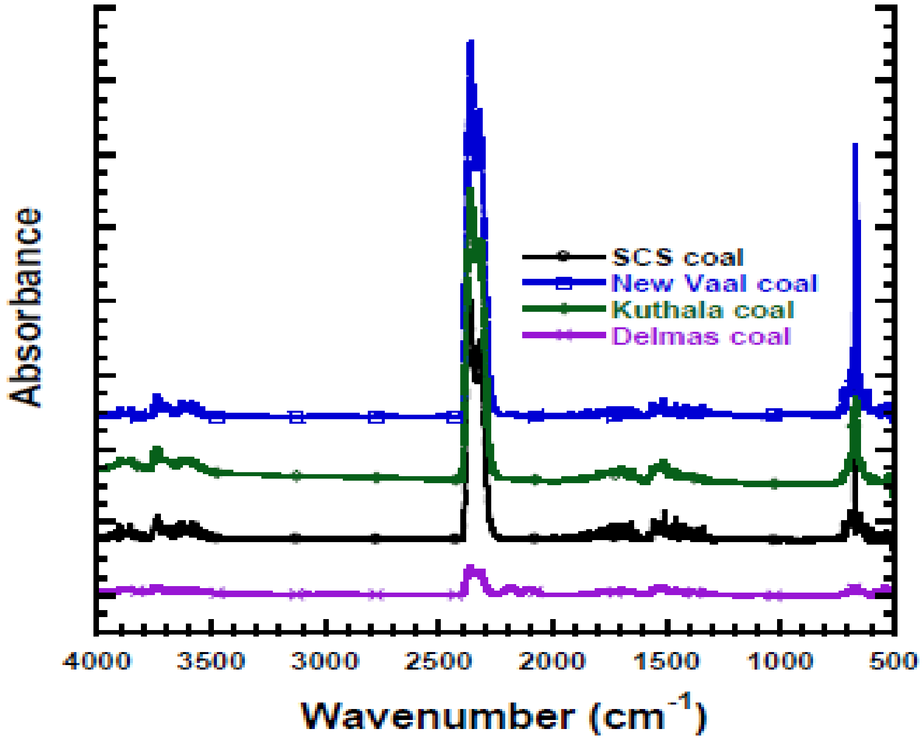


Figure 4. 12: FTIR spectrums for different coals [47]

4.8 Combustion tests of South African coals in fluidised-bed reactors

The objective of this research was to determine the conversion of fuel-N to nitrogen oxides for selected South African coals. Coals at CUT and Eskom are both from South Africa by origin and the combustion of these coals was conducted in a bubbling fluidised-bed and circulating fluidised bed combustion test facility (Fluidised bed combustion technology in its various forms namely: Bubbling fluidised bed (BFBC), circulating fluidised bed combustion (CFBC), pressurised fluidised bubbling bed combustion (PBFC) and pressurised circulating fluidised bed combustion (PCFBC) has the ability to reduce emission. It has been used to burn all types of coals, coal waste and a wide variety of other low quality fuels such as biomass and leather waste either single or co-fired with coal. The principle in fluidised bed combustion is the same. Combustion occurs when the mixture of fuel, a sorbent and fuel ash particles is suspended by using a continuous stream of primary combustion air to create turbulence in the bed). The experimental data contained information on coal composition (proximate and ultimate analyses), nitrogen oxide emissions (in flue gas) and on operating conditions such as air flow rates, bed temperature and flue gas composition etc. Data from Eskom test work enabled us to quantify the conversion of nitrogen to NO_x under fluidized-bed combustion conditions (this test work could therefore not be included under experimental procedures). The assumption is that the formation of nitrogen oxides via the thermal mechanism was negligible. This assumption is justified by low combustion temperature (about 850°C). Then, from the nitrogen mass balance the fraction of coal-N converted to nitrogen oxides was calculated. The coal tested at CUT is from Secunda and one of the coals tested for the researched topic is from Secunda. It seemed reasonable to compare the results as coals used in this work were similar to that used for the project and to compare to literature findings.

Combustion tests at Eskom

Several South African coals were tested by Moodley [48] and Papo [49] in the Eskom BFB combustion test facility. This facility is seven meter in height with a bed zone region that has an ID of 230 mm and a freeboard region that expands to an ID of 360 mm as shown in Figure 4.13. Table 4.8 shows proximate and ultimate analyses of coals tested by [48] and [49]. Operating conditions at which these coals were burned are shown in Table 4.9.

Table 4.8: Proximate and ultimate analyses of coals tested at Eskom [48], [49].

Reference	[48]			[49]		
Proximate analysis						
Coal	MA	MB	MC	PA	PB	PC
Ash	42.4	41.8	38.2	36.3	52.5	45.2
VM	21.0	20.0	20.2	19.8	19.7	18.1
FC	33.8	36.0	38.3	41.8	25.1	33.9
Moisture	2.8	2.2	3.3	2.1	2.7	2.8
Ultimate Analysis						
C	80.13	81.72	81.48	50.12	33.88	39.29
N	1.99	1.98	1.74	1.14	0.60	0.79
H	5.27	4.28	2.97	2.41	2.19	2.07
S	1.90	6.88	3.19	1.84	1.46	2.80
O	10.71	5.14	10.62	6.09	6.67	7.05

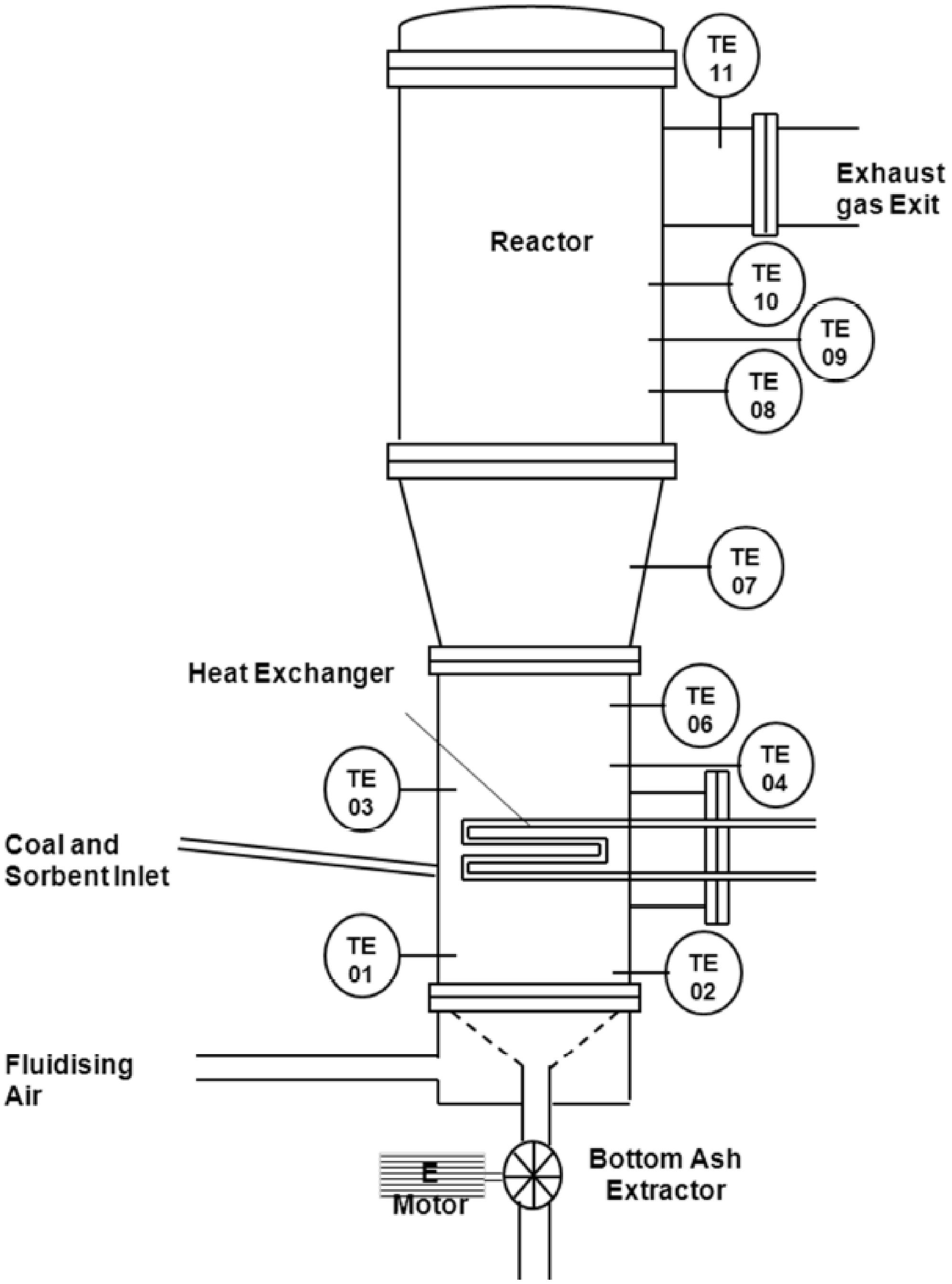


Figure 4.13: Schematic of BFB reactor at Eskom [49]

Table 4.9: Operating conditions in the Eskom BFB combustor (adapted from [48] and [49])

Avg. temp. ˚C	Coal feed rate kg/h	Total air kg/h	O_2 %vol.	CO_2 %vol.	NO ppm	N_2O ppm	CO ppm
Coal MA							
794	4.14	64.7	13.1	8.19	162	101	105
818	4.66	65.5	12.4	9.24	188	94.3	79.6
838	4.71	65.2	11.9	9.75	164	85.7	65.7
850	5.14	65.3	11.6	10.1	216	77.5	54.4
885	5.89	65.8	10.2	11.5	230	63.1	45.3
895	5.61	66.0	10.2	11.6	228	55.2	41.9
Coal MB							
798	4.18	65.2	11.1	8.35	188	106	155
820	4.84	64.9	9.78	9.13	202	106	142
840	5.31	67	8.49	10.5	307	114	137
864	5.79	63.1	7.27	11.7	333	108	124
890	6.17	65.8	6.84	12.1	342	87	97
912	6.55	65.2	6.25	12.6	358	72	84
CoalMC							
802	6.60	87.1	11.69	8.22	208	–	201
826	6.90	87.2	10.92	8.88	209	–	163
842	7.11	87.3	10.63	9.16	217	–	152
862	7.20	87.3	10.30	9.47	236	–	134
876	7.25	87.3	9.97	9.75	258	–	114
903	7.20	86.9	9.46	10.21	285	–	100
CoalPA							
830	8.50	74.70	5.62	12.30	112.31	218.42	173.73
850	8.50	74.74	6.06	11.94	145.45	188.18	164.13
870	8.50	75	6.05	12.01	159.08	176.61	168.55
CoalPB							
830	8.00	72.00	5.41	12.24	210.62	123.08	116.09
850	8.00	71.24	5.67	12.27	206.31	133.77	83.19
870	8.00	71.59	5.76	12.16	165.43	212.51	110.90
CoalPC							
830	8.00	70.17	5.03	13.03	137.16	170.06	122.05
850	8.00	69.96	4.85	12.97	160.75	158.43	102.63
870	8.00	69.44	4.58	13.10	179.04	136.05	94.49

Tables 4.10 and 4.11 show conversions (fractions of coal-N that has transformed to NO and N_2O) of coal-N to NO and N_2O for tested coals. For coal combustion in CFB the conversion of fuel-N to NO_x and N_2O can be calculated as follows:

$$NO_x = \frac{[NO_x]\,Q/V_m}{R_f X_f/M_f} \tag{29}$$

$$N_2O = \frac{2[N_2O]\,Q/V_m}{R_f X_f/M_f} \tag{30}$$

Where $[NO_x]$ and $[NO_2]$ are the NO and N_2O concentrations, Q is the mass flow rate, V_m is the molar volume. R_f and X_f is the mass flow rate of coal and nitrogen fraction of fuel, volatile and char.

These conversions were calculated using an assumption that NO and N_2O detected in the flue gas were formed only from the coal-N. Concentrations of N_2O decrease with temperature as expected. This is also consistent with most other studies [21],[23],[24],[49], however, the trend for NO is not very clear. Because differences between minimum and maximum values are relatively low, the influence of temperature on NO formation can, in this case, be neglected.

Table 4.10: Conversion of coal-N to NO and N_2O for coals tested by [48], %wt.

Coal MA		**Coal MB**		**Coal MC**	
NO	**N_2O**	**NO**	**N_2O**	**NO**	**N_2O**
10.9	13.6	10.4	11.7	13.0	–
11.6	11.6	9.9	10.3	12.1	–
9.6	10.0	13.4	10.0	12.2	–
12.2	8.8	13.3	8.6	12.8	–
11.3	6.2	13.2	6.7	13.6	–
11.2	5.4	13.3	5.3	14.4	–
Avg. 11.1		Avg. 12.3		Avg. 13.0	

Table 4.11: Conversion of coal-N to NO and N_2O for coals tested by [49], %wt.

Coal PA		**Coal PB**		**Coal PC**	
NO	**N_2O**	**NO**	**N_2O**	**NO**	**N_2O**
4.1	16.0	8.0	16.9	5.5	13.6
5.5	14.2	9.8	12.8	6.4	12.5
6.0	13.3	9.9	11.6	7.0	10.6
Avg. 5.2		Avg. 9.2		Avg. 6.3	

Combustion test at CUT

Figure 4.15 shows a CFB combustor at Czestochowa University of Technology [50]. The unit comprises of 0.1 m I.D. combustion chamber (riser) of approximately 5.0 m in height. Solids leaving the riser go to the cyclone where they are separated from the gas stream and returned to the combustion chamber through a 0.075 m I.D. down comer. The test was conducted using staged combustion i.e. the combustion air was split into primary air and secondary air.

The test was carried out with –6 mm fraction of Secunda coal. Table 4.12 shows proximate, ultimate and CV analyses of this coal. Table 4.13 shows test conditions and the flue gas analysis is reported in Table 4.14. The calculated conversions of coal-N to NO and N_2O were 8.1 and 12.3%wt. respectively. The conversion of coal-N to NO is lower than the average value calculated for coals tested by Moodley. However, conversions of coal-N to NO calculated for coals tested by Papo are even lower (except coal PB). In the case of conversion to N_2O, the result obtained in the CFB combustor is similar to values obtained in the BFB reactor at Eskom.

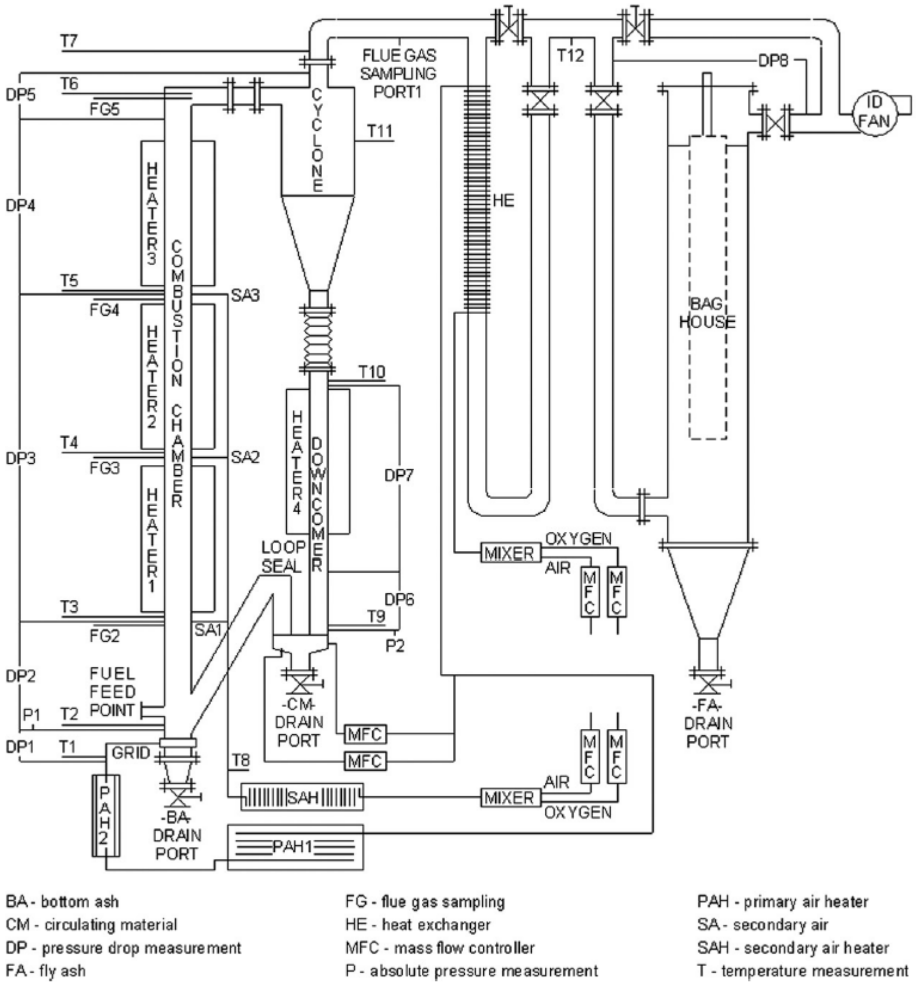


Figure 4.14: **CFB combustion test rig at CUT [50].**

Table 4.12: Analysis (as received basis) of the Secunda coal [50]

Proximate analysis, %wt.	
Moisture	6.0
Ash	20.5
Volatiles	24.5
Fixed carbon	49.0
Ultimate analysis, %wt.	
C	59.46
H	2.95
N	1.30
S	0.99
O (by diff.)	8.80
Calorific value	
HHV, MJ/kg	22.33
LHV, MJ/kg	21.54

Table 4.13: Test conditions [50]

Coal feed rate, kg/h	3.97
Air flow rate, m^3/h	29.0
Excess air, %	24
Primary/secondary air split, %	80/20
Thermal load (LHV), kW	23.75
Superficial gas velocity in the riser, m/s	4.56
Average temperature in the riser, °C	850
Limestone feed rate, kg/h	0

Table 4.14: Flue gas analysis [50]

	Unit	**Average**	**Standard deviation**	**Corrected to 6% O_2 (dry basis)**
Flue gas composition				
CO	ppm	140	62	140
CO_2	%vol.	13.51	0.34	13.51
H_2O	%vol.	6.35	0.19	–
N_2O	ppm	163	7	163
NO	ppm	214	19	214
NO_2	ppm	0.4	1.3	0.4
O_2	%vol.	4.66	0.52	
SO_2	ppm	394	46	394

4.9 Influence of coal properties on the conversion of coal-N to nitrogen oxides

South African coals from different origin were studied with the objective to examine the influence of coal properties on the conversion of coal-N to NO_x. The main coal properties which were of interest are: nitrogen content, fuel ratio and ash composition.

4.9.1 Nitrogen content

Figure 4.15 shows the relationship between nitrogen content and the conversion of coal-N to NO for coals tested in BFB combustor by Moodley [48] and Papo [49]. There is no evident correlation between the conversion and nitrogen content for both sets of tested coals.

Coals tested by [49] have lower nitrogen content. The conversion of coal-N to NO is also low (as indicated in Table 4.11). However, there is higher conversion of coal-N to NO in coal PB compared to other coal as this coal is characterized by high ash content. In literature it is reported that coals with high ash content and moisture produce a high emission of NO_x. This is attributed to delayed ignition and prolonged char combustion. A delayed ignition results in increased mixing of the coal and combustion air prior to volatile combustion. This results in higher local oxygen concentration [48].

Coals tested by [48] have high content of nitrogen, yielding higher conversion of coal-N to NO compared to those by [49]. Similar findings in a study by [61] were seen where an increasing trend of the conversion of coal-N to NO with nitrogen was observed. Also [51] noted that coals with high nitrogen content are found to correlate with high emissions of both NOx and N_2O (These findings could not be related to our own findings as oxides of nitrogen could not be measured).

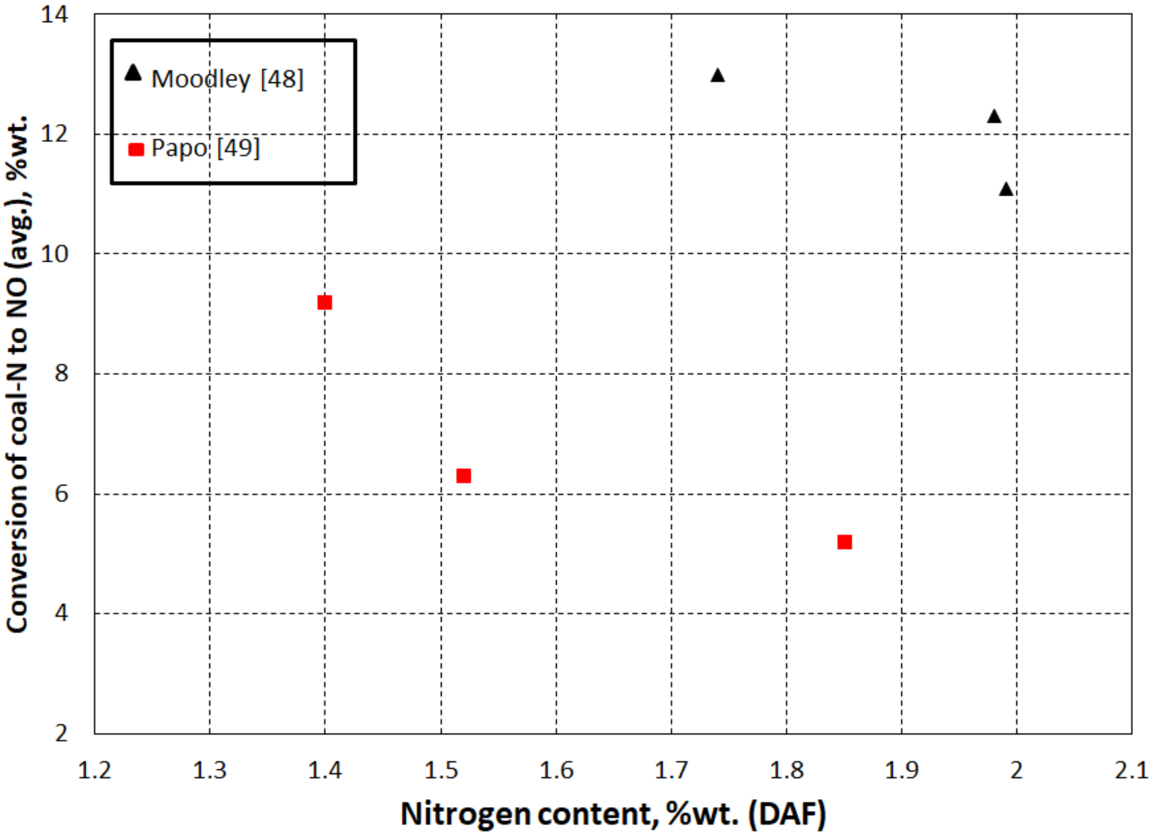


Figure 4.15: The relationship between nitrogen content and the conversion of coal-N to NO.

4.9.2 CH/N mass ratio

Vermeulen et al. [52] developed a correlation between conversion of coal-N to NO and CH/N mass ratio that is based on several data sets for bituminous coals. This correlation is described by equation 31.

$$y = 6.84x + 13.26 \qquad (31)$$

Where y is the conversion of coal-N to NO in %wt. and x is the CH/N mass ratio. This correlation allows to estimate the conversion of fuel-N to NO using the elemental composition of the solid fuel in the form of CH/N ratio (C, H and N are values of the evaluated coals taken from the Table 4.2 on page 29).

The proposed correlation was then applied to the two sets of results reported by [48] and [49]. The Vermeulen's correlation was also used for coals tested in the TG instrument as shown in Table 4.15 and the data obtained from the tested coals compared pretty well to those of [49] and [48]. Correlation for the conversion of fuel-N in terms of CH/N developed by Vermeulen averaged 0.87. An even better regression coefficient of 0.9728 and 0.9993 for coals tested by [48] and [49] was obtained. It is generally accepted that a good correlation corresponds to a correlation coefficients of 0.81 Although this correlation can be applicable to our bituminous coals it cannot however be used to estimate the conversion of coal-N to nitrogen oxides.

The conversion of coal-N to NO predicted using the Vermeulen's correlation was high for all tested coals compared to the measured conversions. The Vermeulen's correlation for some reasons overestimates the coal-N conversion to nitrogen oxides in the case of coals tested at Eskom. It is not clear what these reasons are, but they can be related to the difference in origin of the coals as European coals were used by Vermeulen et al. or its composition etc.

New correlations for coals tested at Eskom were developed. They are in the form of the Vermeulen's correlation but have different values of fixed coefficients. These correlations are shown in Figure 4.16. New correlations for the coal samples tested in this study could not be obtained NO values could not be measured as it was already indicated.

Figure 4.16 shows the relationship between the conversion of coal-N to NO and CH/N mass ratio for coals tested by [48] and [49]. It can be seen that there is a good linear correlation between conversion of coal-N to NO and CH/N although in opposite directions for both coals. For coals tested by [48] the conversion of coal-N to NO decreased with CH/N and for coals tested by [49] CH/N increases so does the conversion of coal-N to NO.

Table 4.15: Measured conversion of coal-N to NO and calculated conversion of coal-N to NO using Vermeulen’s correlation

	Sample ID	**Avg. conversion of coal-N to NO (measured values)**	**Conversion of coal-N to NO from the Vermeulen’s correlation**
[48]	MA	11.2	27.8
	MB	12.3	25.3
	MC	13.0	22.8
[49]	PA	5.2	20.5
	PB	9.2	21.7
	PC	6.3	20.3
	Secunda	–	16.05
	Kuthala	–	16.30
	New Vaal	–	16.34
	Delmas	–	16.21
[38]	CUT	8.1	25

The Vermeulen's correlation has only one variable - CH/N ratio. We can expect that if we use CH/N ratios for our coals, the calculated conversions should be close to our experimental values. However, this is not a case because our coals are different. The Vermeulen's correlation overestimates our experimental data. That is why new correlations were developed. These correlations have the same form and predict experimental values with high accuracy. The only thing that cannot be explained are opposite trends for [48] and [49] coals.

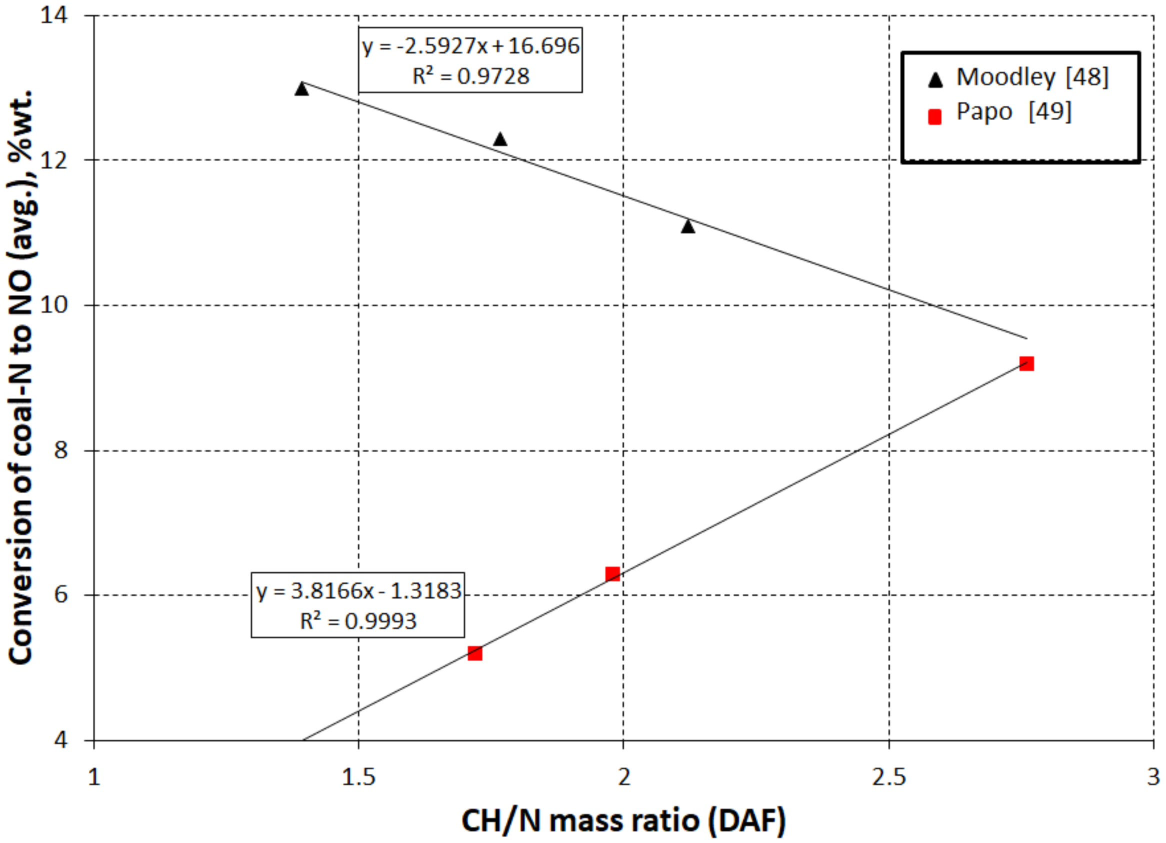


Figure 4.16: The relationship between CH/N ratio and the conversion of coal-N to NO

4.9.3 Fuel ratio

Fuel ratio, FR, is the ratio of fixed carbon content to the volatile matter content of the coal. The fuel ratio of the four tested coals was calculated by using the determined FC and VM from the proximate analysis shown in Table 4.1 on page 28. It is reported in literature [53] that FR for good quality coals is less than 1.5, for average quality coals it is in the range1.5–2.0 and for low quality it is higher than 2.5. All coals tested were average quality coals whose fuel ratio is 1.71, 2.45, 1.82 and 2.22 for Secunda, Kuthala, New Vaal and Delmas respectively. The correlation between the conversion of coal-N to NO and fuel ratio is shown in Figure 4.17. It is noted that a strong linear correlation exists between conversion of coal-N to NO and fuel ratio for both Moodley's and Papo's coals. The correlation coefficient of R^2 =0.9987 and R^2 = 0.9999 were obtained respectively. The conversion of coal-N to NO in the case of Moodley's coals increases with FR while Papo's coals reveal an opposite tendency. Although good linear correlations were obtained between coal-N and CH/N mass ratio and FR, the correlation obtained with FR is slightly better than correlation obtained with CH/N.

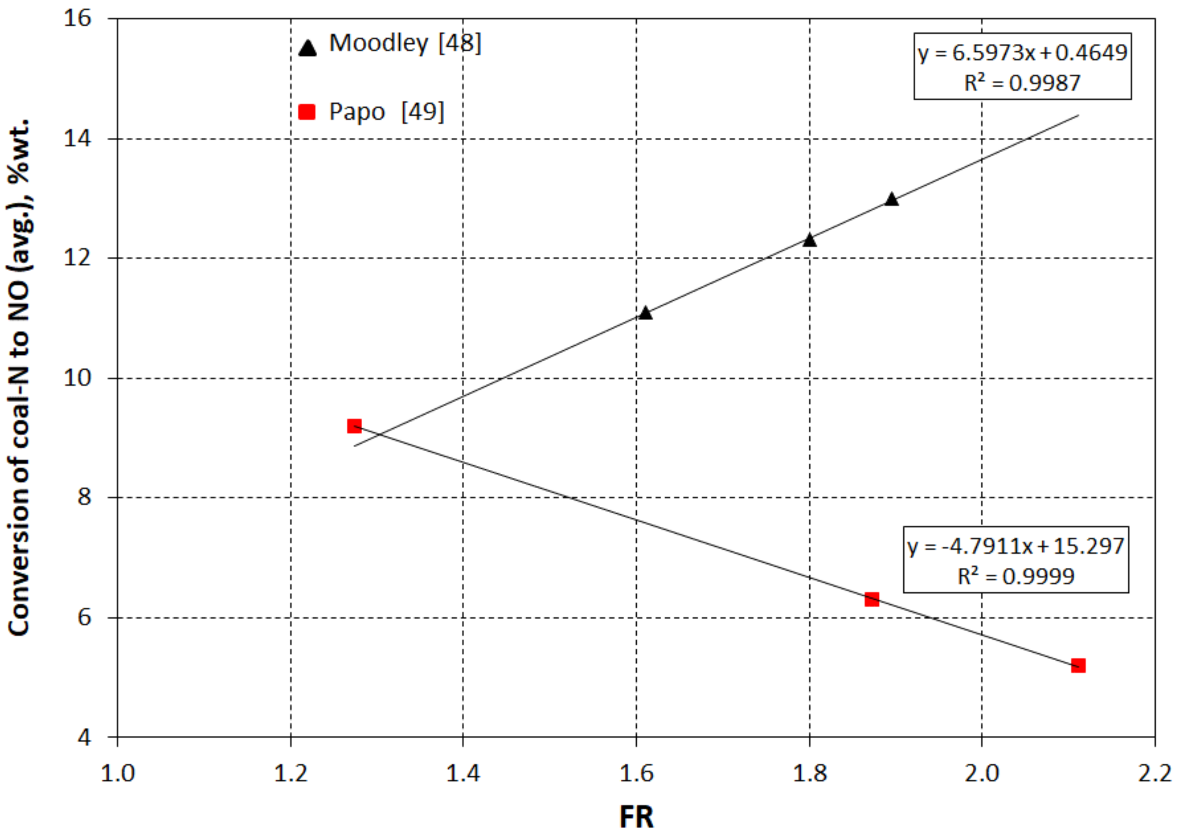


Figure 4. 17: The relationship between fuel ratio and the conversion of coal-N to NO

Looking at the results of the coals tested by Moodley and Papo it can be seen that the CH/N and FR are the most important properties influencing NO emission from fluidized-bed combustion although opposite tendency is observed. Considering that coals tested by Moodley had a higher carbon content compared to those tested by Papo, the conversion of fuel-N to NO_x was expected to be high (See Figure 4.16). This was not the case. This is attributed to the fact that functional form of fuel-N is strongly dependant on carbon content. As the carbon content of the fuel increases nitrogen preferably bounds itself in heterocyclic structure particularly as pyrollic-N leading to the formation of HCN than in the form of amines or quaternary-N structure leading to the formation of NH_3 [52]. HCN which is a primary intermediate reacts with O, H and OH radicals to form principal intermediates like NCO and NH that are then subsequently oxidised to NO. These can be shown by reactions given below:

$$HCN + O \rightarrow NCO + H \tag{31}$$

$$NCO + O \rightarrow NO + CO \tag{32}$$

It is also generally accepted that coals with high fuel ratios and higher nitrogen content produce higher NO_x emissions. Although this was evident from Moodley's coals in order to clarify the effect of coal properties on conversion of coal-N to NO_x, it thus seem particularly important to do this through a wide range of coals types so as to obtain valid conclusions.

4.9.4 Ash content

Figure 4.18 shows the conversion of coal-N to NO as a function of ash content (DB). Coal PB tested by [49] shows a higher conversion of coal-N to NO (see Fig 4.18). Its ash content is also significantly higher than for other coals. This coal possesses a high ash content of 52.5%wt. The reason for higher conversion of coal-N to NO can be attributed to the potential catalytic activity of some minerals in coal. Coal MA, MB and MC tested by Moodley had similar ash content however the conversion of coal-N to NO was different, with coal MB and MC producing a little higher conversion of coal-N to NO_x than coal MA.

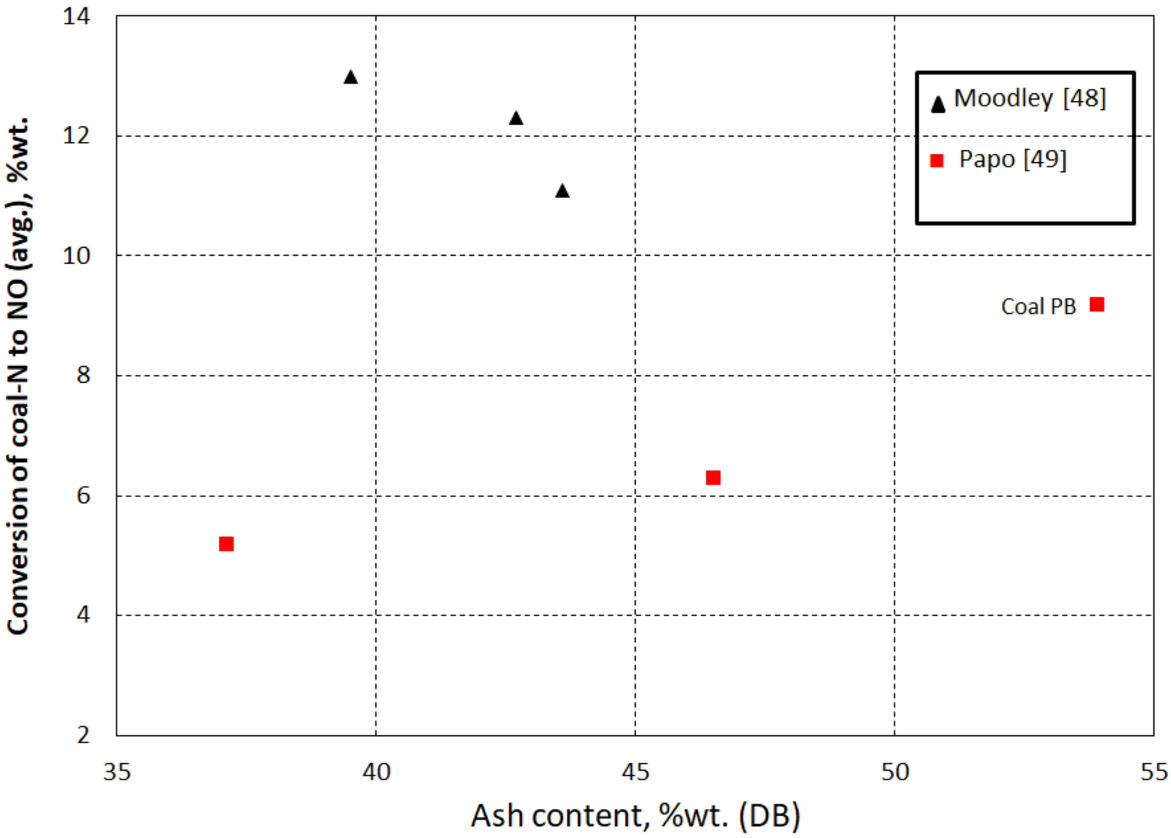


Figure 4.18: The conversion of coal-N to NO as a function of ash content

4.9.5 Maceral composition

South African coals are generally found to be characteristically rich in inertinite and partly rich in vitrinite. As expected this was evident from four South African coals which were tested in

TGA instrument. All coals indicated to be rich in inertinite with the exception for Delmas coal which showed high vitrinite content (see Table 4.6). In a study by [10] for five coals which included a vitrinite-rich Colombian coal, a vitrinite-rich U.S coal and three inertinite-rich South African coals showed NO emissions to decrease with combustion temperature in the case of vitrinite-rich coals and to increase in the case of inertinite-rich coals. Unfortunately due to the inability to measure the NOx emission it was not possible to relate the maceral influence of the four coals used in this study. The only finding which was consistent with literature is that South African coals are high in inertinite.

4.9.6 Maximum possible conversion of coal-N to NO_x

The theoretical flue gas composition was calculated to show the hypothetical maximum possible concentration of NOx in the flue gas and compare it with both the compliance target and the real emissions from the experiments. This comparison shows how far the real emissions are from the theoretical maximum emission. For Eskom experiments the real emissions are lower because not all coal-N is converted to nitrogen oxides. And this comparison, indirectly, provide information on the conversion of coal-N to nitrogen oxides.

The theoretical flue gas composition for the combustion of any fuel can be obtained from the stoichiometric calculations based on the fuel's elemental composition. In the case of FB combustion, it can be assumed that all NO comes from the oxidation of fuel-N. The following reactions, (29)–(32), describe coal combustion assuming complete oxidation of carbon, hydrogen, sulphur and nitrogen to their oxides:

$$C + O_2 \rightarrow CO_2 \tag{33}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{34}$$

$$S + O_2 \rightarrow SO_2 \tag{35}$$

$$Coal - N + \frac{1}{2}O_2 \rightarrow NO \tag{36}$$

Typical excess air for combustion of coal is 20%. It is usually lower for gaseous fuels and higher for solid fuels like coal.

The concentration of NO calculated from Eq. (32) represent the maximum value that would be expected in the case when 100% of coal-N is converted to NO.

Table 4.16 shows the theoretical flue gas composition for Delmas, Kuthala, New Vaal and Secunda coals assuming 20% excess air. Flue gases from these coals would theoretically have high concentrations of NO which would be significantly higher than limits set in the emission standard for existing and new plants (see Table 4.14).

Table 4.16: Off-gas composition of Delmas, Kuthala, New Vaal and Secunda (DB)

	NO in flue gas, mg/m^3_n	NO in flue gas, mg/m^3_n at 10% O_2	NO as NO_2 at 10% O_2
	NO from coal-N	NO from coal-N	
Delmas	4555	2868	1870
Kuthala	4543	2859	1864
New Vaal	9706	6105	3982
Secunda	4875	3069	2001

Table 4.17 represent the minimum emission standards applicable to existing and new plant as stipulated in the Air Quality Act, 2004 (Act NO. 39 of 2004) by National Environmental Management.

Table 4.17: Emission compliance targets [54]

Substance or mixture of substances		Plant status	mg/Nm^3 under normal conditions of 10% O_2, 273 K and 101.3 kPa dry gas
Common name	Chemical name		
Particulate matter	N/A	New	50
		Existing	100
Sulphur dioxide	SO_2	New	500
		Existing	3500
Oxides of nitrogen	NO_x expressed as NO_2	New	750
		Existing	1100

Figures 4.19 and 4.20 compare the emission from the Eskom BFB combustor (without limestone addition) to the AQA 2004 minimum emission standards. The results in both graphs indicate that the NO emissions are lower than the minimum emission for new plants which is 750 mg/Nm^3 and existing plants which is 1100 mg/Nm^3. Emissions of NO_x from FBC have been reported to be lower compared to emissions from the PC boilers [7],[8],

[9], [10]. This has been attributed to low operating temperatures of (800–900°C) compared to those in PC boilers (1300–1700°C). The South African coals tested in FBC by [48] and [49] clearly show that this technology has a potential to produce lower NO emissions than those stipulated in the Air Quality Act. The current South African emission standards (see Table 4.17) do not recognize N_2O as a pollutant that requires an emission limit.

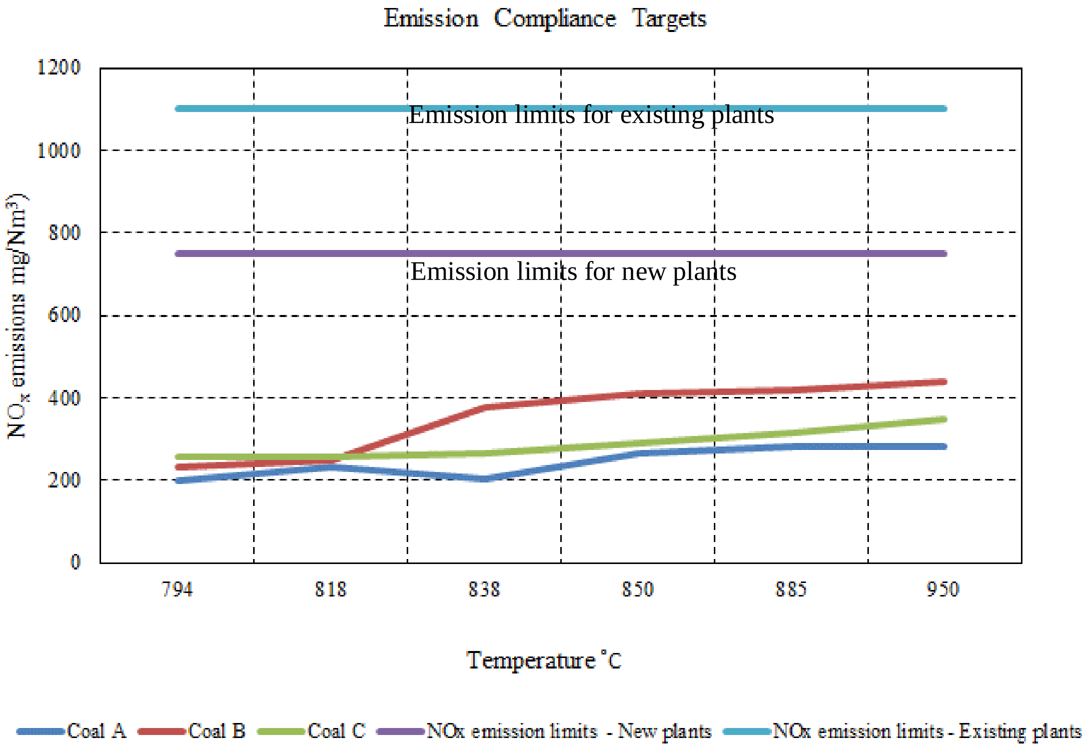


Figure 4.19: BFBR NO_X emission comparison to AQA 2004 emission limits [48]

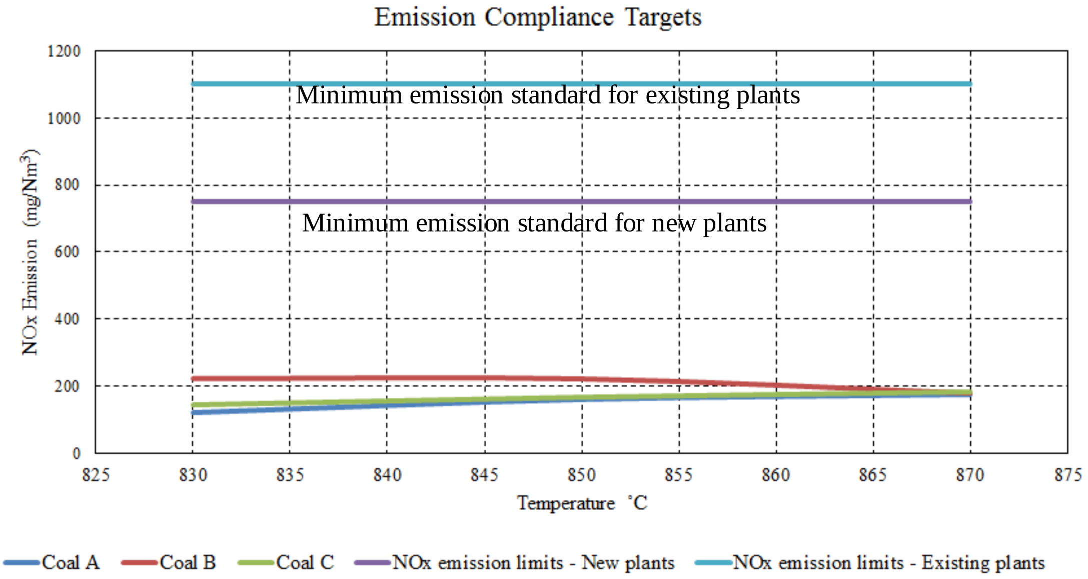


Figure 4.20: BFBR NO_x emission comparison to AQA 2004 emission limits [49]

Chapter 5: Conclusions

The objective of this project was to assess the conversion of coal-N to nitrogen oxides under conditions prevailing in a fluidized-bed combustor. On the basis of conducted analyses and calculations the following conclusions can be drawn:

- Contents of FC in Secunda, Kuthala and Delmas coals and their respective chars are similar. The New Vaal coal and its char have the lowest FC content. The low FC content as well as low HHV of New Vaal coal can be attributed to its high ash yield. Differences in VM contents for tested coals and their chars are small except for Secunda coal and Delmas char. With respect to the ash analysis, the chemical composition of ashes is dominated by SiO_2 and Al_2O_3. All tested coals are inertinite rich with Delmas coal having relatively high vitrinite content. All tested coals were classified as bituminous, with three coal samples falling in the medium rank C range and one in the medium rank D range.
- The TGA combustion tests revealed that Secunda, Kuthala and Delmas coals follow a similar trend during the devolatilization stage. The rate of mass loss in the second region was much higher compared to the mass loss in the first and third region indicating that oxidation reactions are much faster than other processes responsible for mass loss during heating. The TG/DTG curve of the New Vaal coal displayed a different behavior during devolatilization stage compared to other coals. Devolatilization occurred at higher temperatures later in time than in the case of the other three coals. The final mass loss was also low. This was attributed to high content of incombustible material (ash).
- An initial attempt to determine the extent of coal-N and char-N conversion to nitrogen oxides analysis in the TG-MS instrument (at the School of Chemistry, University of the Witwatersrand) failed. Unfortunately, the N-containing species in the flue gas could not be detected. The samples were then analyzed at CSIR in TG-FTIR instrument. This instrument could not detect nitrogen oxides either as nitrogen was used instead of air as requested.
- The analysis of experimental data on the combustion in FB reactors revealed different trends in the conversion of coal-N to nitrogen oxides for different South African coals. The conversion of coal-N to NO decreased with nitrogen content for coals tested by Moodley [48] and Papo [49]. The conversion of coal-N to NO in the case of Papo's

coals was in the range of 4.1–9.9%wt. and was lower than that for coals tested by Moodley, 9.6–14.4%wt.

- An attempt to find a relationship between the conversion of coal-N to NO and CH/N ratio, as suggested by Vermeulen et al. [52], revealed an almost linear correlation between these parameters. However, the trends for two sets of tested coals have opposite directions. For Moodley coals the conversion decreases with increasing CH/N ratio whereas for Papo coals the conversion increases with increasing CH/N ratio. The original correlation proposed by Vermeulen et al. significantly over predicts the conversion of coal-N to NO in the case of South African coals.
- Even better linear correlation was found between the conversion of coal-N to NO and FR. And again, two sets of tested coals show excellent linear trends but in opposite directions.
- As coals tested by Papo and Moodley did not provide clear relationships between nitrogen content, ash content, CH/N ratio, fuel ratio and the conversion of coal-N to nitrogen oxides these factors could not be related to the coals that were tested.
- Looking at the results of the coals tested by Moodley and Papo it can be seen that the CH/N and FR are the most important properties influencing NO emission from fluidized-bed combustion although opposite tendency is observed. Considering that coals tested by Moodley had a higher carbon content compared to those of Papo the conversion of fuel-N to NO_x was expected to be high (looking at the correlation between the conversion of coal-N to NO and CH/N in Figure 4.16) but this was not the case. It is also generally accepted that coals with high fuel ratios and higher nitrogen content produce higher NO_x emissions. Although this was evident from Moodley's coals in order to clarify the effect of coal properties on conversion of coal-N to NO_X, it thus seem particularly important to do this through a wide range of coals types so as to obtain valid conclusions.

- Coals with high ash content yielded a high conversion of coal-N to NO. This finding can be attributed to the potential catalytic activity of some minerals (like iron) in coal such as CaO.

The theoretical flue gas composition calculated for Delmas, Kuthala, New Vaal and Secunda coals assuming that 100% of coal-N is converted to NO indicated very high potential concentrations of NO in the off gas which were higher than the limits set in the emission standards for existing and new plants. However, the combustion tests conducted in FB reactors at Eskom and CUT revealed that less than 15% of coal-N is converted to NO. This means that NO emissions from FB combustion of some South African coals can be lower than current limits (i.e. Stoichiometric combustion calculations and experimental values on NOx emissions show that only a small fraction of coal-N is converted to NOx in FB combustors. Therefore, it might happen that for some SA coals emissions of NOx from FB combustors can be lower than current emission limits).

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