

Low-smoke fuel production via low temperature pyrolysis of lump coal

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DECLARATION

I, Mathys Johannes Kühn, hereby declare that the dissertation entitled: "*Low-smoke fuel production via low temperature pyrolysis of lump coal*", submitted in fulfilment of the requirements for the degree of Master in Chemical Engineering, is my own work except where acknowledged in text, it has been language edited as required and has not been submitted to any other tertiary institution in whole or in part.

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Signed at Potchefstroom on the _____ day of November 2015.

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ABSTRACT

Coal is used on a large scale in the Kwadela Township, Mpumalanga, South Africa with the means to fulfil the basic energy requirements of low-income households. Energy within the coal is utilised via combustion thereof in household appliances, resulting in significant quantities of air pollution being produced. Consequently, a need exists for a fuel that would still provide sufficient energy to the low-income households, whilst fewer pollutants are released into the atmosphere during combustion. Hence, the suggestion to produce low-smoke fuels from raw coal. The aim of this investigation was therefore to produce a technically feasible low-smoke fuel that would serve as a viable alternative to replace coal. Anthracite, which is known to have an inherently low volatile content that may lead to less air pollutants released during combustion, was also investigated as a possible alternative to low-smoke fuel production from coal.

The production of low-smoke fuels can be achieved through thermal decomposition of raw coal. A fundamental understanding of the devolatilisation process requires extensive knowledge regarding the intrinsic properties of the raw coal and its subsequent products formed that include char (low-smoke fuel), water, tar and gas. In an attempt to produce such a low-smoke fuel, a coal sample was acquired from within the Kwadela Township, from which four respective low-smoke fuels were produced: each thermally decomposed at a different temperature. The Kwadela coal sample was found to be a medium rank C bituminous coal rich in inertinite (82vol.% mineral matter free basis), with a high ash content (30.6wt.% air dry basis), typical of South African Highveld seam 4 coals.

Kwadela coal devolatilisation behaviour of three particle size fractions (20mm, 30mm and 40mm) was studied under inert, atmospheric pressure conditions in the North-West University (NWU) Fischer Assay setup at temperatures of 450°C, 550°C, 650°C and 750°C. The effects of temperature and coal particle size on the derived pyrolysis products were evaluated, and it could be concluded that final pyrolysis temperature was the dominating factor controlling both product yield and quality. It was found that char yield decreased, while volatile- and gas yields increased significantly with an increase in temperature. In addition, the effects of particle size was deemed negligible throughout the in depth devolatilisation study. Tar evolution increased until a maximum yield (4-5wt.%) was obtained at temperatures ranging between 550°C and 650°C, after which it decreased slightly, due to possible manifestation of secondary cracking reactions at higher temperatures. The gas species evolved were found to consist primarily of H₂, CO, CO₂ and CH₄, of which CO₂ was the most predominant. Advanced analytical techniques (Simdis, GC-MS/FID, SEC-UV) were employed to analyse the condensable volatile fractions and revealed that the tar consisted mainly of higher-molecular weight olefins and paraffins.

Combustion performance tests of the low-smoke fuels produced, concluded that there are significant differences between the behaviour of coal, anthracite and the four low-smoke fuels produced in this study, from both an emissions and practical performance perspective. The low-smoke fuels investigated consisted of the Kwadela coal having a particle size distribution ranging between 9mm and 60mm, which was devolatilised at the respective temperatures of 450°C, 550°C, 650 °C and 750°C. Emissions investigated included gas emissions (NO_x, CO, CO₂ and SO₂), total suspended particulate matter (TSP) and volatile organic compounds (VOC's), while the time it took to boil 1L of water, fuel ignition time and total space heating provided constituted the tangible practical performance parameters. Combustion efficiencies of the low-smoke fuels decreased with increasing pyrolysis temperature, with anthracite having the highest efficiency. Substantially lower TSP and VOC emissions were released into the atmosphere during combustion of the anthracite and low-smoke fuels in comparison to coal. NO_x and SO₂ gas emissions decreased with an increase in pyrolysis temperature, whereas CO and CO₂ emissions followed similar trends. Hence, the emissions increased up to a maximum at a devolatilisation temperature of 650°C, followed by a decrease, however quantities were still higher than that measured during raw coal combustion. From an emissions perspective the low-smoke fuel produced at 750°C performed the best, however this fuel is not practically viable as water boiled only after one hour in comparison to the 17 minutes observed for the coal and anthracite. The boiling time for low-smoke fuels produced at 450°C and 550°C were relatively acceptable at 30 minutes. All the low-smoke fuels and anthracite, provided space heat for a longer period than that produced by raw coal. Accordingly the anthracite and low-smoke fuel produced at 550°C is the best practically viable fuel, while the benefits thereof include reductions of approximately 80% and 90% less particulate and volatile organic compound emissions respectively. Reductions of 10% and 35% in SO₂ emissions were found for the low-smoke fuel produced at 550°C and the anthracite in comparison to the Kwadela coal.

A techno-economic feasibility study regarding a low-smoke fuel production facility in the Secunda area indicated that such a venture would be economically sound by a slight margin only as a result of the low-smoke fuel produced being sold at a very low price. Due to the market for low-smoke fuels being low-income households, the price thereof should be as low as possible. It would cost approximately R1.50/kg anthracite to acquire and transport the fuel from Komatipoort to Secunda. Low-smoke fuels produced (locally in Secunda) from coal, on the other hand, have the possibility to be sold at approximately R1.00/kg, which increases the viability of low-smoke fuels in comparison to anthracite.

Keywords: Low-smoke fuel, Kwadela Township, pyrolysis, devolatilisation, char, tar, gas, combustion performance tests, TSP, VOC's, community upliftment, job creation, air pollution, techno-economic feasibility

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NOMENCLATURE

ABBREVIATIONS

Acronym	Description
ACE	Associated Chemical Enterprises
ACT	Advance Coal Technology
a.d.	Air dry basis
Afrox	African oxygen
Ant	Anthracite
Ar	Argon
ASTM	American Society for Testing and Materials
BNM	Basa Njengo Magogo
BTX	Benzene, toluene, xylene
C/H	Carbon to hydrogen ratio
CFC	Chlorofluorocarbon
Char-450	Low-smoke fuel (char) produced at 450°C
Char-550	Low-smoke fuel (char) produced at 550°C
Char-650	Low-smoke fuel (char) produced at 650°C
Char-750	Low-smoke fuel (char) produced at 750°C
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
CSIR	Council for Scientific and Industrial Research
CV	Calorific value
D	Direct costs (manufacturing costs)
Da	Dalton
d.a.f	Dry, ash free basis
DCFR	Discounted cash flow rate of return
d.b.	Dry basis
DEAT	Department of Environmental Affairs and Tourism
d.m.m.f.	Dry, mineral matter free basis
EIA	Energy Information Administration
exp	Experimental
FBP	Final boiling point
FC	Fixed carbon
FCI	Fixed capital investment
FID	Flame ionisation detection/detector
GC	Gas chromatograph/chromatography
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography mass spectrometry
GPAD	Gross profit after depreciation
GPBD	Gross profit before depreciation
H ₂	Hydrogen
He	Helium

ABBREVIATIONS (CONTINUED)

Acronym	Description
I	Indirect costs (non-manufacturing costs)
IBP	Initial boiling point
IR	Infrared
IRR	Internal rate of return
I	Indirect costs (non-manufacturing costs)
IBP	Initial boiling point
IR	Infrared
IRR	Internal rate of return
ISO	International Standard Organization
L.O.I	Loss on ignition
LSF-450	Low-smoke fuel (char) produced at 450°C (Same as Char-450)
LSF-550	Low-smoke fuel (char) produced at 550°C (Same as char-550)
LSF-650	Low-smoke fuel (char) produced at 650°C (Same as char-650)
LSF-750	Low-smoke fuel (char) produced at 750°C (Same as char-750)
m.m.m.f.	Moist, mineral matter free basis
m.m.f.	Mineral matter free basis
mol. %	Mol percentage
NL	Normal litres
NMP	N-methyl-2-pyrrolidinone
NO _x	Oxides of nitrogen
NWU	North-West University
O ₃	Tropospheric ozone
O/C	Oxygen to carbon ratio
PAH's	Polycyclic aromatic hydrocarbons
PBP	Payback period
PFD	Process flow diagram
PSD	Particle size diagram
Rr%	reflectance of vitrinite
Rn	Net return
R & D	Research and Development
ROI	Return on investment
SABS	South African bureau of standards
Sasol	South African Coal, Oil and Gas Corporation
SANS	South African National Standard
SEC	Size-exclusion chromatography
SEC-UV	Size-exclusion chromatography ultraviolet fluorescence spectroscopy
Simdis	Simulated distillation
TCI	Total capital investment
TCD	Thermal conductivity detection/detector
TGA	Thermogravimetric analysis
TPC	Total production cost
TSP	Total suspended particulate matter
UV	Ultraviolet

ABBREVIATIONS (CONTINUED)

Acronym	Description
VM	Volatile matter
VOC's	Volatile organic compounds
vol. %	Volume percentage
WABP	Weight average boiling point
WCA	World Coal Association
WCI ^a	World Coal Institute
WCI ^b	Working capital investment
wt. %	Weight percentage
XRD	X-ray diffraction
XRF	X-ray fluorescence

ROMAN SYMBOLS

Symbol	Description	Dimension
C_n	New capital investment	R
$Cost_{year}$	Cost of inflation	R
$Cost_{0,years}$	Initial cost	R
E	Cost of purchased equipment	R
f_n	Multiplying factor for purchased equipment	-
i'	Annual inflation rate	%
j	Number of years for which inflation is charged	-
M	Inherent moisture	g
m_0	Coal sample weight	g
m_1^a	Coal particle weight	g
m_2^a	Submerged coal particle and plunger weight	g
$m_{plunger}$	Submerged plunger weight	g
m_1^b	Water weight from entrainment	g
m_2^b	Tar weight	g
m_3	Char residue weight	g
$m_{rv,i}$	Empty rotary evaporation flask weight	g
$m_{rv,f}$	Rotary evaporation flask weight after toluene removal	g
MW	Molecular weight	g/mol
ρ_p	Coal particle density	kg/m ³
R	Molar gas constant	J/(mol.K)
R_r	Mean random vitrinite reflectance	%
T	Temperature	°C
T_{10}	Temperature at which 10% of tar mass loss	°C
T_{30}	Temperature at which 30% of tar mass loss	°C
T_{50}	Temperature at which 50% of tar mass loss	°C
T_{70}	Temperature at which 70% of tar mass loss	°C
T_{90}	Temperature at which 90% of tar mass loss	°C
V	Volume	m ³
yr	Year	-

CHAPTER 1: INTRODUCTION

This chapter provides the necessary motivation to investigate the possibility of using devolatilised coal as a fuel for low-income households in South Africa as opposed to raw coal. Brief background information concerning the production of low-smoke fuel from coal (coal pyrolysis), and air pollution originating as a result of coal use on a residential level is outlined in Section 1.1. Section 1.2 contains the problem statement, followed by the research objectives presented in Section 1.3. The scope of this investigation is discussed in Section 1.4 and lastly, Section 1.5 states the relevance of the study.

1.1 Background and motivation

Coal is one of the world's most important sources of energy with abundantly available reserves outlasting that of both oil and natural gas at current production rates (WCI, 2009). According to the WCI, (2009), coal has been the fastest growing energy source over the last decade, with South Africa being the fifth largest producer of coal, with the seventh largest coal reserve globally. Due to the abundance of coal in South Africa, it is utilised in many industrial processes such as electricity generation, steel production, cement manufacturing and the production of liquid fuel for the petrochemical industry.

South African townships are characterised by low-income households; this type of housing is further characterised by domestic burning activities when air quality is examined. Domestic combustion of coal has become a major source of urban air pollution in South Africa, contributing to approximately 20% of the total air pollution related to coal use (Palmer Development Consulting, 2004). According to Balmer (2007), and SACRM, (2011), residents in South African townships prefer the use of coal due to the large installed infrastructure enabling the utilisation of coal, and the affordability of coal while serving as a dual utility. Especially during the cold winters, coal is used for both heating and cooking purposes, resulting in extremely high levels of air pollution in the rural settlements. Statistics South Africa indicated that 63% of the households in the rural settlements in the Vaal Triangle areas of Vanderbijlpark, Vereeniging and Sasolburg are reliant on coal (Barnes *et al.*, 2009). It has been reported that domestic burning of coal has become a strong cultural element in township households with several social and familial attributes. A study performed by Hoets, (1994), in the township of Evaton, South Africa, indicated that families valued gathering around their coal-fire heated houses, whilst the use of electricity was preferred for lighting, fridges, ironing and entertainment. In a similar study by Scorgie *et al.*, (2001), in the townships of Embalenhle and Qalabotja, also in South Africa, respondents

showed a preference towards the use of electricity for lighting and entertainment. These households also stated that electricity was very expensive in comparison to coal when cooking, heating water, ironing and space heating was taken into account. Therefore, Hoets, (1994), concluded that the problem of localised air pollution in townships across South Africa, as a result of the domestic burning of coal, may not be solved by electrifying households, as residents only use electricity for activities that consume low amounts of power such as lighting and entertainment (radio and television).

Household burning of coal in South African townships is predominantly performed via a traditional coal stove (Palmer Development Consultants, 2004). According Barnes *et al.*, (2009), Palmer Development Consultants, (2004), and Pemberton-Pigott *et al.*, (2009), incomplete combustion of coal in traditional coal stoves result in the production of air pollutants which are released into the atmosphere. These pollutants include carbon monoxide (CO), oxides of nitrogen (NO_x), methane (CH₄), sulfur dioxide (SO₂), particulate matter (PM) and volatile organic compounds (VOC's). The greenhouse gas, carbon dioxide (CO₂), is also emitted and together with the other carbon based pollutants, emitted as a result of domestic coal combustion, play a significant role in alterations to the global carbon cycle. Engelbrecht *et al.*, (2001), found that D-grade lower quality coal is widely used in low-income urban communities throughout South Africa as a multifunctional fuel for domestic heating and cooking purposes owing to its abundance, availability and affordability. South African D-grade coal typically has a calorific value of less than 25.5MJ/kg a.d. (Steyn, 2009).

A possible solution to the problem of indoor air pollution may be through the use of a low-smoke fuels, produced from coal, which, in essence, is coal that has been devolatilized to a specified extent. Devolatilized coal possibly contains fewer pollutants than raw coal and may still produce the sufficient amount of heat energy required. Therefore, a reduction in air pollution may result if the low-smoke fuel is proven successful. Low-smoke fuel production from coal as feedstock is performed via pyrolysis at relatively low temperatures ranging from about 350°C to 900°C (Bunt and Waanders, 2008). Typical products obtained from coal pyrolysis/devolatilisation include char (a solid residue), water, tar and gas, of which the char is the so called "low-smoke fuel". Tar and gas products from pyrolysis processes have the potential to be recovered, and sold, in order to increase the economic viability of such a process, furthermore it could also be circulated back into the process to provide additional heat-energy (Skodras and Amarantos, 2004).

1.2 Problem statement

From Section 1.1, it is evident that coal is a popular fuel used for cooking and heating purposes in low-income households throughout South Africa, hence an increase in air pollution was observed (Balmer, 2007; Barnes *et al.*, 2011; Engelbrecht *et al.*, 2001; Pemberton-Pigott *et al.*, 2009; Scorgie, 2012). Numerous authors have proposed that indoor coal combustion may possibly be related to adverse health effects of humans living in such conditions (Barnes *et al.*, 2009; Balmer, 2007; Norman *et al.*, 2007; Scorgie *et al.*, 2001).

The coal utilised in this study was obtained in Kwadela Township situated approximately 55 km east of Secunda, South Africa, where the fuel use patterns of the residents in Kwadela were investigated. According to Nova, (2013), approximately 90% of the residents in Kwadela utilise coal with the intention to provide energy for cooking and space heating, which results in air pollution. Consequently, the need for a viable low-smoke fuel to replace coal as a household fuel exists, and although devolatilised coal was used in previous studies, the extent to which the coal was devolatilised is unclear, moreover, the coal was mostly combusted in self-made braziers and umbawulas (Engelbrecht *et al.*, 2001; Le Roux *et al.*, 2004; Scorgie *et al.*, 2001; Surridge *et al.*, 2004). In this study, however, the different degrees of devolatilisation were specified, and the fuels characterised in order to form comparative conclusions. In addition, little is known regarding the potential of the tar and gas products derived from coal pyrolysis on a relatively small scale. Due to the fact that anthracite has a relatively similar volatile content to that of devolatilized coal, the combustion behaviour thereof was also investigated and compared with that of the low-smoke fuels produced from raw coal. This anthracite was acquired locally in Vanderbijlpark from Klipkor Building Materials, however the exact origin thereof is uncertain. Another feasible solution that has been proposed in the past is the “Basa Njengo Magogo” (BNM) or “Top Down” method of ignition, in which the coal is ignited from the top and combusts downwards. Although proved to successfully reduce the amount of air pollution, and is economically sound, it was concluded that the BNM ignition method is difficult to implement within townships across South Africa. A map indicating the location of Kwadela Township in South Africa is provided in Figure 1.1.



Figure 1.1: Map showing location of Kwadela Township.

1.3 Objectives of investigation

The chief aim of this study was to produce a technically viable low-smoke fuel (char), via pyrolysis of large coal particles obtained in Kwadela Township. A secondary aim was to determine the economic and technical potential of pyrolysis by-products consisting of tar and gas components, with the intent to possibly increase the feasibility of the low-smoke fuel implementation. In order to achieve this, the following objectives were identified:

- Characterisation of the parent coal sample obtained from Kwadela, characterisation of a typical South African anthracite, and the low-smoke fuels produced, through chemical, mineralogical and petrographic analyses so as to form a basis with which low-smoke fuels can be compared.
- Determine the effect of final pyrolysis/devolatilisation temperature and coal particle size on the quantity and quality of the resulting products yielded.
- Determine the effect of final pyrolysis temperature on the practical performance and emissions released from combustion of the low-smoke fuels versus that of the raw coal and anthracite.
- Determine the techno-economic feasibility of a typical process in which low-smoke fuel would be produced in comparison to the procurement of anthracite to be sold to low-income communities.

1.4 Scope of investigation

In order to meet the objectives identified for this investigation it was necessary to construct a well-defined scope. A coal sample obtained from Kwadela Township and a typical South African anthracite were prepared and characterised accordingly, however the exact origin of the anthracite was not known. Thermogravimetric analyses (TGA) was performed on the coal particles of sizes 20mm, 30mm and 40mm respectively to determine the degree of devolatilisation at different temperatures. An in depth devolatilisation investigation on large coal particles (20mm, 30mm and 40mm) was performed at multiple temperatures (450°C, 550°C, 650°C and 750°C, as identified from TGA) with the intent to provide a better understanding regarding product yields, quality and behavioural traits of large particles during pyrolysis. The NWU Fischer Assay setup was used for pyrolysis experiments in which the respective products were recovered (Bean, 2013; Roets *et al.*, 2014). Pyrolysis experiments of a fraction of the same coal sample, but with a particle size distribution that ranged between -75mm and +9.5mm, were conducted with the use of a Lenton tube furnace at temperatures identical to that used in the investigation using the NWU Fischer Assay setup. This large particle size range was selected as it is typical of the coal used for cooking and heating purposes by residents in Kwadela Township, and the char products obtained from pyrolysis were labelled as low-smoke fuel (devolatilised coal). Combustion experiments of the raw coal, anthracite and low-smoke fuels were conducted in a coal stove (Union 7), which is commonly found in low-income households of Kwadela. Emissions produced during combustion of the respective fuels were measured, and included the total suspended particulate matter (TSP), volatile organic compounds (VOC's), NO, NO_x, CO, CO₂ and SO₂. Emissions were measured with the intent to indicate whether a reduction in emissions are observed, and several practical parameters were also investigated such as the ignition time, total time heat is provided, time to boil 1L of water and the combustion efficiency of the low-smoke fuels in comparison to the coal and anthracite. The techno-economic feasibility study was based on a selection process in which the low-smoke fuel with the best balance between a reduction in emissions and practical viability was selected as a possible fuel to replace coal. The selection process was followed by the development of a typical pyrolysis process based on the requirements of Kwadela Township, and in which the possibilities of by-products from pyrolysis were evaluated. An alternative solution from an economic point of view is to acquire anthracite in bulk, which is inherently a low-smoke fuel. The price thereof is however, expensive (for a plant situated in the Secunda area) as this study is based on household coal use in the Highveld area. The cost to acquire and transport anthracite from the Nkomati anthracite mine in Komatipoort to Secunda would cost approximately R1.50/kg. The purpose of the techno-economic feasibility study is therefore to determine if low-smoke

fuels produced from coal, acquired locally in Secunda, can be produced at a cost to sell the low-smoke fuel product at a price lower than that of the anthracite.

This dissertation is sub-divided into 7 chapters, the outline of each chapter is briefly discussed below:

- The introduction, as per this chapter (Chapter 1), provides brief background information regarding coal utilisation in South Africa with associated air pollutants. The problem statement, objectives, scope and relevance of the study are also discussed.
- In Chapter 2, a detailed literature survey is provided in which residential coal use in South Africa, air pollution as a result thereof, and information regarding coal pyrolysis are presented.
- Characterisation properties of the coals used in the Fischer Assay investigation are presented in Chapter 3.
- Chapter 4 provides the experimental equipment and methods used throughout the investigation for the numerous experiments.
- The results obtained from the Fischer Assay investigation are evaluated and discussed in Chapter 5.
- Chapter 6 contains a detailed discussion regarding characterisation of the fuels and the results generated during combustion performance tests.
- A techno-economic feasibility study with regards to a process to produce the ideal low-smoke fuel selected is provided in Chapter 7.
- The conclusions and recommendations made based on the experimental findings in this study are provided in Chapter 8.

1.5 Relevance of this study

If the use of low-smoke fuel is proven to be successful in fulfilling the energy requirements, as well as reduce the amount of air pollution resulting from low-income household applications, the possibility exists that, if implemented on a large scale, it may lead to a significant reduction in air pollution. In addition, it might also result in job creation for residents in Kwadela, as the low-smoke fuel production facility would preferably be within close proximity of the township. Hence, the upliftment of low-income communities. The investigation is therefore driven from a strategic rather than an economical perspective.

CHAPTER 2: LITERATURE SURVEY

2.1 Introduction

Chapter 2 contains the literature survey providing the necessary background information in order to form a basis for this study. The nature of coal, and more specifically South African coals, is discussed in Section 2.2. Section 2.3 provides information regarding the numerous uses of coal in South Africa, whereas the use of coal on residential level (in South Africa) is discussed in Section 2.4. Section 2.5 elaborates on the relationship between the domestic use of coal and the air pollution as a result thereof. The process of coal pyrolysis is described in Section 2.6 along with various parameters such as temperature and particle size that affect the pyrolysis of coal. Section 2.7 discusses the definition of a low-smoke fuel, and the method of validating low-smoke fuels produced from coal, while Section 2.8 provides information concerning possible alternative solutions to the problem of air pollution, which is in competition with low-smoke fuels. A summary of the literature presented in this Chapter is included in Section 2.9.

2.2 Coal nature

History stated that the name “coal” is derived from the Old English “col”, which was a type of charcoal used at the time (Speight, 1994). In some areas it was also referred to as “sea” coal due to the fact that coal was occasionally found washed up on beaches, especially in north eastern England. Written records indicate that the mining of coal to any large extent did not commence until after the Middle Ages, however, the use of coal escalated phenomenally during the nineteenth and early twentieth centuries. (Vorres, 1993; Speight, 1994)

Coal is a solid, brittle, combustible, carbonaceous rock that consists mainly of organic components containing carbon, oxygen, hydrogen, nitrogen, sulfur and minerals. The formation of coal takes place through the decomposition and alteration of vegetation as a result of various factors such as compaction, temperature and pressure. Coals from the Gondwana provinces (Southern Africa, India, Australia and South America) have been found to be characteristically rich in minerals, relatively difficult to beneficiate, and highly variable in rank and organic-matter composition (Falcon and Ham, 1988). These characteristics indicate the significant difference between the Carboniferous coals of the northern hemisphere (i.e. Laurasian region) and those of the southern hemisphere (i.e. Gondwana region). Such differences may be attributed to the reigning conditions at the time of coalification in accordance with the subsequent history of geological events in each region. In contrast to the hot and humid coastal Carboniferous coal-forming swamps of the Laurasian region, the

Permian swamps in the south formed under cold (increasing to warm) temperature conditions associated with the diminishing of a massive ice age. Coal bearing sediments accumulated in continental depressions along the margins of glacial valleys, continental lakes and shallow inter-continental seas, while the existence of highly inconsistent topographic and sedimentary environments resulted in numerous degrees of degradation of plant matter (Speight, 1994).

Coal swamps of the northern hemisphere comprised mainly of giant water-loving sub-tropical equatorial types of locopod horsetails and freshly-barked trees, with abundant ferns, whereas, the Gondwana region was characterized by vegetation ranging from sub-arctic through cold-cool temperature deciduous forests to warm savannah-like woodlands with reed-infested swamps. These vegetational differences resulted in various kinds of plant tissues in addition to varying proportions of plant organs which include leaves, pollen and waxy plant excreta. Consequentially, the combined effect of the conditions in the Gondwana region gave rise to inconsistent, largely mineral-rich peat-forming swamps, which developed into widespread, fairly thick coal seams with the passage of time (Falcon and Ham, 1988). Due to the fact that coals in the Gondwana region were never subjected to any great depth of burial, as in the case of the Laurasian coals, Southern African coal seams are relatively shallow, are virtually horizontal in dip, and are therefore generally easier to mine in comparison to their Laurasian counterparts. While the rank of Laurasian coals in the northern hemisphere increased reasonably consistently over time, the coal-bearing strata in the Gondwana provinces remained at generally shallow depths, but have frequently been subjected to intrusions of hot volcanic lavas in vertical, as well as horizontal streams, through the strata. This resulted in the vastly uneven maturation (rank) of coals within very localised areas, portraying yet another major difference between the Gondwana coals and their Laurasian counterparts (Falcon and Ham, 1988; Speight, 1994).

Coal can be classified according to rank, which is directly dependent on the extent of coalification. Therefore, the different ranks consist of lignite, sub bituminous coal, bituminous coal and anthracite, with anthracite having the highest rank. Lignite, often referred to as brown coal with high inherent moisture content (up to 45%), is the lowest rank coal with a calorific value ranging from 9MJ/kg to 17MJ/kg, and is used almost exclusively as fuel for steam generation at power stations. Southern African coals consists mostly of bituminous coal with an inherent moisture content of approximately 3-6%, and is used in power generation, the petroleum industry and steel manufacturing industries (Falcon and Ham, 1988; Everson *et al.*, 2013). Anthracite is a hard, brittle and black lustrous coal containing a high fixed carbon content of approximately 80%.

2.3 Coal in South Africa

The formation of the South African coal deposits occurred during the late Palaeozoic times when an area of the Gondwanaland supercontinent progressively subsided due to the collision of crustal plates. Hence, the Karoo Basin was created with the development of peat swamps on the margins of glaciated lakes and valleys (Baruya *et al.*, 2003). South African coal deposits vary greatly in rank as a result of the frequent igneous (volcanic) intrusions associated with the uplift of the Drakensberg, which supplied the necessary heat and pressure to improve the coal rank. These geographical alterations also contributed to the tendency of South African coals to decrease in rank from northeast to southwest, with the occurrence of anthracite deposits in eastern Mpumalanga and Kwazulu-Natal. Economically recoverable coal reserves in South Africa are estimated to be between 15 and 55 billion tons, where bituminous coal represents roughly 96% of the reserves, whilst metallurgical coal and anthracite each account for approximately 2% (Eberhard, 2011). The area consisting of the Witbank, Highveld and Ermelo coalfields represent the Central Basin, where the majority of South African coal reserves and mines are found.

With South Africa being the 6th largest producer, 5th largest exporter and 4th largest consumer of coal, it is clear that the coal industry is of utmost importance to the country (WCI^a, 2009; Eberhard, 2011; SACRM, 2011). Coal is not just the primary energy source, it also plays a crucial role in South Africa's economy. Approximately 90% of South Africa's electricity, roughly 30% of the liquid fuel, and around 70% of the country's total energy needs are produced from coal, consequently, large amounts of direct and indirect employment result from the industry. In 2011, the coal mining sector alone was accountable for the employment of about 78,600 people producing approximately 245Mt of marketable coal, contributing significantly to the generation of export revenues. On a national level, coal is predominantly used in the generation of electricity by Eskom (70%) and production of liquid fuels by Sasol (20%), while the manufacturing of steel and ferroalloys is responsible for approximately 8%. Lastly, the combined consumption of coal by residential areas and small businesses accounts for 2% (DMR, 2009; Eberhard, 2011). Table 2.1 contains quantities of coal used in South Africa in relation to the various methods of utilization. Coal used in conversion technologies consumes the largest quantity (161.4Mt) of coal by a large margin. Annual consumption of the industry and construction sector is 10.4Mt, while that of household and other consumers is 8.4Mt. From these statistics it is clear that coal is being used in South Africa on a relatively large scale as a household fuel.

Table 2.1: South African Domestic coal use in 2007 (UNdata, 2011)

Domestic uses of coal (2007)	Quantity (Mt)
Conversion to other forms of energy	161.4
Coke ovens	2.6
Gas works	6.7
Thermal power plants	116.4
Other energy-producing plants (eg. Sasol)	35.7
Non-energy uses	2.0
Industry and Construction	10.4
Iron and steel industry	4.0
Other industries and construction	6.3
Households and other consumers	8.4
Households	5.6
Agriculture	0.03
Other consumers	2.8

2.4 Residential coal use in South Africa

Terblanche *et al.*, (1994), defined household energy as the energy consumed by people in their homes for the purposes of cooking, space and water heating, lighting and recreational activities. Household energy sources making up the lower part of the energy ladder are likely to be available at low cost, however, will have low combustion efficiencies and cause high adverse impacts (Terblanche *et al.* 1994). The energy ladder is displayed in Figure 2.1, and shows the cleanliness, efficiency, cost and convenience of the fuels in relation to the prosperity thereof. It is clear that coal is found in the lower section of the energy ladder. According to Terblanche *et al.*, (1994), the energy ladder is not applicable to developing countries as it is regarded to be too simplistic. Households in developing countries do not necessarily move up along the energy ladder as income increases, they rather prefer to increase the security of their customary energy sources (Terblanche *et al.*, 1994). Furthermore, Bruce, (2002), noted that low-income households make use of multiple energy sources, consequently there is no simple linear progression up the energy ladder.

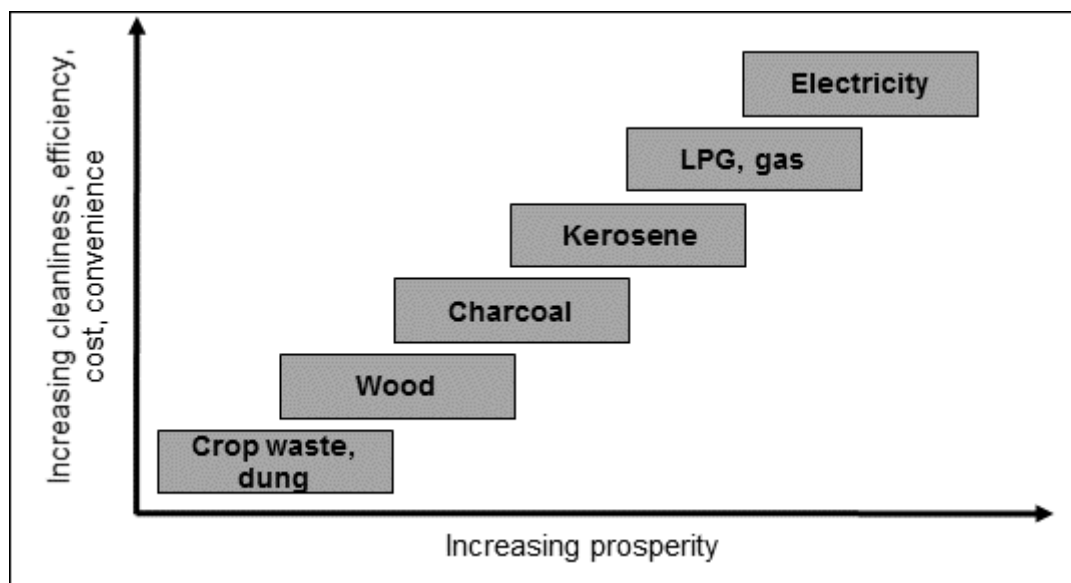


Figure 2.1: Energy ladder adapted from Bruce, (2002).

2.4.1 Fuel use patterns

Coal is a widely used and is the preferred source of energy for numerous low-income households across South Africa, largely owing to its abundance, availability and associated low cost in comparison to other accessible fuels (Engelbrecht, 2000; Balmer, 2007; SACRM, 2011). It was estimated that approximately 1 Mt of coal is being utilized annually in residential areas. Most residents in low-income households have a low and sporadic income, especially those situated inland near coal mines, which greatly affects their selection of energy services in three ways. First and foremost, poor households with low and inconsistent levels of income will be unable to afford costly fuels or even modern end-use appliances like energy efficient and low-pollution stoves. South Africa is a perfect example where households have been electrified through the subsidized electrification programme, only to be disconnected later on due to the inability to pay their electricity bills (SACRM, 2011; SACRM, 2013). Secondly, from a market share view, services and/or products that are obtainable in small discrete quantities will be favoured, forming the reason why LPG is not a preferable fuel as it is only economic when purchased in large volumes. Thirdly, rural villagers do not have the capital strength to meet the expense of modern day energy appliances as it can be prohibitively costly (SACRM, 2011; SACRM, 2013). Coal is used as a dual utility in providing both space heating and the energy required for cooking purposes, thus, one fuel is used in one appliance while simultaneously providing energy for two end-uses. This fact that coal serves as a dual utility is the reason why other energy sources find it difficult to compete with coal (Balmer, 2007; SACRM, 2013).

The public perception concerning the affordability of electrical appliances is also a contributing factor ensuring that coal remains a popular choice of fuel despite the progressive electrification of rural settlements and the low energy efficiency of coal usage (Wenzel, 2006; Howells et al., 2005; Mdluli, 2007; Visagie, 2008). Coal consumption in the inland regions, such as Gauteng, persists for household applications as preference above fuels derived from crude oil (paraffin and LPG) due to the close proximity of coal mines and the associated costs of transporting crude oil to inland refineries (Strydom & Surridge, 2009).

In a study by Mdluli, (2007), the energy consumption patterns of residents in the townships of Doornkop and KwaGuqa were determined by conducting a survey in each township. The number of households included in the study amounted to 100 for each of the two townships. In Doornkop 79% of the households were electrified, whereas 91% of the households had access to electricity, indicating a high incidence of electrification in accordance with the national electrification programme (Spalding-Fecher, 2002). Even though such a large amount of households were electrified, 80% of the electrified households in both Doornkop and KwaGuqa still burnt coal at the time of the study. It was found that multiple fuel types were used by the residents in the two study areas (Mdluli, 2007; Annecke, 1999), which is evident of a non-linear transition of fuel patterns and choices. Table 2.2 specifies an overview of the different fuel sources used by the households in the study area. It should be noted that these values do not add up to a 100% as the residents made use of multiple fuels simultaneously in order to fulfil their energy needs. Therefore the information presented in Table 2.2 is a mere indication of the percentage of people that make use of the respective fuels.

Table 2.2: An overview of the patterns of fuel use in Doornkop and KwaGuqa (Mdluli, 2007).

Purpose	Electricity	LPG	Paraffin	Candles	Coal	Wood	Other
	% people that use fuel						
Lighting	85.0	0.0	3.0	14.0	-	-	-
Cooking	58.5	3.5	42.0	-	32.5	2.0	0.5
Space Heating	24.5	0.5	11.5	-	57.0	2.5	15.5
Heating Water	53.5	1.5	33.0	-	28.5	1.5	0.5

It is clear from Table 2.2 that coal forms a large constituent of the fuels used by the low-income households in both study areas. It should be noted that most of the households do not make use of only one type of fuel and use a combination of multiple fuels. For example: one household makes use of predominantly coal for space heating, but they also use wood and LPG for the purpose of initiating the fire before coal is added (Mdluli, 2007). Coal was predominantly used for space heating and secondly for cooking, with electricity being used

mainly to provide lighting. A study by Röllin *et al.*, (2004), noted a decline in the use of solid fuel after electrification of households in the rural areas of South Africa, however, this study also found a significant persistence in the combustion of coal in township households. Other studies by Hoets (1994), Hoets, (1998), Qase *et al.*, (2000) and Scorgie *et al.*, (2003) confirmed the persistence of household coal combustion, indicating that the electrification of township communities has not been successful in phasing out the domestic burning of coal. From Table 2.2 it can be observed that 32.5%, 57% and 28.5% of the households in the Doornkop and KwaGuqa townships still use coal for cooking, space heating and water heating respectively. The seasonal coal consumption on a monthly basis by the households in the Doornkop and KwaGuqa townships is summarised in Table 2.3.

Table 2.3: Seasonal household consumption of coal in Doornkop and KwaGuqa (Mdluli, 2007).

Average Number of Bags per Month (1 bag = 70 kg)	Doornkop		KwaGuqa	
	Summer	Winter	Summer	Winter
	% households that use coal			
2	8	34	13	12
5	4	22	6	21
8		4		7
11				8
14				1
Van (±500kg)				9
Total	12	60	19	58

From Table 2.3, it can be observed that coal consumption on a monthly basis increased drastically for both of the townships included in the survey (Mdluli, 2007). For Doornkop it was observed that 34% of the inhabitants used 2 bags of coal monthly, whereas 22% used 5 bags per month during the winter months. According to the survey by Mdluli (2007), 21% of the residents in KwaGuqa used 5 bags of coal monthly, while 7% and 8% made use of 8 and 11 bags respectively. Another observation made was that 40% and 42% of the residents in Doornkop and KwaGuqa respectively did not make use of coal as a fuel during the winter months. It was anticipated that households in KwaGuqa burnt more coal on a monthly basis in comparison to those living in Doornkop for which there may be several reasons. One of which may be the fact that the KwaGuqa Township is situated in close proximity of the coal mines enabling the residents to buy their coal supply directly from the coal yards at the mines (where the coal merchants also buy coal). The merchants usually buy a van-load of coal at a time to transport the coal to the relevant township, after which township residents buy coal in smaller amounts from them. Qase *et al.*, (2000), concluded that township households within a distance of 150km from coal mines burn a larger quantity of coal than

those townships located further away. The price of the coal could be another reason for the households in KwaGuqa burning more coal than those in Doornkop, which is visible in Table 2.3. During the winter of 2004 one bag of coal weighing approximately 70 kg in KwaGuqa cost residents R27, whilst the same bag would cost R35 in Doornkop, therefore it was expected that more coal would be bought where it was cheapest (Qase *et al.*, 2000). Lastly, the average ambient temperatures in the two townships differed. According to Mdluli (2007), the average ambient temperatures observed for the KwaGuqa and Doornkop Townships during the winter of 2004 were 16°C and 17.5°C respectively, signifying the statement that more coal is consumed in the colder study site. This is in line with another study by Mathee and von Schirnding, (2003), which specified that township households usually burn more coal in colder conditions. Results from the study by Mdluli, (2007), showed that the monthly coal consumption during winter, in Doornkop, by 57% of the coal-burning households was 140kg, whereas 37% burnt 350kg and 7% burnt 560kg of coal per month respectively. In KwaGuqa, 21%, 36%, 15%, 12%, 14% and 2% of the coal burning households burnt 140kg, 350kg, 500kg, 560kg, 770kg and 980kg of coal monthly respectively during the winter period. During the summer months, 67% and 68% of the coal burning households in Doornkop and KwaGuqa used 140kg of coal.

Another factor influencing the persistent use of coal from a societal point of view is the existence of coal supply networks. Decades of coal burning in townships resulted in the establishment of several of these coal supply networks. These networks form part of the reason it has been difficult to phase out the extensive usage of coal in townships. Results obtained from the survey performed in Doornkop and KwaGuqa indicated that coal merchants sell coal on a door-to-door basis in the townships with their coal yards situated within the townships. A similar observation of coal merchants selling the coal door-to-door in townships was made by Qase *et al.*, (2000), making it easy for residents to buy coal in large quantities without having to travel great distances in the case of coal fields situated far away (like Doornkop). The Energy Research Centre (ERC) found that the main incentive for household burning of coal by poor communities is due to the affordability, as well as availability of coal, which greatly affects people's choices of fuel use (ERC, 2004).

As a result of coal being used for decades in township households across South Africa, a 'coal lifestyle' has been adopted where coal is used to supply the essential energy required for both cooking and space heating. Residents have adapted and learnt to employ coping strategies in order to deal with the problems originating from the burning of coal indoors. It is difficult for the households to immediately switch to an alternative fuel source since coal is what they have known to be a major source of energy over the years. A change in attitude is

therefore necessitated to ensure a switch-over to an alternative 'cleaner' fuel. Rogan *et al.*, (2005), stated that first-hand environmental experiences have a substantial influence on people's perceptions and behaviour regarding fuel use. Despite reports indicating that health impacts from exposure to pollutants caused by the indoor burning of coal, residents taking part in the survey performed by Mdluli, (2007), still preferred to make coal fires during cold winters above any other energy sources (Mdluli, 2007; Spalding-Fecher, 2002).

A study performed by Scorgie *et al.*, (2003), specified that various electrified households continue to use coal to provide space-heating particularly due to its dual functionality as it supports cooking as well as heating. Several respondents taking part in the survey performed by Mdluli, (2007), stated that "Coal is best when it is cold". Therefore, coal fires are still made during the cold winter months in low-income township households. White *et al.*, (1998), performed a questionnaire survey on multiple fuel use patterns by low-income households in the areas of Mzimhlope, Lusaka city, Powa Park and Mandelaville. Results from the survey showed that 7% of the households, included in the study, used coal for cooking, whereas 64% used coal for space-heating. According to White *et al.*, (1998), non-electrified households using coal as fuel for space heating in Powa Park and Mandelaville were 60% and 29% respectively. Non electrified households using both coal and paraffin for space heating amounted to 13% and 29% in Powa Park and Mandelaville.

The School of Geo- and Spatial Sciences of the North West University in association with the Nova Institute, performed a quality of life baseline survey in selected communities surrounding Sasol Secunda (Nova, 2013). The survey was performed during the winter months of 2013. A total of 1100 interviews were conducted with multiple households in the townships of Embalenhle, Emzinoni, Lepogang and Kwadela, with 500 interviews being conducted in Embalenhle and 200 each for the other townships respectively. The survey focused mainly on Kwadela Township. Consequently it was found that electricity is the primary energy carrier in all towns, except Kwadela as 76% of all respondents identified electricity as their main energy source for cooking, while 89% indicated that they use electricity some of the time for cooking. The use of several energy sources however, is still a reality as 43% of the respondents sometimes also use coal for cooking purposes. A total of 68% of the respondents use electricity some of the time for heating, whereas 47% use coal some of the time. The pattern of multiple fuels being used to fulfil the energy needs of low-income township households is thus apparent (Nova, 2013).

2.4.2 Cost of different fuels

Table 2.4 shows the different fuel types generally used by low-income households, and the respective cost of each adapted from SACRM, (2011).

Table 2.4: Fuel price comparison of fuels utilized by low-income households (SACRM, 2011).

Fuel	Cost (R/GJ)
Coal	21
Paraffin	187
Electricity	185
LPG	405

As indicated in Table 2.4, it is clear that coal is the cheapest form of energy (R21/GJ) when compared to paraffin, electricity and LPG. The appliance efficiency associated with each fuel, however, can determine whether the fuel becomes expensive to use (Senatla, 2011). The study by Senatla, (2011), incorporated data from several sources, which include the Community survey of 2007, and energy reports from the cities of Tshwane, Johannesburg and Ekurhuleni. Households using coal pay a different energy price relative to other households using paraffin, electricity and LPG respectively (Cowan, 2005). Table 2.5 serves as an indication of the fuel costs incurred by low-income households for cooking, in Gauteng.

Table 2.5: Cost of fuels used for cooking in low-income households (Senatla, 2011).

Fuel	Energy used (GJ/annum)	Cost to household (Rand)	Energy used for cooking (GJ/annum)	Useful energy service cost (Rand)
Coal	23.3	480.13	1.9	38.41
Paraffin	1.5	274.89	0.6	74.80
Electricity	1.1	200.18	0.7	130.12
LPG	1.0	404.93	0.7	263.20

From Table 2.5, a low-income household using coal for cooking purposes has an annual energy bill of 23.3GJ, and in the cases of paraffin, electricity and LPG the respective annual energy requirements for cooking amounts to 1.5GJ, 1.1GJ, and 1.0GJ per household. Senatla, (2011), carefully integrated the concept of useful energy in determining the energy requirement for the different fuels, and found that coal is the most expensive fuel to cook with, although it appears to be economically sound. Households using coal for cooking pay R280, R205 and R75 more, in comparison to households using electricity, paraffin and LPG respectively, due to the low efficiency of the associated appliances.

The need therefore, exists, for the improvement of coal and paraffin appliances as low-income households may continue using these fuels. Space heating is the other energy requirement of low-income households that has to be fulfilled, especially during cold winters. Table 2.6 presents the costs related to space heating for different fuels used by low-income households in the Gauteng residential area.

Table 2.6: Fuels used for space heating in low-income households (Senatla, 2011).

Fuel	Energy used (GJ/annum)	Cost to household (Rand)	Energy used for space heating (GJ/annum)	Useful energy service cost (Rand)
Coal	24.1	495.15	14.2	292.14
Paraffin	2.3	435.71	1.7	318.07
Electricity	1.4	253.93	1.4	253.93

It can be seen in Table 2.6 that coal is the most expensive fuel. In terms of useful energy required for space heating in low-income households, coal and electricity is approximately 8% and 20% less expensive than paraffin. Nevertheless, the cost per household to buy coal is still approximately 12% and 50% higher than for households using paraffin and electricity separately.

2.5 Air pollution

Coal burning households in townships across South Africa utilize “in shop-bought or makeshift”, home-made technologies that include: braziers, coal stoves and the locally well-known “imbhwawula” also called an “mbawula”, which was adapted from the word “barrel”. (Pemberton-Pigott *et al.*, 2009; Balmer, 2007; Barnes *et al.*, 2009). The coal stoves used are mostly made of cast iron. Approximately 61% of the households in the Kwadela Township in Mpumalanga, situated near Secunda, make use of a typical Union coal stove as displayed in Figure 2.2.



Figure 2.2: Typical coal stoves used in low-income households (Anon, 2014).

Typical coal stoves used in low-income households are usually about 550-620mm in length, 870mm in width and 650mm in height, with a chimney diameter of approximately

150mm. These stoves generally contain two compartments consisting of the firebox and the oven. When a fire is made inside the stove, it results in the stove being heated up, which consequently increases the temperature inside the room into which it is installed, while food may be simultaneously cooked atop the stove.

Coal braziers usually consist of a metal vessel containing a wire mesh or grate in the hole drilled bottom. The holes and mesh aid in air access to the burning coal, inherently reducing cooking time and fuel consumption, while improving the combustion rate (Pemberton-Pigott *et al.*, 2009). Initiation of a fire in a brazier is generally performed via a sequence of layering and lighting of coal and wood kindling upon the wire mesh. After some time, depending on the method of ignition, a burning bed of coke is produced which delivers the necessary energy to cook and provide space heating (SACRM, 2011).

Coal burning appliances such as those used by low income households in townships throughout South Africa are defined by inefficient combustion, which results in the production of high levels of air pollution. The constituents of the air pollutions include particulate matter, volatile hydrocarbons, CO, as well as gases containing sulfur such as SO₂ and H₂S (Pemberton-Pigott *et al.*, 2009). It has been estimated that roughly 65% of ambient air pollution in the Gauteng province, and 48% of the quantifiable particulate emissions in the Johannesburg area, are a result of inefficient coal burning in residential areas (Scorgie *et al.*, 2003; Mathee, 2004). Moreover, mobilisation of fine ash particles by wind in residential areas where coal is used may occur, and exacerbate the local air pollution. Although household coal reliance in South Africa, on a national level, is relatively low (3% for cooking and 7% for space heating), the problem however is highly localised (Statistics South Africa, 2003). The Vaal Triangle area of Vanderbijlpark, Sasolburg and Vereeniging is an example where over 63% of households in rural settlements are reliant on coal as energy source.

Low combustion efficiencies of household coal burning appliances lead to incomplete combustion, and therefore the formation of pollutants such as CO, NO_x, SO₂ and volatile organic compounds. Small amounts of O₃, as well as heavy metals are also released into the atmosphere during combustion (US EPA, 1993). Greenhouse gases CO₂ and CH₄, are also produced through household combustion of coal, and together with all the other pollutants emitted, play a major role in changes to the global carbon cycle (Jaques, 1992). Respirable particulate matter is a very common pollutant resulting from household coal burning activities, and is classified into two categories namely: Particulate matter with a diameter of 10µm or less (PM₁₀), and those with a diameter of 2.5µm or less (PM_{2.5}). In South Africa, particulate matter (PM), and more specifically the PM₁₀ size, is a common pollutant associated with smoke emitted from local burning activities (Engelbrecht *et al.*,

2000). The combustion of poor quality coal contributes to the release of particulate matter into the atmosphere resulting in air pollution Engelbrecht *et al.*, 2000).

Volatile organic compounds consist of volatile, semi-volatile and condensable organic compounds that may be present in the coal, or formed as a result of incomplete combustion (National Academy of Sciences, 1972; National academy of Sciences, 1976). These organic emissions are usually characterised as unburned vapour-phase hydrocarbons, and include alkanes, alkenes, aldehydes, alcohols, and substituted benzenes such as benzene toluene and xylene (National Academy of Sciences, 1972; National academy of Sciences, 1976). Oxides of sulfur formed as products of coal combustion are primarily in the form of SO₂, as the sulfur present in the coal is oxidised through the combustion process (U.S. EPA, 1993). The sulfur contained within the coal is the largest contributor to SO_x emissions emitted during coal combustion (U.S. EPA, 1993). The formation of tropospheric ozone (O₃), commonly known as smog emissions, is encouraged when VOC's and NO_x's react in the atmosphere in the presence of sunlight (Federal Register, 2015). The speed at which smog is formed greatly depends on the type of VOC's present as different VOC's have different levels of reactivity (U.S. EPA, 2015).

Engelbrecht *et al.*, (2000) conducted in depth particulate emission monitoring field campaigns lasting 30 days respectively, in the Qalabotjha Township, and in an adjacent community in Villiers in South Africa during the winter of 1997. Combustion of typical lower quality D-grade coal was compared to low-smoke fuels in the residential neighbourhood. The purpose of the study was to determine the extent of air quality improvement via switching fuels used for household cooking and space heating. The U.S. EPA 24hr (standards over a period of 24h) PM_{2.5} and PM₁₀ National Ambient Air Quality Standards (NAAQS) were 65µg/m³ and 150 µg/m³ respectively at the time of the study (U.S. EPA, 1997). Results concluded that the ambient levels of PM_{2.5} and PM₁₀ in Qalabotjha often exceeded the values provided by the NAAQS during the 30-day field campaign. Lower quality D-grade coal was used during the first 10 sampling days when PM mass concentrations were the highest (93µg/m³ for PM_{2.5} and 110µg/m³ for PM₁₀). During the 11th and 20th days, low-smoke fuels were implemented reducing the PM_{2.5} and PM₁₀ mass concentrations significantly to 56µg/m³ and 62µg/m³ respectively. In the Qalabotjha site, PM_{2.5} constituted more than 85% of PM₁₀ and more than 70% at the similar site in Villiers. The primary constituent, accounting for approximately 50% and 33% of the PM mass at the Qalabotjha and Villiers study sites respectively, was carbonaceous aerosols, containing about 75% organic carbon. Sulfate, nitrate and ammonium constituted secondary aerosols, which were also significant and accounted for approximately 8% to 12% at Qalabotjha and 15% to 20% at the Villiers site

respectively. On average, the sulfate concentrations are three times the corresponding nitrate concentrations Engelbrecht *et al.*, (2000).

The major pollutants resulting from coal combustion on a household level can be summarised as follows:

- Gas emissions: CO, CO₂, NO_x, SO_x,
- Particulate matter (PM_{2.5}, PM₁₀)
- Volatile organic compounds
- Smog (tropospheric ozone)

2.6 Coal pyrolysis

Now that an understanding of the emissions resulting from coal combustion has been obtained, it is clear that the need for a low-smoke (low emission) fuel exists. Therefore, it is necessary to gain further insight into the process through which low-smoke fuels are produced, and will be discussed in the text to follow.

Gasification of coal, or any other solid feedstock, is an incomplete combustion of the feedstock, with the primary goal being to convert the total non-ash fraction of the feedstock to gas, and to produce gases that preserve the heat of combustion value of the feedstock as much as possible (Kandyoti *et al.*, 2006). Gas produced from the feedstock (coal) through gasification can be burned to produce energy, or another possibility is to chemically convert the gas to form other products. In contrast, the gas resulting from a combustion process cannot be further burned to produce energy. Pyrolysis is the thermal decomposition of a chemical compound (such as coal) or a mixture of chemical compounds, and occurs prior to gasification at lower temperatures.

Coal pyrolysis dates back to the 18th century where coal was used in England to replace charcoal, and to produce coke by using various types of ovens (Longwell *et al.*, 1995; Kandyoti *et al.*, 2006). When pyrolyzed in an inert atmosphere, coal typically undergoes a de-polymerization reaction through which a semi-liquid intermediate state, known as a metaplast, is formed (Bunt and Waanders, 2008). The metaplast usually decomposes to form the pyrolysis products, which may be in the form of a volatile component, consisting of condensable tar, gas, and solid char. A coal particle undergoing heating is first subjected to drying (100-350°C), followed by primary (fast) and secondary (slow) pyrolysis, with gasification (in the case of packed beds) being the penultimate region, which normally occurs at temperatures higher than 900°C as well as combustion. The moisture content of the coal is removed during drying, resulting in an endothermic process, after which the dried

coal starts to de-volatilize at a temperature of about 350-400°C where the production of gases, oils and tars are initiated. Primary pyrolysis of coal is often described as the process whereby tars, oils and hydrocarbon gases are produced, along with the formation of the main product, referred to as “semi-char”, at temperatures normally between 400°C and 600°C (Bunt and Waanders, 2008). In the case of applying further heat to a temperature of 700°C, the coal will de-volatilize further with the evolution of mostly hydrogen to form a char product.

Now that the process of coal pyrolysis has been described, the relationship thereof with low-smoke fuels will be discussed. A low-smoke fuel derived from coal can be defined as the solid product formed as a result of coal pyrolysis at temperatures ranging between 400°C and 750°C (Ladner, 1988). The solid residue yielded after pyrolysis is called char/semi-char, and may also be referred to as devolatilised coal. The degree/extent of devolatilisation is dependent on the final temperature to which the coal is devolatilised. This study investigated the production of low-smoke fuels to multiple degrees (temperature variation), as well as the combustion behaviour of the respective low-smoke fuels, in comparison to that of the raw coal sample obtained in Kwadela Township. Further investigation to determine the effects of pyrolysis conditions on the behaviour of the coal being treated was conducted to gain a better understanding of the low-smoke fuel production process.

2.6.1 Effects of pyrolysis temperature and particle size on volatile yield

The final pyrolysis temperature is a significant variable controlling the devolatilization behaviour of coals. In the case of heating a low-to-middle rank bituminous coal at a heating rate of several degrees per minute in inert conditions, the initial products evolving generally consist of water vapour, hydrogen, and light hydrocarbon gases along with some H₂S. It is expected to observe the scission of covalent bonds at temperatures between 310°C and 350°C during the evolution of large volumes of hydrocarbons and other gases (Kandiyoti *et al.*, 2006). A rapid increase in sample weight loss may be observed between 350°C and 400°C along with the initial cracking of tar precursors, leading to the evaporation of the lighter products. At relatively slow heating rates such as 5-10°C/s, the weight loss curve is most likely expected to level out at roughly 550°C. It is a well-known fact that high temperatures favour the devolatilization of coal (Fu *et al.*, 1987; Kandiyoti *et al.*, 2006; Wang *et al.*, 2010; Cui *et al.*, 2006; Bunt and Waanders, 2008).

A study on the pyrolysis behavior of different large coal particle sizes by Yang *et al.*, (2013), indicated that the volatile yield of the different particle sizes has an identical variation trend with the final bed temperature. This is in line with what Hattingh, (2012), found with 5mm and

20mm particles at temperatures of 450°C and 750 °C. Hattingh, (2012), observed that the total volatile matter yield increased with an increase in temperature, irrespective of particle size. This observation corresponds to the findings of numerous authors which include: Kristiansen (1996), Ladner (1988), Hu *et al.*, (2004) and Smith *et al.*, (1994).

According to numerous authors (Kandiyoti *et al.*, 2006; Anthony *et al.*, 1976; Devanathan and Saxena, 1987), volatile yields are likely to diminish with increasing particle size that may be attributed to intra-particle secondary reactions. This is in agreement with the observations of Yang *et al.*, (2013) for 2mm and 6mm particles. However, Yang *et al.*, (2013) also observed that at temperatures above 500°C, that the volatile yields of different particle sizes tend to decrease initially, until a minimum is reached, after which it increased substantially. Seebauer *et al.*, (1997), made a similar observation during a devolatilization study on coal particles of sizes ranging between 0.1mm and 2.0mm. Another study by Suuberg, (1977), stressed the difficulty assessing the effect of particle size on devolatilization at high heating rates on a quantitative basis. Consequently, propagation of heat from the outer surface of the coal particle towards the centre may be limited by the thermal conductivity of the coal (Hattingh, 2012). During the pyrolysis of coal, the volatiles produced have to escape to the outer surface through the pore structure within each individual coal particle. This mitigation of volatiles through the particle may result in the cracking, condensing and polymerizing of the volatiles, along with the deposition of some amounts of carbon. It is expected that these intra-particle secondary reactions might become significant at temperatures higher than 500°C with an increase in particle size (Yang *et al.*, 2013).

2.6.2 Effect of heating rate on pyrolysis products

In the event of coal samples being heated very rapidly, it may occur that the speed of the temperature rise overtakes the normal sequence of pyrolytic events observed in slow pyrolysis. This rapid heating rate (above 100-200°Cs⁻¹) consequently, does not permit each of the pyrolysis steps to complete at or near the same temperature, before moving on (Kandiyoti *et al.*, 2006). Therefore, the sequence of pyrolytic events, is shifted up alongside the temperature scale, and occur in progressively shorter time intervals. At a rapid heating rate of 1000°Cs⁻¹, tar evolution is found between 600°C and 700°C, while tar is produced between 550°C and 600°C when coal samples are heated more slowly at 1°Cs⁻¹.

Tar precursors survive better at faster heating rates, where the rapid build-up of internal pressure forces the tar precursors rapidly through the pore network to exit the coal particles. Fragmentation of coal particles is an important factor influencing the volatile yield as the particle size increases (Yang *et al.*, 2013; Kandiyoti *et al.*, 2006). Particle fragmentation

increases linearly with increasing pyrolysis temperature and particle size, due to higher internal pressure and thermal stress. The extent of fragmentation is thus dependent on the particle properties, particle size and also the pyrolysis temperature. High pyrolysis temperatures tend to create a large temperature gradient inside the coal particle, and therefore high thermal stress. Large particles often possess a fairly large volatile content, resulting in high inner pressures within the particles during pyrolysis. During the formation of cracks and fissures, and the breaking of particles into smaller fragments, the inherent volatiles are immediately released without further intra-particle reactions taking place. The maceral/chemical composition of each individual coal particle may also be a factor contributing to the variation in volatile yields (Stubington and Sumaryono, 1984). The observed increase in volatile yields according to numerous authors may be explained by particle fragmentation, as displayed in Figure 2.3.

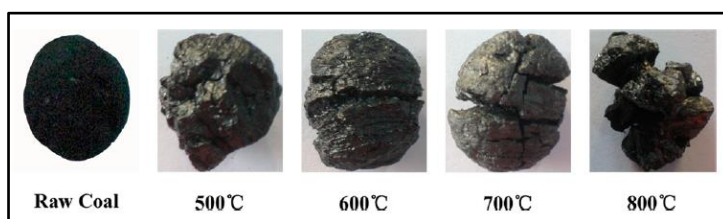


Figure 2.3: Frame photographs of 14 mm size coal particles at different pyrolysis temperatures (Yang *et al.*, 2013).

From Figure 2.3 it is clearly visible that the degree to which large coal particles fragment increases with an increase in temperature. No obvious cracks and fissures can be observed at the lower temperatures (500°C and 600°C) depicted in Figure 2.3 as these only start to develop as the temperature is further increased. Such large particles have the tendency to fragment into smaller pieces at high temperatures, due to the larger inner pressure and thermal stress. The extent of the fragmentation is therefore dependent on the particle size and temperature, as well as the inherent properties of the coal (Yang *et al.*, 2013). The formation of cracks and fissures restricts the intra-particle secondary reactions.

2.6.3 Effects of pyrolysis temperature and particle size on liquid and gas pyrolysis products

The value of coal derived tar as a source of chemicals was comprehended in the 1870's, and up until the end of World War II, the entire organic chemical industry was based on the utilization thereof. However, there are still uses for speciality chemicals such as aromatic hydrocarbons and coal tar pitch. The rising crude oil price is a factor that may contribute to

considering the tar yielded from gasification as an advantage rather than a disadvantage (Bell *et al.*, 2011; Casal *et al.*, 2008).

Tar evolution possibly continues up to about 525-550°C according to Taupitz, (1977), while Yang *et al.*, (2013), observed that tar yields started to level off after 600°C. Tars produced from pyrolysis processes operated at a relatively low temperature of 500°C, were found to contain large amounts of alkyl aromatic material and alkanes. In comparison, tars obtained from high temperature (greater than 1000°C) coking processes, may be distilled to produce light oils, creosote and anthracene oil (Kandiyoti *et al.*, 2006). During distillation of coal tars, some of the substituent alkyl groups may be lost due to the light alkanes and alkyl substitution found in pitches that are limited to predominantly methyl groups. Two significant products derived from coal tars include naphthalene, which is used for the production of phthalic anhydride, and anthracene, the source of anthraquinone. Other important profitable products yielded from coal tars on a smaller scale include hydrocarbons, phenols and N₂ containing compounds. Hydrocarbons produced include fluorene, phenanthrene and pyrene, while phenols are a necessity for the plastic manufacturing industry (Menendez *et al.*, 2000). Tars yielded from coal are of significant importance, because they provide useful information regarding the thermal breakdown characteristics of the coal (Kandiyoti *et al.*, 2006).

The O/C and H/C ratios are important indicators of the liquid product quality, and although conclusions regarding the tar quality cannot be reached from it, the ratio still provides a hint of the tar quality to some extent (Gavalas, 1982; Stubington *et al.*, 1997). Furimsky and Ripmeester, (1983), found that the molecular structure of the chars obtained from devolatilisation move towards a more aromatic nature as the O/C and H/C ratios decreased with increasing final pyrolysis temperature. The behaviour of tars and gases do not follow the general trend of the evolution of the total amount of volatiles during coal pyrolysis. This statement is confirmed by numerous authors from literature that performed pyrolysis experiments on various coals. Hattingh, (2012), investigated four different coals and found that an increase in temperature did not have a significant effect on the respective tar yields for three of the coals, however a substantial decrease in tar yield was observed for the fourth coal.

A study by Yang *et al.*, (2013), investigated four different particle sizes (2mm, 6mm, 10mm and 14mm) of one coal, and found the liquid product yield trends for the 2mm and 6 mm to be similar, with trends of the 10mm and 14mm particles being similar. The liquid yields for the 2mm and 6mm particles seemed to increase initially up to a maximum temperature, after which a rapid decrease in yields was observed. This observation may be as a consequence of the rapid increase in secondary cracking reactions. In contrast, the 10mm and 14mm

particle size fractions displayed an initial decrease in liquid product yield to a minimum temperature, and then increased (Yang *et al.*, 2013). This observation regarding the trend variation agrees well with that of other researchers, which include: Wang *et al.*, (2013); Cui *et al.*, (2006); Xiong *et al.*, (2010).

In general, the gas yield was found to increase with an increase in temperature, as well as particle size, however, the increase in relation to particle size is only minor (Hattingh, 2012; Yang *et al.* 2013). This increased gas yield may be caused by the evolution of small molecular compounds from the secondary decomposition of tar, and the larger quantity of volatiles released at elevated temperatures (Yang *et al.*, 2013). Pyrolysis gas consists mainly of CO, CO₂, and CH₄, with small quantities of H₂ and C_xH_y. The respective yields of CO, CO₂, CH₄, H₂ and C₂H₄ all displayed a relatively similar pattern as a function of temperature. These gases are produced in small quantities during primary decomposition at 500 °C, where the secondary reactions are insignificant, whereas the yields increase profoundly at higher temperatures. This phenomenon suggests that a qualitative analysis of the pyrolysis gas in terms of CO, CO₂, CH₄, H₂ and C₂H₄ serves as a good indicator of the extent of secondary reactions.

2.6.4 Effect of pressure

Conducting pyrolysis experiments under reduced pressures (vacuum) conditions, tend to increase both the volatile and tar yields in comparison to operation at atmospheric pressure (Kandiyoti *et al.*, 2006). It has been found that the increase in tar yield could be as high as 5%, suggesting that the reduced external pressure allows the tar precursors to escape more easily through the pore structure of the coal particles to the surface.

As discussed in this section, the process utilised to produce low-smoke fuel (char) from coal, is known as pyrolysis, and now that an understanding is gained thereof, the process through which low-smoke fuels can be validated will be discussed in the following section.

2.7 Low-smoke fuel validation

In the event of claiming the production of a low-smoke fuel from coal, it is essential to employ a method of validation with the means to prove the success rate of the process utilized. Le Roux *et al.*, (2004), developed a standard comparative combustion test method for evaluating low-smoke fuels. Besides the analyses performed to determine the chemical properties of the char such as the proximate, ultimate and petrographic analyses, multiple other tests have to be included in the evaluation process. Determination of the calorific value, ignition time, boiling time for 1L water and the total solid emissions provide the chief

characteristics of the low-smoke fuel in comparison to the original coal sample used to produce the low-smoke fuel. The fuel ratio, stipulating the amount of fixed carbon in relation to the volatile matter (FC/VM) content is also an important parameter to be tested as it is indicative of the ignitability, how rapidly it will burn out and flame quality of the fuel being tested (Schobert, 2013). Another factor which is to be considered is the “Time to Cooking”, defined as the time progressed since the fire has been lit until cooking can commence (Le Roux, 2009).

Mangena, (2004), performed a comparative study in which devolatilized binderless briquettes produced from coal discards were evaluated according to the criteria developed by Le Roux *et al.*, (2004). These fuels investigated in the study by Le Roux *et al.*, (2004), and Mangena, (2004), consisted of D-grade coal, low volatile coal and anthracite. In addition, the Basa Njengo Magogo or “Top-down” method of ignition was employed to ignite the D-grade coal which is discussed in Section 2.8. The equipment used for the combustion tests consisted of mbawulas as displayed in Figure 2.4. The mbawulas used in the different experiments were identical to minimise experimental errors due to design inequalities. Fires conducted according to the traditional “bottom up method” consisted of firstly putting four separately rolled and twisted double newspaper pages into the mbawula after which one kilogram of wood was added. Approximately 200g fine wood was added initially before addition of the rest of the wood. The coal batch consisting of about 6kg was then added on top of the wood, and lastly placing the mesh and chimney on top of the mbawula before lighting the paper. Iso-kinetic sampling was also initiated at this stage along with the logging of CO, CO₂, and temperature.



Figure 2.4: Combustion tests: Comparison of devolatilized binderless briquettes, raw binderless briquettes and D-grade sized coal (Mangena, 2004).

The iso-kinetic sampling was performed for one hour prior to the water-boiling test, and the chimney was removed once the smoke had subsided. Ash samples collected the following day were milled, homogenised and sent for sulfur analysis (Le Roux, 2009).

Preparation of the Basa Njengo Magogo method firstly consisted of adding 5kg of coal and/or low volatile fuels into the mbawula. Four double newspapers were separately rolled and twisted and placed atop the coal, after which 200g fine wood and 800g “coarse” wood was added in that order. One kilogram of coal was added on top of the coal before introducing the mesh and chimney, and finally lighting of the fire. Iso-kinetic sampling also started at this point and continued for approximately 45 to 60 minutes, however the chimney was removed after only 10 minutes compared to 1 hour for the traditional method. Ash was treated according to the same method employed for the traditional method.

Table 2.7 displays the properties of the fuels evaluated in the combustion tests and it can be observed that the binderless briquettes compared relatively well to the other fuels. For the time taken for boiling 1L of water, the binderless briquettes took the longest, however it outperformed all the fuels, including anthracite, in terms of the total solid/particulate emissions. In context of the method developed by Le Roux *et al.*, (2004), the ignition time, taken as the time when the fuel started to glow, was defined as the time when the first sharp temperature increase could be observed on the temperature profile of a particular fuel (Mangena, 2004). However Mangena, (2004), found the ignition time to vary greatly from one combustion test to the next according to the temperature profiles provided in Figure 2.5.

Table 2.7: Comparison of the performance of devolatilised binderless briquettes with that of the fuels tested in the national study by Le Roux *et al.*, (2004).

Property	Unit	KK binderless devolatilised briquettes	Coal	Anthracite	Low-volatile coal	Basa Njengo Magogo method (Coal)
Calorific value	MJ/kg	24.3	25.8	29.9	29.6	25.0
Volatile matter	% (a.d.)	12.4	23.5	12.0	20.8	23.5
Ignition time	min	34.5	41.0	23.0	33.0	5.4
Boiling time for 1L of water	min:s	08:18	04:50	04:17	05:28	07:12
Total solid emissions (TSP)	mg/MJ	15.7	355.1	20.2	135.0	71.2

Particulate emission measurements were performed by means of iso-kinetic sampling, which is in accordance to the method acknowledged by the Department of Environmental Affairs and Tourism (DEAT), published in CSIR Report No. CE-I-93001, Method 2 (Le Roux *et al.*, 2004). It is evident from Table 2.7 that a significant reduction in particulate emissions was observed for the other fuels in comparison to coal. Gas sampling consisted of measuring oxides of sulfur (SO_x) and expressed in terms of SO_2 as it was assumed that all sulfur lost during combustion is converted to SO_2 . The SO_2 quantity emitted during each combustion test was calculated by determining the difference in sulfur concentration of the fuel prior to the burn, in comparison to the residual SO_2 content of the ash (Le Roux *et al.*, 2004). Le Roux *et al.*, (2004) investigated the SO_2 emissions produced during combustion of coal,

anthracite and devolatilised coal and found the respective SO₂ concentrations to be approximately 287mg/MJ, 1035mg/MJ and 1207mg/MJ. Thus a sharp increase in SO₂ emissions were observed for both the anthracite and devolatilised coal used in the study by Le Roux *et al.*, (2009).

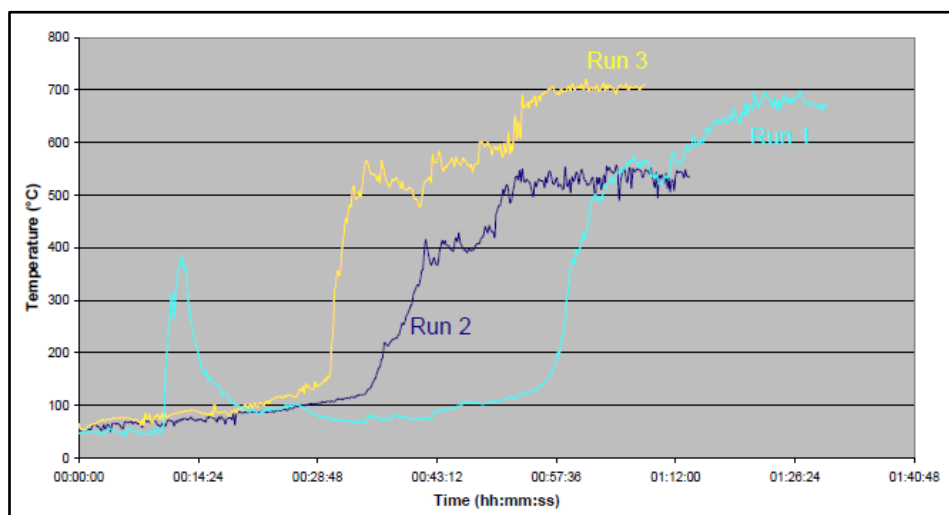


Figure 2.5: Temperature profile devolatilised binderless briquettes (Mangena, 2004).

2.8 Alternative household energy interventions and strategies

In order to curb coal-based indoor and outdoor air pollution, the Department of Minerals and Energy (DME) has embarked on implementing an integrated clean household energy strategy (Van Niekerk and Swanepoel, 2002a). This strategy identified three phases to address residential air pollution which consist of: (1) Popularisation of the Basa Njengo Magogo low-smoke fire lighting method; (2) Successful manufacturing and distribution of an acceptable and affordable low-smoke fuel; and, (3) Promotion of energy efficient housing design that includes proper insulation. Some of the proposed household interventions consist of the following (Palmer Development Consulting, 2004; Van Niekerk and Swanepoel, 2002a):

- Basa Njengo Magogo method
- Vesto stove
- Solar cookers
- Energy efficient housing design

From Figure 2.6 it can be observed that there is a significant difference in the constituent layering of the two fire-lighting methods as described in Section 2.7. The methodology for “top-down” ignition of a fire was promoted by the National Association for Clean Air during the 1980’s under the name of “Scots fire”. Mrs Mashinini of Embalenhle perfected the

methodology during a clean air project undertaken by Nova with Sasol support (Van Niekerk & Swanepoel, 2002a). Consequently, the project was named “Basa Njengo Magogo” in her honour, meaning “make your fire like the old lady”.

2.8.1 Basa Njengo Magogo (BNM) method

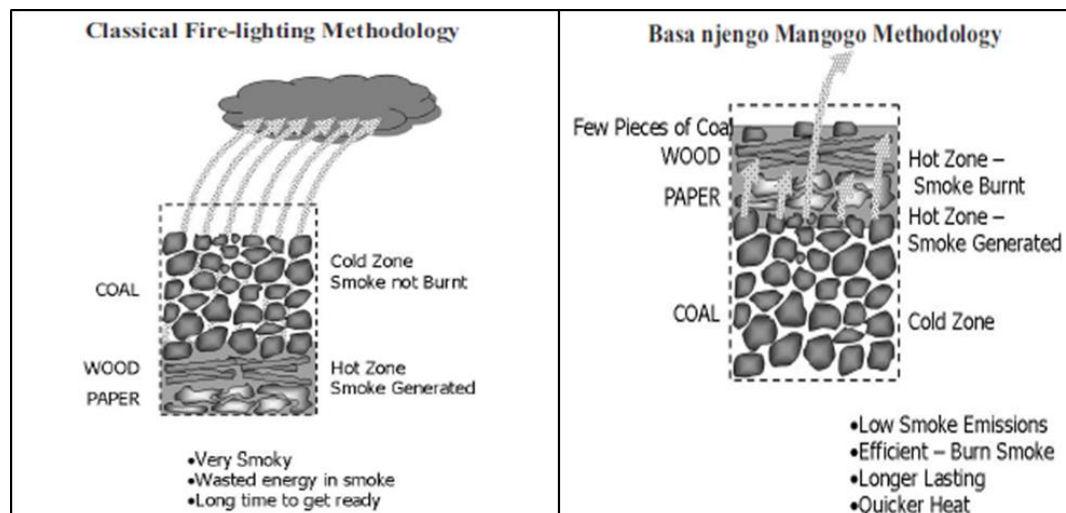


Figure 2.6: Principal differences between the classical fire lighting method (a) and Basa Njengo Magogo method (b), (SurrIDGE et al., 2005)

Despite the purpose of the BNM technology being the reduction of smoke, it is appealing to households because (Palmer Development Consulting, 2004):

- It costs nothing
- Applicable to existing appliances
- Less coal is burnt resulting in lower costs
- Fire's time to cooking is less
- Reduction in air-pollution
- BNM method may be utilized in all coal burning appliances (stoves, mbawulas and even in a heap on the ground)

There however consists one barrier limiting the success of this possible solution on a national level, and that is the difficulty of effectively implementing it (SurrIDGE et al., 2004).

2.8.2 Vesto stoves

New Dawn Engineering are producing different types of upgraded stoves at a price of roughly R430, which is useable for both indoor and outdoor purposes, as it is small and does not emit smoke (Anon, 2014). These stoves make use of biomass types of fuel such as wood, charcoal, twigs, dung and biomass briquettes (Palmer Development Consulting,

2004). One can cook for up to 10 people at a time, while saving 40-66% of fuel depending on how it is used.

2.8.3 *Solar cookers*

A Solar Cooker Field Test was performed by a joint initiative between the governments of South Africa and Germany during the time period of 1996-2003. This program consisted of two phases, with Phase 1 being the global market status quo of solar stoves and social acceptance testing, whilst Phase 2 estimated the market potential in South Africa, the manufacture of stoves, as well as the testing and marketing thereof (Van Niekerk and Swanepoel, 2002). The reason behind implementation of the pilot program in South Africa lies in the possibility to significantly contribute to solving the problem of household energy (Palmer Development Consulting, 2004).

2.8.4 *Energy efficient housing design*

The principle, on which energy efficient housing design is based, is that it is easier to build conservation measures into a house during the initial stages of construction, compared to the case of retrofitting an existing house. Such measures have the potential to significantly reduce fuel usage rates and energy expenditures (Palmer Development Consulting, 2004). Designing an energy efficient house definitely, has advantages as it improves indoor comfort levels and saves energy, whilst indoor air pollution is reduced thereby improving health and safety. Some energy efficient design measures include proper insulation of walls and ceilings, and to design windows and roof overhangs in such a way as to provide shade during summer, and allow sunlight in winter (Palmer Development Consulting, 2004).

2.9 Summary

This chapter provided background information with regard to the use of coal in South Africa (more specifically on a household level), the air pollutants produced as a result of coal combustion, the principles of a typical process in which low-smoke fuels can be produced, and alternatives other than low-smoke fuels to combat air pollution resulting from residential coal use.

Coal is used extensively in South Africa by low-income households with the intent to provide energy for cooking and space heating, hence the combustion thereof results in air pollution. Residents of low-income households do not only use coal as it is affordable, but it is also socially acceptable. The emissions resulting from coal combustion are well-known and include gaseous components (NO_x , CO, CO_2 , SO_2), as well as particulate matter, volatile

organic compounds and smog. Therefore, the need exists for a low-smoke fuel that produces less air pollution during combustion in typical household appliances such as cast iron coal stoves. Research in relation to low-smoke fuels has been conducted in South Africa, however not extensively, and there is a lack regarding the holistic combustion performance (according to emissions and practical aspects) of different fuels that can be used as possible replacements for coal. It is of the utmost importance that a low-smoke fuel must be able to fulfil the energy requirements of low-income households, whilst the amount of air pollution is reduced in comparison to coal being used as fuel. Pyrolysis is a typical process through which low-smoke fuels with different properties can be produced from coal depending on the process conditions. Although low-smoke fuels have been produced via coal devolatilisation/pyrolysis in the past, the extent of thereof was not specified, indicating a discrepancy in the available literature. Alternatives to combat air-pollution resulting from coal use in low-income households across South Africa have been investigated, and some found to be viable options, however, most proved difficult to implement within the low-income residential areas.

CHAPTER 3: COAL PREPARATION AND CHARACTERISATION

This chapter consists of the coal characterisation, and the subsequent sample preparation necessary to prepare the required quantity of coal samples used in this study. Section 3.1 describes the origin of the sample, followed by Section 3.2 in which the sample preparation is discussed. Information regarding the characterisation procedures employed according to which the coal was prepared is provided in Section 3.3. Section 3.4 discussed the results obtained from the various characterisation analyses, with a summary of the findings in this chapter provided in Section 3.5.

3.1 Sample origin

The coal sample investigated in this study is a typical Highveld coal obtained from Kwadela Township, situated approximately 55km east of the town of Secunda. Residents in the township of Kwadela utilize coal as a major fuel source to fulfill their basic household energy needs such as cooking and space heating. There is however, no concrete evidence of the actual origin of the acquired coal sample; therefore a need for extensive characterization existed. The anthracite sample was obtained locally in Vanderbijlpark from Klipkor Building Materials, however characterisation thereof is discussed in Chapter 6 along with that of the low-smoke fuels produced in this study. The exact origin of the anthracite sample is however unknown.

3.2 Sample preparation and analyses standards

A coal sample of approximately 300kg was obtained from a local dealer within Kwadela Township, and air-dried for approximately 4 days to establish equilibrium with the immediate atmosphere. Once air-drying was completed, the bulk coal sample was cone and quartered according to the procedure provided by Wills and Napier-Munn, (2006) with the intent to obtain a sample representative of the 300kg coal sample obtained in Kwadela. The representative sample was crushed in a jaw crusher (Samuel Osborne (SA) LTD, Model: 66YROLL) until a size fraction of <10mm was achieved and division of the sample into smaller representative samples was performed via the use of a rotary splitter (SMC rotary sample splitter. 220 Hz. 50/1 A. serial no.: 09/01/005). The smaller representative samples were stored in sealable bags under N₂ atmosphere and sent to the respective laboratories for analyses.

The largest portion of the characterisation analyses were outsourced to Bureau Veritas South Africa, who conducted the final sample preparation prior to analyses according to ISO

13939-4, (2001). The conventional coal analyses consisted of the proximate analysis, ultimate analysis, calorific value, forms of sulfur, crucible swelling number, ash constituents (XRF), mineralogical (XRD) and petrographic analysis. The purpose of performing XRF and XRD analyses was to gain a better understanding of the coal properties in an attempt to form a more accurate comparison to the coals reported in Pretorius *et al.*, (2002). The standards used by the various institutions according to which the respective analyses were performed are shown in Table 3.1.

Table 3.1: Coal characterisation analyses standards.

Procedure	Standard used	Laboratory
Sample preparation	ISO 13909-4, (2001)	Bureau Veritas South Africa
Moisture content (%)	ISO 11722, (1999)	
Ash content (%)	ISO 1171, (2010)	
Volatile matter content (%)	ISO 562, (2010)	
Total sulfur (%)	ISO 19579, (2006)	
Gross calorific value (MJ/kg)	ISO 1928, (2009)	
Crucible swelling number	ISO 501, (2003) (Not SANAS Accredited)	
Ultimate analysis	ISO 29541, (2010) (Not SANAS Accredited)	
Petrographic analysis	ISO 7404 Part 1-5, (1994)	
Forms of sulfur	ISO 157	NWU
Mineral (XRD)	Rietveld method	
Ash (XRF)	ISO/IEC 17025	Sci-ba Laboratoties and scientific consultants

3.2.1 Size preparation

The remainder of the bulk coal sample was sieved in order to find the particle size fractions shown in Table 3.2.

Table 3.2: Particle size distribution of Kwadela coal.

Particle size (mm)	Fraction (%)
+75	14
-75+53	36
-53+37.5	28
-37.5+26.5	10
-26.5+19	4
-19+13.2	2
-13.2+9.5	1
-9.5	5

The particle size fractions included in this study consisted of the +19mm to -26.5mm, +26.5mm to -37.5mm and +37.5mm to -53mm size fractions, and were classified as 20mm, 30mm and 40mm particles respectively. All the particles investigated were handpicked according to a dimensional basis, where the particles were fitted onto grids constructed of different sizes (20, 30 and 40mm) in order to select particles with similar physical geometric properties within each size fraction.

3.2.2 Density preparation

By increasing the homogeneity of the lump coal samples used during the experimentation process may lead to an increase in similarity of the results obtained. Differences in particle density reflect the variations in chemical composition between the maceral groups of coal particles. The particle density of the selected coal particles was determined using the mercury submersion analysis (as described in Section 3.3.1). In order to increase the homogeneity of the coal samples, it is necessary to use a density cut for each of the particle size fractions in order to conduct experiments on the coal samples having a density within the specified density cut.

3.3 Coal characterisation procedures

3.3.1 Particle density analysis

The mercury submersion technique is a qualitative method used for the determination of the volume and particle density of either single particles or multiple coal particles during a single experiment. Equipment used in the analysis included a laboratory mass balance (Sartorius ED 42025, maximum weight: 4.2kg, accuracy: 0.01g) and double/triple distilled mercury with purities higher than 99.5%. The experimental setup for the mercury submersion analysis is given in Figure 3.1.

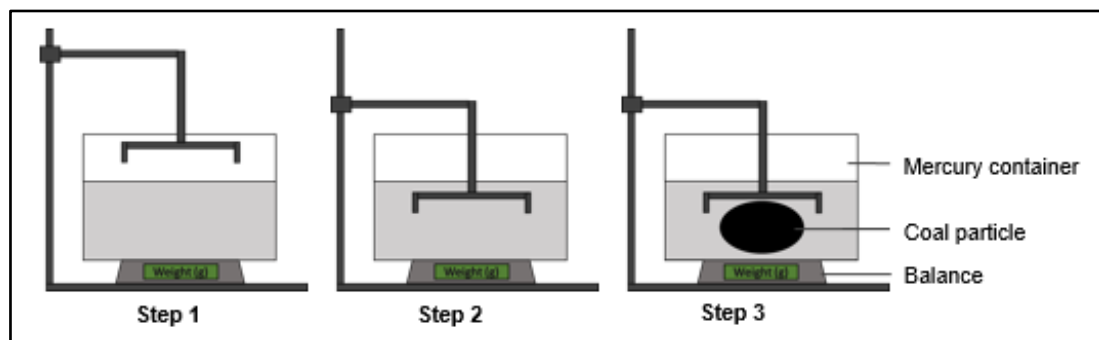


Figure 3.1: Mercury submersion analysis of lump coal particles.

Due to the poisonous nature of mercury, the setup is located inside a ventilation chamber to ensure the removal of any mercury vapour that may form. As seen from Figure 3.1, a stand provides the necessary foundation and is connected to an adjustable arm and plunger, which is used to submerge the coal particle into the mercury. The adjustable arm can be moved up or down and set at the desired height, depending on the level of the mercury inside the container. The mercury container is stationed atop the mass balance where it remains for the duration of the analysis. Different plungers were used for the different particle sizes.

The procedure for performing the mercury submersion test entails the submersion of single large coal particles in mercury. Three weight measurements are required in order to determine the particle density of a coal sample/particle as illustrated in Figure 3.1. It is clear that the three weight measurements required, comprise of the weight of the particle (m_1), weight of the submerged plunger ($m_{plunger}$) and the weight of the submerged particle and plunger (m_2). The particle density can then be calculated from Archimedes' principle according to Equation 3.1 (Van der Merwe, 2010):

$$\rho_p = \left(\frac{m_1}{m_2 - m_{plunger}} \right) \quad \text{Eq 3.1}$$

Each experiment for every particle was repeated in triplicate in order to ensure repeatability regarding the equipment used to determine the particle density.

3.3.2 Final physical preparation

After a density cut of the selected coal particles had been established, the particles to be used in the Fischer Assay experiments have to undergo a final stage of physical preparation. This entailed the drilling of a 3mm hole into the core of each particle (for 30mm and 40mm particles) in order to fit a thermocouple into the particle. For the 20mm size fraction, multiple particles were combined to create coal samples equal in weight forming a coal bed inside the Fischer Assay retorts (reactors). Accordingly, the thermocouple could be placed into the coal bed within the retorts during experimental runs.

3.3.3 Ash analysis (XRF)

The compositional analysis of the ash (XRF) was outsourced to Sci-Ba Laboratories and Scientific Consultants. Sample preparation for the XRF analysis were similar to that described in Section 3.2 as Sci-Ba Laboratories also performed the final preparation before

analysis. The bulk of the ash content in coal is constituted by inorganic compounds, which are intimately mixed with organic compounds in their matrix (Meyers, 1982).

3.3.4 Mineral-matter analysis (XRD)

The mineralogical composition of the Kwadela coal sample was analysed at NWU and preparation of the sample was as follows. A representative sample obtained from the rotary splitter described in Section 3.2 was further reduced in size via a rotary mill (Wenman Williams & Co. (PTY) LTD. 503A). After completion of particle size reduction, the sample was sieved using a Fritsch Analysette (Type 03.5025, no.: 4822) Spartan vibratory sieve-shaker from which a <75µm representative sample was obtained. Lastly, the sample was placed in a sealable bag under argon atmosphere and sent for analysis.

3.3.5 Petrographic analysis

The purpose of conducting a petrographical analysis is to provide deeper insight into the organic composition, maturity and carbon-mineral associations within coal, and may be classified as the microscopic examination of coal (Du Cann, 2010). The petrographic analysis of the coal in this study was outsourced to Bureau Veritas Testing and Inspections South Africa. Petrographic blocks used for the analysis were prepared and polished in accordance with ISO Standard 7404-2, (1985). Accordingly, the sample blocks were subjected to a maceral point-count analysis and vitrinite reflectance measurements to provide information regarding the petrographic composition and rank (maturity) of the coal sample respectively. A 500 point-count technique was employed to quantify the different maceral groups in accordance with the ISO 7404-3, (1994) method. One hundred random reflectance measurements of vitrinite within the coal was conducted according to ISO Standard 7404-5, (1994) after which the coal rank was determined in accordance with ISO Standard 11760-Classification of coals. The reactive inertinite macerals were determined according to the method developed by Smith *et al.*, (1983) for South African inertinite rich coal.

3.4 Results and discussion

3.4.1 Particle density analysis

The particle density range for the different particle size fractions of the Kwadela coal was found to be between 1200kg/m³ and 2000kg/m³. It can be observed from Figure 3.2 that the density distribution trend for each particle size fraction differs by a relatively large extent with respect to the other sizes. The bulk of the 20mm particles analysed, were found to have a

density ranging from 1400kg/m^3 to 1500kg/m^3 , while that of the 30mm particles range between 1600kg/m^3 and 1700kg/m^3 . The 40mm particles, however showed equal amounts for the respective ranges of $1300\text{--}1400\text{kg/m}^3$, $1400\text{--}1500\text{kg/m}^3$, and $1500\text{--}1600\text{kg/m}^3$. Saghafi *et al.*, (2008) found a density range ranging from 1500 to 1900 kg/m^3 for Highveld coals, which is relatively similar to that for the Kwadela coal. It is nevertheless clear that the majority of the coal particles have a particle density between 1400kg/m^3 and 1700kg/m^3 , hence the particles having a density within the range of $1400\text{--}1700\text{kg/m}^3$ qualified to be assessed further in the Fischer Assay investigation to follow in Sections 4 and 5 of this study.

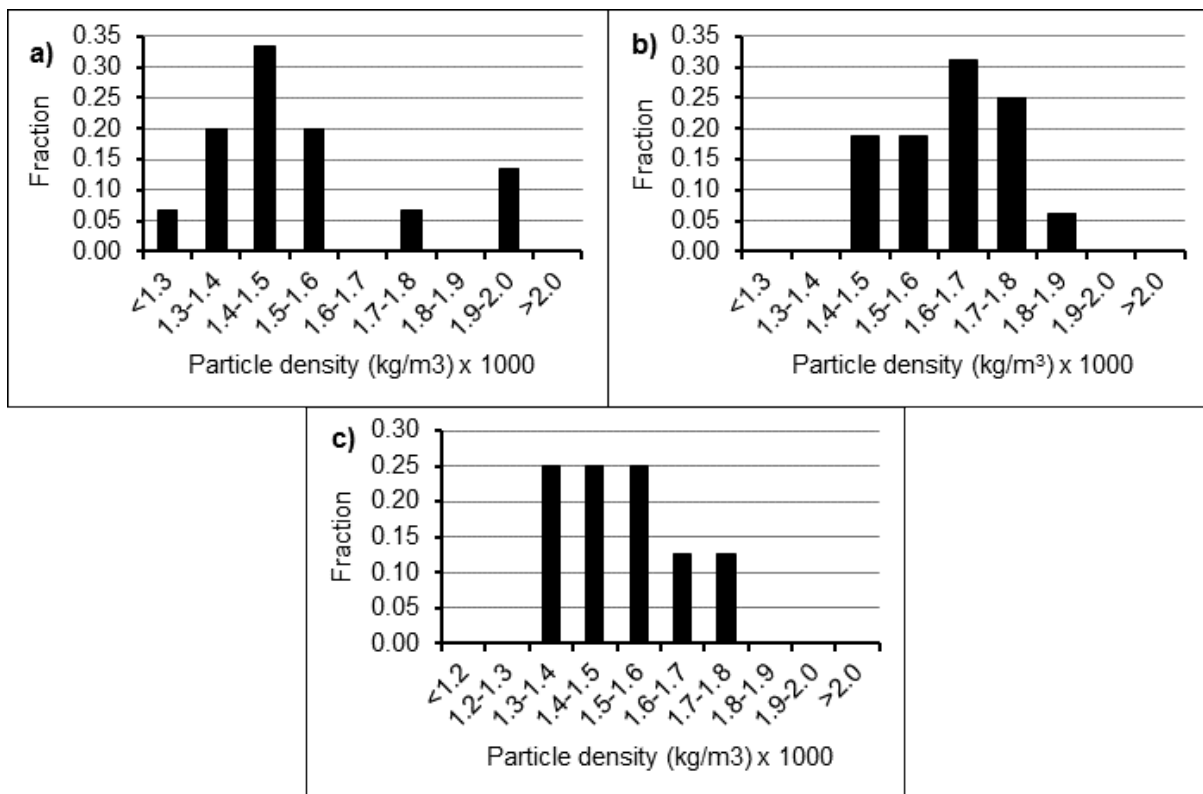


Figure 3.2: Particle density analyses results for a) 20mm, b) 30mm and c) 40mm particle size fractions.

3.4.2 Conventional analyses

The results obtained from the proximate analysis, calorific value, sulfur-, crucible swelling number and ultimate analysis for the Kwadela coal used in this study are summarised in Table 3.3. A representative sample, as well as the individual size fractions to be investigated in the Fischer Assay analysis, were characterised in order to gain in depth knowledge regarding the coal. It is important to note that the exact origin of the Kwadela coal was not known, therefore other coals with similar conventional properties have been identified in order to form a comparison between the coals. Accordingly, the properties of three other

Highveld coals that consist of New Denmark, Brandspruit and Middelbult coals (Pretorius *et al.*, 2002) were identified. The Brandspruit and Middelbult mines are utilised by Sasol Secunda and situated approximately 50km to the west of Kwadela township, whereas the New Denmark mine is located approximately 85km south west in the Standerton area. The respective basis on which the proximate and ultimate analyses were reported are significant and these analyses were performed on raw coal.

All the Kwadela coal samples analysed were characterised as high ash coal with respective ash contents of 30.6wt.%, 23.5wt.%, 24.9wt.%, and 24.3wt.% (air-dry basis), which compares relatively well with that of the New Denmark and Middelbult coals. The ash value for all the coals fall within the high ash value range of 20-40wt.% for Highveld coals as reported by Van Niekerk *et al.*, (2008), Van Dyk *et al.*, (2009) and Everson *et al.*, (2008). In terms of the volatile matter and fixed carbon content, the Brandspruit coal aligns better with the Kwadela coal than the other two Highveld coals. The fixed carbon content of all four coals falls within the range (41-60wt.%) for Highveld coals as reported by Campbell *et al.*, (2010), Hattingh *et al.*, (2011) and Saghafi *et al.*, (2008). Although there are marginal differences in the ash content and volatile matter properties between the representative sample, and the three size fractions obtained from Kwadela, the fuel ratios are relatively constant. The fuel ratio of a coal serves as an indication of the ignitability, flame quality and how rapidly it will burn out, consequently, coal with a low fuel ratio could ignite easily but will burn out relatively quickly and tends to burn with a long, smoky flame. In contrast, a high value of the fuel ratio may signal a coal that is difficult to ignite, while it will burn for a longer period with a short and clean flame. The fuel ratio for all the coals shown in Table 3.3 are within the range for South African bituminous coals (Hattingh *et al.*, 2011). A relatively constant atomic H/C ratio is observed throughout except for the New Denmark coal which has a slightly higher value of 0.67. The 30mm size fraction displays a marginally higher O/C ratio of 0.17 which is indicative of a shift to higher aromaticity (Furimsky & Ripmeester, 1983).

The calorific value of coal is the heat produced through the combustion of a unit quantity of coal via a bomb calorimeter in the presence of oxygen and under specific conditions (ASTM D-121; ASTM D-2015; ASTM D-3286; ISO 1928). The gross calorific value of the Kwadela coal samples varies between 20.5MJ.kg⁻¹ and 22.5MJ.kg⁻¹ and is within the range (15 - 35.4 MJ.kg⁻¹) for other Highveld coals (Hattingh *et al.*, 2011; Wagner and Hlatshwayo, 2005; Kruszewska, 2003). The slightly higher gross calorific values of the 20mm and 40mm Kwadela coal samples may be attributed to their fixed carbon content being higher to some extent in comparison to the other coal samples.

The crucible swelling number is a value that specifies any increase in volume when a coal is heated without restriction. Results from this analysis may be used as an indication of the caking characteristics of the coal when it is burned as a fuel (Speight, 2005). The Kwadela coal has a crucible swelling number of 0 that designates it as a non-caking coal, consistent with results reported for seam 4 Highveld coals (Coetzee *et al.*, 2014).

During the ultimate analysis of coal, the weight percentage of C, S, N and H are determined while the O content is calculated by difference. Results obtained for the ultimate analysis of the Kwadela coal samples are relatively similar to each other and to that of the Brandspruit and Middelbult coals reported by Pretorius *et al.*, (2002), with the sulfur content being the only exception.

The total sulfur value of 0.62wt.% (a.d.b) of the Kwadela coal is well below the limit for South African coals, which is usually less than or equal to 1.0wt.% (Milne, 2004; Thomas, 2002). The higher sulfur content of the other three Highveld coals can possibly be as a result of the higher pyrite contents of these coals. The slight difference in properties of the New Denmark coal in comparison to the other coals may be due to it being located in another area of the Highveld coal field. The sulfur present in coal comprises of different forms of sulfur which are organic and inorganic sulfur (Larsen 1978; Klaus, 1984; Meyers, 1982). Organic sulfur compounds are generally grouped into thiophenes, mercaptans and sulfides, whereas the inorganic constituent comprises of mainly pyritic, sulfate and silicate forms of sulfur. From Table 3.3, it can be observed that organic sulfur is the greatest constituent of the total sulfur, followed by pyritic and sulfatic sulfur respectively. According to these results, the New Denmark, Brandspruit or Middelbult mines may not be the sources of the coal used in Kwadela Township, however further investigation is required in order to confirm the origin of the coal as these three mines are tied to companies that utilise the coal. Another possibility is that the coal could have been bought by the local dealer at another mine in the area.

3.4.3 Ash analysis (XRF)

Only the representative sample obtained from Kwadela was characterised, and not the respective particle size fractions as it was only desired to achieve an understanding of the ash composition for the sample as a whole. Consequently a comparison could be formed between the representative Kwadela coal sample and the other three coals obtained from Pretorius *et al.*, (2002).

Table 3.3: Conventional analyses results of Kwadela coal samples vs. results obtained from Pretorius et al., (2002) for New Denmark, Brandspruit and Middelbult coals.

Analyses		KwaDela- Representative	Kwadela- 20mm	Kwadela- 30mm	Kwadela- 40mm	New Denmark	Brandspruit	Middelbult
Proximate analysis (a.d.)								
Inherent moisture	wt.%	2.1	3.0	2.9	2.8	3.5	4.2	3.9
Ash	wt.%	30.6	23.5	24.9	24.3	29.8	26.9	29.7
Volatile matter (VM)	wt.%	20.4	22.5	25.8	22.1	22.0	21.5	22.2
Fixed Carbon (FC)	wt.%	46.9	51.0	46.4	50.8	44.7	47.4	44.2
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fuel ratio (FC/VM)		2.3	2.3	1.8	2.3	2.0	2.2	2.0
Gross calorific value	MJ.kg ⁻¹	20.5	22.4	21.3	22.5	20.9	20.9	20.2
Total sulfur	wt%	0.62	0.49	0.76	0.52	1.20	1.23	0.92
Forms of sulfur (a.d.)								
Pyritical sulfur	wt.%	0.13	0.08	0.31	0.07	-	-	-
Sulphatic sulfur	wt.%	0.06	0.09	0.14	0.01	-	-	-
Organic sulfur	wt.%	0.43	0.32	0.31	0.44	-	-	-
Total	wt.%	0.62	0.49	0.76	0.52	-	-	-
Crucible swelling number		0	-	-	-	-	-	-
Ultimate analysis (d.a.f.)								
Carbon	wt.%	79.0	78.9	75.8	79.8	80.6	78.6	79.6
Hydrogen	wt.%	4.0	4.1	3.9	4.1	4.5	3.9	4.0
Nitrogen	wt.%	1.9	1.4	1.7	1.8	2.1	2.0	1.9
Oxygen (by difference)	wt.%	14.1	15.0	17.5	13.6	11.1	13.6	13.2
Sulphur	wt.%	0.9	0.7	1.1	0.7	1.8	1.9	1.3
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Atomic H/C ratio		0.61	0.62	0.61	0.62	0.67	0.60	0.60
Atomic O/C ratio		0.13	0.14	0.17	0.13	0.10	0.13	0.12

According to the ash analysis results in Table 3.4, it is clear that all four coals are rich in SiO_2 and Al_2O_3 , although, the New Denmark coal has a slightly larger amount of SiO_2 and also a slightly less amount of Al_2O_3 . The third and fourth most predominant inorganic species present in the coals consisted of CaO and SO_3 . Ash from the Kwadela coal sample (used in this study) has 49.01wt.% and 31.38wt.% SiO_2 and Al_2O_3 respectively. The large quantities of SiO_2 and Al_2O_3 may correspond to large amounts of clay and quartz (kaolinite and quartz) minerals present in the coals, however a XRD analysis of the coal mineral constituents would have to be conducted to confirm the kaolinite and quartz quantities (Spears, 2000). Calcite and dolomite minerals present in the coal influence the amount of CaO detected during the ash analysis. Typical values of CaO quantities reported for Highveld coals range from 4.27wt.% to 8.50wt.% (Matjie *et al.*, 2011; Mishra *et al.*, 2010; Van Dyk *et al.*, 2009). The Middelbult coal contains the largest amount of CaO (6.15wt.%), followed by the Kwadela, Brandspruit and New Denmark coals with 5.70wt.%, 5.29wt.%, and 4.13wt.% respectively. The Kwadela coal also contains a relatively large amount of SO_3 in comparison to the other three Highveld coals. According to the results obtained from the XRF analyses of the respective coals it is unlikely that the Kwadela coal originates from one of the three selected mines as the results differ by relatively great margins.

Table 3.4: XRF-ash analysis results.

Loss on ignition free basis				
Ash species	Kwadela- Representative wt.%	New Denmark wt.%	Brandspruit wt.%	Middelbult wt.%
SiO_2	49.01	59.14	53.33	53.30
TiO_2	1.94	1.29	1.53	1.52
Al_2O_3	31.38	24.02	28.58	26.85
Fe_2O_3	1.24	5.22	3.72	3.52
MnO	0.03	N/D	N/D	N/D
MgO	0.76	1.62	1.65	2.34
CaO	5.70	4.13	5.29	6.15
Na_2O	0.19	0.70	0.42	0.42
K_2O	2.13	1.21	1.22	1.11
P_2O_5	0.92	0.24	0.52	0.80
Cr_2O_3	0.03	N/D	N/D	N/D
SO_3	6.65	2.43	3.73	3.98
Total	100.00	100.00	100.00	100.00

3.4.4 Mineral-matter analysis (XRD)

Mineral XRD analysis is a useful technique used for the identification of mineral crystalline compounds and amorphous carbon forms present in coal (Huggins, 2002; Pinetown *et al.*, 2007; Ward, 2002). Results from the mineral XRD analysis reported in Table 3.5, indicate that 68wt.% of the sample weight is represented by amorphous carbon content, while the mineral matter constitutes the remaining fraction of 32wt.%. Similar to the ash analysis, the mineral matter of only the representative Kwadela coal sample was analysed for mineralogical properties in order to gain a better understanding of the specific minerals present in the coal. The most predominant crystalline mineral species present in the coal are kaolinite (14.1wt.%), dolomite (7.4wt.%), calcite (3.6wt.%) and quartz (4.4wt.%). Previous studies by Hattingh, (2012), and Roets, (2014), found that kaolinite to be the mineral species present in the largest quantity. During coal pyrolysis, kaolinite transforms at temperatures between 450°C and 800°C to form metakaolinite and water (Alpern *et al.*, 1983; Ilić *et al.*, 2010; Prinsloo, 2008; Van Dyk, 2006; Vassilev *et al.*, 2009). Refer to appendix D.2 for a detail discussion regarding the decomposition of kaolinite during devolatilisation.

Table 3.5: XRD mineral analyses results.

Mineral species	Kwadela-Representative wt.%
Amorphous carbon content	68.0
Quartz	4.4
Calcite	3.6
Dolomite	7.4
Kaolinite	14.1
Pyrite	0.5
Micricline	0.4
Goyazite	0.4
Anatase	0.2
Graphite	0.8
Muscovite	0.3
Total	100.1

Refer to Appendix A for a chromatogram of the mineral matter analysis.

3.4.5 Petrographic analysis

Petrographic analysis of the coal in this study was used to determine the random reflectance of vitrinite, as well as the quantities of the respective macerals within the coal. Actual analysis

was performed on the Kwadela coal sample only, whereas results for the other three coals were obtained from Du Cann, (2010). Vitrinite reflectance analysis is a suitable method to establish the rank (degree of maturity) of a specific coal. The reflectance property of vitrinite increases uniformly throughout the coalification process proving to be independent of the vitrinite quantity and coal grade (Du Cann, 2010). The reflectance results are shown in Table 3.6.

Table 3.6: Vitrinite random reflectance and rank classification (adapted from Du Cann, 2010).

Maceral counted	KwaDela (vol.%)	New Denmark (vol.%)	Brandspruit (vol.%)	Middelbult (vol.%)
Mean Rr%	0.83	0.62	0.61	0.64
Rank	Medium rank C	Medium rank C	Medium rank C	Medium rank C

It has been reported by Du Cann, (2010) that the range of the random reflectance of vitrinite for Highveld coals are between 0.57vol.% and 0.80vol.%, which confirms that the New Denmark, Brandspruit and Middelbult coals are of Highveld coal origin. Although the Kwadela coal has a random vitrinite reflectance value of 0.83vol.%, it is very close to the range specified in literature (Campbell *et al.*, 2010; Hattingh *et al.*, 2011; Van Dyk *et al.*, 2009). According to ISO 11760(2005) the Kwadela coal sample analysed was classified as a medium Rank C bituminous coal, which is typical for Highveld coals (Hattingh *et al.*, 2011). A maceral point count analysis was performed on the raw Kwadela coal sample only to determine the organic (maceral) composition of which the results are provided in Table 3.7. Organic compositions for the New Denmark, Brandspruit and Middelbult coals were obtained from Pretorius *et al.*, (2002). From the maceral point count analysis' results in Table 3.7, it is clear that all four coals are classified as inertinite rich coals. This may be expected from Highveld seam 4 coals according to Van Niekerk, (2008). A low liptinite content was observed for all four coals, which is also a typical characteristic of Highveld coals (Everson *et al.*, 2006; Hattingh *et al.*, 2011; Van Niekerk, 2008). Coal from the Middelbult mine displayed a relatively similar maceral composition to that of the Kwadela coal used in this study, whereas the New Denmark and Brandspruit coals compare well.

Table 3.7: Maceral point count comparison (mineral matter free basis) (adapted from Du Cann, 2010).

Mineral matter free basis				
Maceral counted	KwaDela (vol.%)	New Denmark (vol.%)	Brandspruit (vol.%)	Middelbult (vol.%)
Vitrinite	11	29	33	17
Liptinite (Exinite)	7	5	5	3
Inertinite	82	66	62	80
Total	100	100	100	100

It is important to note that the observations made regarding the comparison between the measured coal characteristic properties of the Kwadela coal and the three Highveld coals cannot be validated as the analyses were performed on the Kwadela coal only. All the characteristic properties for the three Highveld coals were obtained from literature (Pretorius *et al.*, 2002) with the purpose of finding a possible location of the Kwadela coal. The differences observed for the petrographic properties of the respective mines may be attributed to the possibility that the mines may be mining in different areas at present, which may differ from the coal reported in Pretorius *et al.*, (2002).

3.5 Summary

The particle size fractions selected to be used for this study consisted of the 20mm, 30mm and 40mm lump coal particles, with the bulk of the particles having a density ranging between 1200kg/m³ and 2000kg/m³. As a result of the heterogeneous nature of large coal particles, a density cut (1400-1700kg/m³) was selected to increase the homogeneity of the coal samples to be used for experiments. Results from the proximate analysis indicated that the Kwadela coal is rich in mineral matter with the ash residue (according to XRF analysis) consisting of mostly SiO₂ and Al₂O₃. Mineral XRD analysis was also indicative of a high mineral content in the coal. Petrographic analysis showed that the Kwadela coal is a medium Rank C, inertinite rich bituminous coal. These results are typical of South African Highveld seam 4 coal when compared to that of known Highveld coals. As Kwadela Township is situated approximately 55km east of Secunda, there is a strong possibility that the source of the coal used by the residents in Kwadela may be from nearby mines in the Highveld coal field.

CHAPTER 4: EXPERIMENTAL EQUIPMENT AND PROCEDURES

4.1 Introduction

Chapter 4 describes the experimental equipment as well as the methodology followed regarding the experiments performed during the progression of this investigation. Results obtained from the thermogravimetric analyses of the Kwadela coal are discussed in Section 4.2. Production of the Fischer Assay products derived from the pyrolysis of lump coal at multiple temperatures is explained in Section 4.3, whereas the determination of the yields of the respective products is discussed in Section 4.4. Analysis of the Fischer tar and char produced during the pyrolysis experiments is included in Section 4.5. Section 4.6 includes a summary of the various analyses conducted on the pyrolysis products. The production of low-smoke fuel from lump coal is discussed in Section 4.7. Lastly, the experimental setup and procedure regarding the combustion performance of the respective fuels investigated is provided in Section 4.8.

4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted with the purpose of identifying the temperatures at which the Fischer Assay investigation, as well as the bulk char preparation, would be conducted. This part of the study was needed prior to combustion testing of the raw coal, produced chars, as well as an anthracite. The Fischer Assay analysis included the investigation of the effects of final pyrolysis temperature and particle size on the pyrolysis product yields (char, water, tar and gas) for the raw coal obtained in Kwadela. The three particle size fractions selected for the thermogravimetric analysis, as well as the Fischer Assay study, consisted of particles with approximate outer diameters of 20mm, 30mm and 40mm respectively. Therefore, these particles were classified as 20mm, 30mm and 40mm particles. TGA's are frequently used in fundamental studies regarding the optimisation of coal conversion technologies as it provides useful knowledge in terms of mass loss with increasing temperature during pyrolysis and gasification (Everson *et al.*, 2006; Fu and Wang, 2001; Hanson *et al.*, 1992; Huang and Watkinson, 1996; Lu and Do, 1992). The experimental setup used is presented in Figure 4.1. A vertical pipe furnace (supplied by Lenton Ltd.) was utilised to provide the necessary heat for thermal decomposition of the large coal particles. The furnace has an inner pipe diameter of 50mm, as the furnace was designed to handle particle size fractions of up to 40mm. A 1mm, K-type thermocouple was used to measure the temperature of the reaction zone within the pipe of the furnace. Heating rates of up to 25°C/min are possible, with 1500°C being the maximum achievable

temperature. N_2 gas flow was used to provide the inert atmosphere required for pyrolysis, and was controlled with a Brooks model 0254 mass flow controller. Sample mass is continuously measured via a Radwag PS 750/C/2 balance. A sample holder consisting of an aluminium tripod and quartz stand contains the coal sample analysed.

The TG analyses, in this instance, was used with the means to provide information regarding the mass loss of the three respective particle sizes up to a temperature of 900°C. The selection of 900°C was motivated by the previous devolatilisation studies that employed temperatures within a similar range (Coetzee, 2011; Roets, 2014). Sample mass and the reaction zone temperature were recorded as pyrolysis experiments progressed from room temperature up to 900°C.

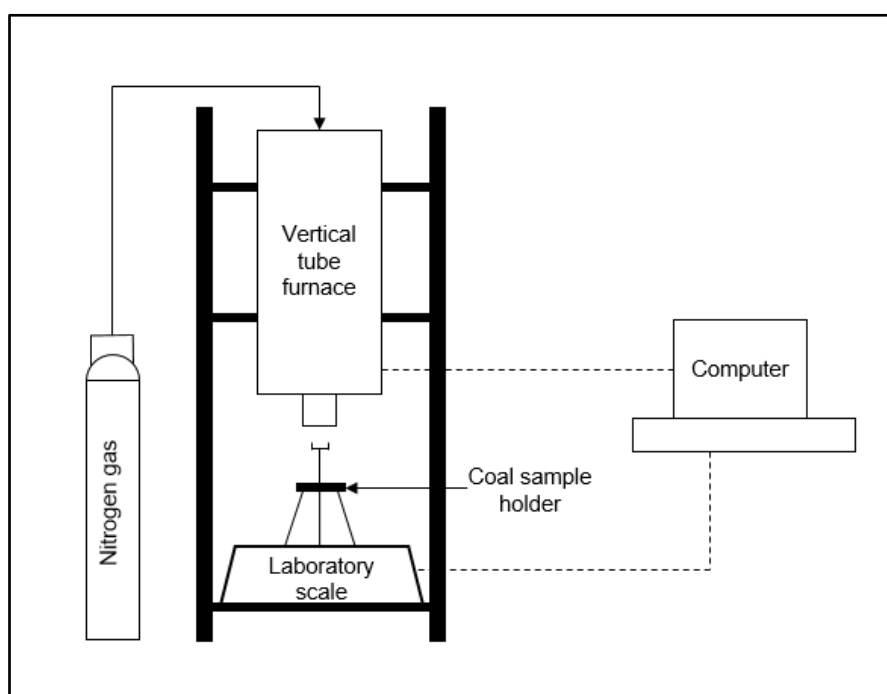


Figure 4.1: Schematic representation of TGA experimental setup.

At the start of each experiment, the coal sample was placed into the sample holder, which was placed on top of the balance. N_2 flow was injected into the reactor, and the software recording the temperature and mass was initiated. Once the furnace was lowered over the sample holder, the heating programme commenced from room temperature up to 900°C, at which the temperature was kept constant for 30minutes after which the furnace was allowed cooled down. Table 4.1 summarizes the conditions employed during TGA operation.

Table 4.1: TGA operating conditions.

Parameter/Condition	Value
Particle size (mm)	20, 30, 40
Maximum temperature (°C)	900
Reactor pressure	Atmospheric (~87 kPa)
Nitrogen flow (NL/min)	2

4.3 Pyrolysis experiments

The NWU Fischer Assay setup was used with the purpose of capturing the products formed during the devolatilisation/pyrolysis of coal, which consists of water, tar, char residue and gas. In this study the effect of particle size, and temperature, on pyrolysis product yields and compositions will be determined. The method used was based on the ISO 647 standard, although there are a few differences.

Stainless steel retorts were used instead of aluminum retorts, and the Fischer products were prepared at temperatures of 450°C, 550°C, 650°C and 750°C, which differs from the single temperature of 520°C as specified by ISO 647. However, repeatability of the NWU Fischer Assay apparatus was performed at 520°C and 750°C respectively. Selection of the temperatures employed in this study are within the temperature range of that studied by previous authors who also investigated the effects of particle size, and final temperature, on the products of pyrolysis (Hattingh, 2012; Yang *et al.*, 2013). The sample mass used in this study was 100g, which also differs from the 50g of powdered coal used in ISO 647 standard, and was due to the mass of the large particle size fraction (40mm diameter) being approximately 100g. Particle size fractions used in this study consisted of particles with diameters of approximately 20mm, 30mm and 40mm respectively.

4.3.1 NWU Fischer Assay setup

Production of pyrolysis products was performed using the modified NWU Fischer Assay setup (Roets *et al.*, 2014; Bean, 2013). This setup contains two modified stainless steel retorts, which were manufactured according to the ISO 647 dimensions, and has the ability to capture the gas, condensable volatiles and tar fractions originating from pyrolysis in order to quantify these products. The experimental equipment constituting the NWU Fischer Assay setup includes an oven, two retorts and various flasks and gas bags. An automatic temperature control system is incorporated into the oven design which employs pre-programmed heating curves.

There is, however, a definite temperature gradient between the chamber temperature of the oven and the temperature within the retorts containing the coal samples. The Fischer Assay setup used is displayed in Figure 4.2.

The Fischer oven, built by Lenton, is specified with a 22amp–48kW rating over 220V. The modified NWU Fischer Assay setup as specified by Roets *et al.*, (2014), is fitted with a TOHO TTM-P4 temperature controller, fulfilling the purpose of controlling the oven temperature via the thermocouple inside the chamber of the oven. The system was further modified by incorporating one additional thermocouple in each retort with the purpose of measuring the inside-bed temperature of both retorts. Furthermore, five Shinko DCL-33A rail mounting type indicating controllers connected to K-type thermocouples combined with a Shinko LMD-100 Console/Data Logger were also installed.

This modification enabled the Fischer Assay setup to store the respective temperature profiles of the chamber as well as the bed and inside-wall temperature of both retorts, consequently the heating rate inside the retorts could be accurately determined and monitored throughout the experimental stage.

The heat curve followed by the oven is based on the fact that a heating rate ranging between 8.7°C/min and 9.1°C/min had to be achieved in this study of lump coal pyrolysis at various temperatures, since it is known that lump coal pyrolysis in fixed-bed gasifiers occurs at approximately similar heating rates (Kandiyoti *et al.*, 2006; Yaw *et al.*, 1980).

The two stainless steel retorts inside the oven were linked via two stainless steel adapters to two 250ml short neck round bottomed Büchner flasks, each provided with a rubber stopper. These two Büchner flasks, containing a solvent, serve as receivers for the condensable volatiles, and are placed inside a single 25L bucket filled with ice (cold bath), to improve the condensation of volatiles, whilst the gas undergoes the first stage of washing. Two additional gas washing bottles with a tapered lid, as supplied by Rochelle Glass, was included as a second and third stage to ensure condensation of as much of the liquid products contained in the gas fraction as possible.

Toluene, and dichloromethane solvents (analytical standard purity $\geq 99.5\%$ supplied by ACE chemicals), were respectively used for quantitative and qualitative experiments. Dichloromethane was utilised as solvent for the reason being that minor quantities of the light tar fractions may be lost during vacuum distillation in the procedure to separate toluene from the tar fraction in order to obtain the tar yield. Each gas washing stage contained approximately 35mL of the solvent. The last receiver in the gas washing system was

connected to a 10L Tedlar gas sampling bag (for quantitative experiments only) supplied by Sigma-Aldrich. After the different Fischer products were obtained from quantitative experiments, the final gas composition was analysed via GC-analysis, whilst the Dean Stark azeotropic distillation and rotary evaporation were used to further separate the moisture and tar fractions. Qualitative experiments entailed the use of simple solvent extraction using a separation funnel.

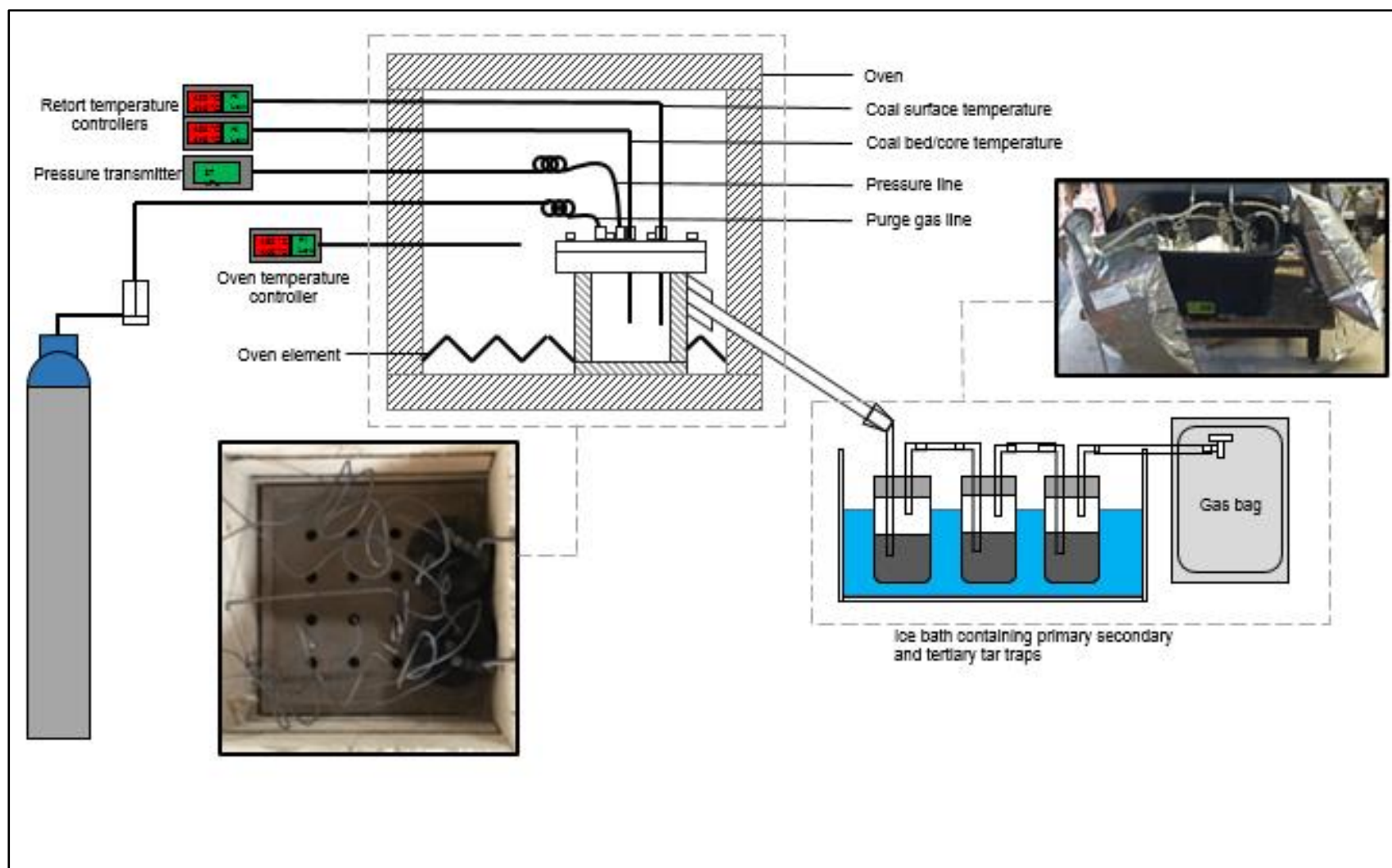


Figure 4.2: NWU Fischer Assay experimental setup.

4.3.2 Operating procedure

The variables and experimental conditions of the experiments conducted with the Fischer Assay apparatus are listed in Table 4.2.

Table 4.2: Fischer Assay experimental details.

Variable	Range specification or composition
Coal feedstock	Kwadela Township coal
Sample weight (g)	100 ± 0.1
Coal particle size fractions (mm)	20, 30, 40
Operating temperatures (°C)	450, 550, 650, 750 (non-isothermal)
Heating rate (°C/min)	8.7 - 9.1
Holding time (min)	10
Operating pressure	Atmospheric (± 87kPa)
Atmosphere	Ar

Each of the two stainless steel retorts were filled with 100g of the sized coal sample to the nearest 0.1g. The retort lids and bolts were smeared with Spanjaard High Temperature copper compound which prevents the loss of volatiles and the bolts from seizing. The retorts, with their respective thermocouples inserted, were then set in place inside the oven. Solvent addition into the receiver flasks and gas wash bottles was completed and the flasks were sealed, linked to the individual retorts, the ice bath filled with ice after which the system was purged for 10minutes with Argon (Ar) at a flow rate of 10NL/min (Roets *et al.*, 2014). Before the oven was started for each experiment, it was imperative to confirm that the correct heat programme was selected to achieve the desired heating rate inside the retorts. Once purging was completed, the 10L Tedlar gas sampling bags were connected and the memory card inserted into the Shinko LMD-100 Console/Data logger. Consequently data logging was initiated and the oven switched on.

The duration of one run varies between 70min and 115min for experiments concluded at 450°C and 750°C respectively. Importantly, the temperatures inside the two retorts should be noted relative to that of the chamber, as there is a significant temperature lag during the first 30 minutes of the experiments.

After the run was completed it was left to cool down to below 100°C, after which the char residue contained inside the retorts was removed, the weight thereof determined and recorded. A Radwag PS 750/C/2 balance was used to determine all the weights of the chars. The pyrolysis products obtained for the quantitative and qualitative experiments were processed and analysed accordingly as specified in Sections 4.3 and 4.4. The temperature profile of each experiment was recorded to determine if the specified heating rate was achieved.

4.3.3 Experimental plan

Experiments conducted with the Fischer Assay apparatus were classified into three categories consisting of the *Repeatability experiments* (Section 4.3.3.1) and *Quantitative and Qualitative experiments*, which are described in Section 4.3.3.2.

4.3.3.1 Repeatability experiments

It is of the utmost importance to determine if an experimental setup is performing as expected, therefore two sets of experiments were identified according to literature, as well as TGA experiments conducted in this study (Refer to Chapter 5, Section 5.2 for a detailed discussion of TGA results). According to Ladner (1988), the production of low-smoke fuels range between 400°C and 900°C. However, 750°C was selected as the highest temperature to be investigated as the evolution of mainly hydrogen occurs at higher temperatures (Bunt and Waanders, 2008). In addition, the average degree of devolatilisation for the three particle size fractions was approximately 70% at 750°C, according to the TG analyses thereof. A temperature of 520°C is specified by the ISO 647 standard, which was the second temperature at which repeatability experiments were performed. The three particle size fractions investigated consisted of 20mm, 30mm and 40mm particles. The 30mm particle fraction was selected as the size to be used in the repeatability experiments since it is the middle size fraction investigated in this study. Six repeats were performed at each of the two respective temperatures, after which it was proven that the experimental setup and procedure was reproducible, and therefore quantitative and qualitative experiments could commence. The repeatability of these experiments was based on the yields of the different pyrolysis products obtained, that included the respective weight percentages of the char, water, tar and gas. The weight of the gas was determined through combining the volumes obtained from the water submersion technique and the molar compositions as determined via GC analysis of the gas as described in Section 4.4.4. Results obtained in the reproducibility experiments performed on the 30mm coal particles at temperatures consisting of 520°C and 750°C are reported in Table 4.3.

Table 4.3: Pyrolysis product yields obtained for repeatability experiments (as determined basis).

Product	Char-520 (wt.%)	Char-750 (wt.%)
Char	87.9 ± 0.4	79.8 ± 1.1
Water	6.4 ± 1.2	11.1 ± 0.8
Tar	3.9 ± 1.0	2.3 ± 0.5
Gas	1.8 ± 0.2	6.8 ± 0.8

From Table 4.3, it can be observed that the experimental error on repeatability (80% confidence interval) for the tar fractions was proportionally the highest in comparison to the other products,

i.e. 26% at 520°C and 22% at 750°C. Although the errors obtained are relatively large, it is still acceptable if the uncertainty in large particle (30mm particle size fraction) homogeneity is taken into consideration. Therefore a 80% confidence interval was selected to determine the experimental errors on repeatability throughout this investigation.

4.3.3.2 Quantitative and Qualitative experiments

Two sets of pyrolysis experiments via the Fischer Assay apparatus were conducted, with the purpose of quantifying the respective products with the first set, whereas the second (qualitative) set was imperative with regards to the advanced tar analyses (Simdis, GC-MS/FID, SEC-UV). The advanced tar analyses are discussed in Section 4.4 of this chapter.

The procedure used during quantitative experimentation was identical to that of the repeatability experiments. During qualitative experiments, only the char, tar and water fractions resulting from pyrolysis were obtained, however the amount of experiments conducted were identical to that of the quantitative experiments. The only notable differences between the two methods were that dichloromethane was used as solvent and that the gas fraction was not captured and analysed for the qualitative experiments. Table 4.4 lists the number of repeats conducted for every particle size at the respective temperatures for quantitative Fischer Assay investigation.

Table 4.4: Experimental plan for quantitative Fischer Assay investigation.

Particle size (mm)	Temperature (°C)	Repeats
20	450	4
20	550	4
20	650	4
20	750	4
30	450	4
30	550	4
30	650	4
30	750	4
40	450	4
40	550	4
40	650	4
40	750	4
Total		48

From Table 4.4, it can be observed that two repeats were conducted for each particle size at the corresponding temperatures, which amounts to 24 experiments for the quantitative and qualitative experiments respectively. Thus, a total of 48 experiments were performed to determine the resulting yields of the pyrolysis products. With regards to the pyrolysis experiments performed to produce tar for the advanced (qualitative) analyses thereof: a total of

24 experiments (2 repeats for each particle size at the respective temperatures) were conducted.

4.3.4 Operating conditions

4.3.4.1 Final operating temperature, particle size, heating rate and heating curve

The temperatures at which the pyrolysis experiments are conducted in this study are within the range of both primary and secondary pyrolysis at which low-smoke fuels are produced, and include the temperature range of 450°C, 550°C, 650°C and 750°C (Ladner, 1988). The selection of these operating temperatures is motivated by previous research, as well as by thermogravimetric analysis performed on the coal used in this study, as specified in Chapter 5, Section 5.2. According to Bunt and Waanders, (2008), primary pyrolysis normally occurs between 400°C and 600°C, with secondary pyrolysis ranging between 600°C and 900°C (Ladner, 1988). As described in Chapter 2, Section 2.6, pyrolysis is the de-compositional process of coal where tars, oils and hydrocarbon gases are produced along with the formation of the main product, referred to as “semi-char”. At temperatures above 700°C coal devolatilises further, mainly with the evolution of hydrogen (Bunt and Waanders, 2008).

The respective heating curves followed by the NWU Fischer Assay oven during the devolatilisation study are presented in Figure 4.3. The heating curves used during repeatability experiments conducted with 30mm particles at 520°C and 750°C are displayed in Figure 4.3a. The ISO 647 heating profile is also included in Figure 4.3a and it is visible that there is an approximate 20 minute difference at which the final pyrolysis temperature was reached between the ISO 647 standard and the heating curve used in this study for 520°C. However, a constant heating rate ranging from 8.5°C/min to 9°C/min was achieved between approximately 200°C and the final pyrolysis temperature for all experiments, irrespective of the final temperature. The delay in heating of the core temperatures was a result of the thick stainless steel walls of the Fischer Assay retorts used in this study. It can be observed that the heating profiles for the 20mm and 30mm particles, Figure 4.3b and Figure 4.3c, were relatively similar, and although the trends for the 40mm particles, Figure 4.3d, were almost identical to that of the smaller particles, the 40mm size fraction heated up slightly slower. This observation may be as a result of the differences in heat transfer properties of the respective coal particles, therefore it was necessary to individually evaluate the heating profiles at the selected temperatures for the three size fractions investigated. Large particles have less reactive surface area available and therefore the heat propagates slower through each particle to its core. The heterogeneity of the large particles used in this study may also have contributed to the anomalies in the heating process.

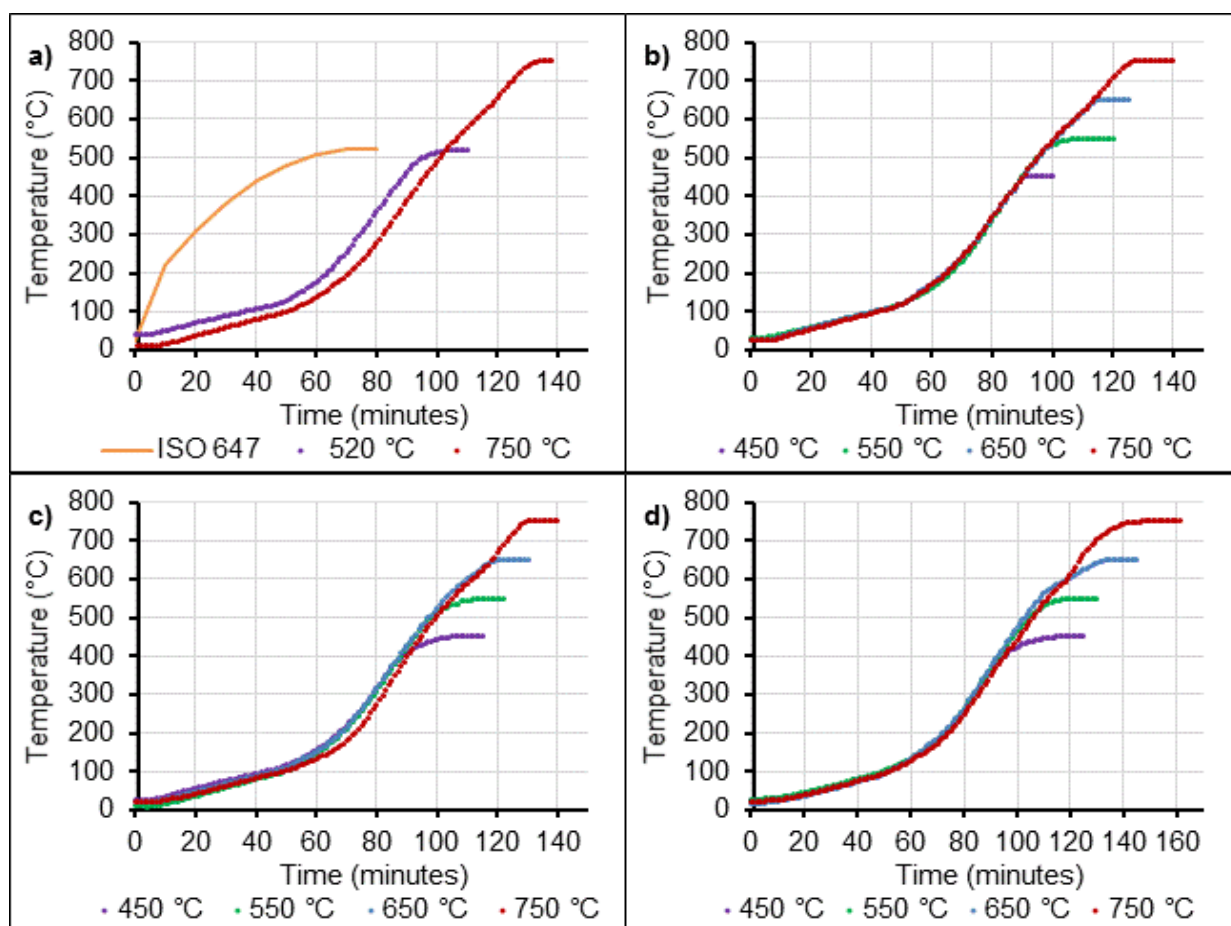


Figure 4.3: Heating curves of the Fischer Assay apparatus during devolatilisation for a) Repeatability, b) 20mm particles, c) 30mm particles and d) 40mm particles

4.3.4.2 Operating pressure and atmosphere

Pyrolysis experiments were conducted at ambient pressure in an inert atmosphere to eliminate the effect of oxidizing reactions. Argon (Ar) baseline 5.0 ultra-high purity grade, supplied by African Oxygen (AFROX) was administered to the Fischer Assay system at a flow rate of 10NL/min for 10 minutes before pyrolysis runs were initiated. The ambient pressure varied between 0.855–0.900bar. Pressure inside the two retorts was measured by a WIKA IPT-1* pressure transmitter, with an operating range of 0–10bar, and capable of reporting pressure differences as small as 0.1mbar (Roets *et al.*, 2014).

4.4 Quantification of product yields from pyrolysis experiments

The purpose of the quantitative investigation was to determine the mass yields of the different pyrolysis product fractions that consist of char, water, tar, and gas. Quantification of the pyrolysis yields were determined by modification of the method described by SANS (1974), and analogous to that done in previous studies (Govender, 2005; Stanton *et al.*, 2005; Slaghuys and Raijmakers, 2004). This method required the addition of toluene into the receiver flasks as a

solvent where the condensable volatiles will be captured. Therefore approximately 35mL of toluene was added to each gas washing stage in every experiment prior to the initiation of a Fischer Assay run. Yields of pyrolysis products were determined according to Equations (4.1 to 4.4) listed in Table 4.5.

Table 4.5: Equations used to determine pyrolysis yields (SANS, 1974).

Parameter (wt.%)	Equation	Equation number.
Water	$= \frac{m_1 \times 100}{m_0}$	(Eq.4.1)
Tar	$= \frac{m_1 \times 100}{m_0} - M; m_2$	(Eq.4.2)
Char residue	$= \frac{m_3 \times 100}{m_0}$	(Eq.4.3)
Gas (plus errors)	$= 100 - (char + tar + total\ water)$ $= \frac{(m_0 - m_1 - m_2) \times 100}{m_0}$	(Eq. 4.4)
where, m_0 is the coal sample mass; m_1 is the water mass determined by entrainment after the inherent moisture, as determined by the Proximate analysis, has been subtracted; m_2 is the tar mass determined by the difference in mass of the empty rotary evaporation flask ($m_{N,i}$) and the mas of the rotary evaporation flask after toluene removal ($m_{RV,i}$); m_3 is the mass of the char residue with M the wt% inherent moisture originally present in the coal sample.		

4.4.1 Char yield

The char residue that remained inside the retort was left to cool to below 100°C, after which the char sample was removed and weighed using a Radwag PS/750/C/4 balance. Consequently, the char yield was determined via Equation 4.3. After the char sample was weighed, it was inserted into a hermetically sealed container, under Argon atmosphere, to prevent oxidation, for further characterisation analysis.

4.4.2 Water yield

The water yield was determined by performing a Dean-Stark distillation. The tar, water, and toluene mixture (Fischer Assay products) are decanted into the round bottomed flask of the

Dean-Stark setup, in which the water and toluene fractions were evaporated through the use of a Seta MTop 5 heating mantle. Once the water and toluene fractions were in the vapour phase, it passed through a reflux condenser, where it condensed back into the liquid phase, and moved down into a reflux reservoir. Due to the fact that the density of water (998 kg/m^3) is higher than that of toluene (865 kg/m^3), the water layer was at the bottom of the reflux reservoir, and constituted the lower layer of the two. From this point onwards, the water was decanted and weighed. Equation 4.1 was then used to determine the water yield. A schematic of the Dean-Stark distillation setup is displayed in Figure 4.4.

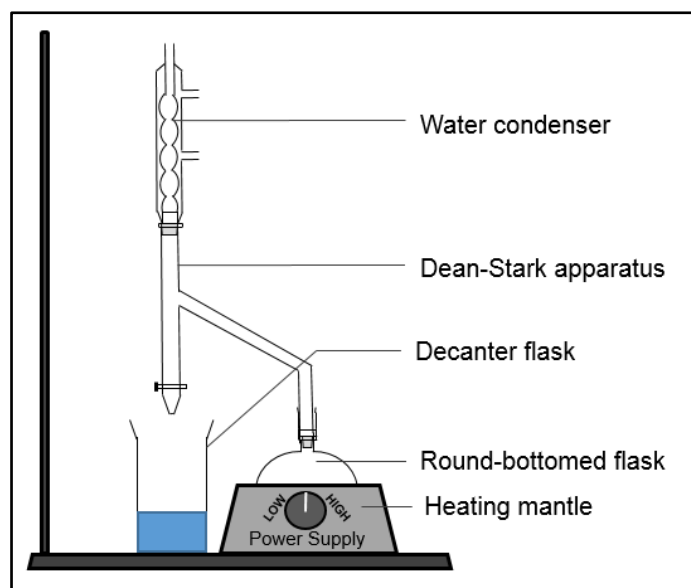


Figure 4.4: Dean-Stark distillation setup.

4.4.3 Tar yield

Once the water removal was completed, the round bottomed Dean-Stark flask contained the tar, light oils and toluene. The toluene was removed from the mixture via rotary evaporation to achieve the tar fraction. The rotary evaporation setup constitutes a Büchi vacuum controller V-850, Büchi vacuum pump V700 and a Büchi Rotavapor R II. A water bath was also included in the setup and filled with water, of which the temperature was controlled at 60°C .

The organic mixture was transferred into the round bottomed flask of the rotary evaporation setup and connected to the setup to commence evaporation. Toluene removal was performed by keeping the organic mixture at a constant temperature of 60°C , while the internal pressure of the system was sequentially lowered from atmospheric pressure to 27 mbar (Hattingh, 2012). Once 27 mbar pressure was reached, the tar fraction was kept constant at the set 60°C for 5 minutes to ensure complete toluene removal. The mass of the tar fraction was determined by weighing the empty rotary evaporation flask prior to the addition of the tar, light oil and toluene mixture, and again after the toluene has been removed from the organic mixture. A Radwag PS

200/C/4 balance was used to weigh the tar fraction, and Equation 4.2 was used to determine the tar yield.

Although this method differs from that specified in ISO 647 (SANS, 1974), it is required to be performed in this manner as a result of the gas washing phase. The rotary evaporation setup is displayed in Figure 4.5.



Figure 4.5: Rotary evaporation setup.

4.4.4 Gas yield and composition

According to SANS (1974), the conventional Fischer Assay method stipulates that the gas yield is determined by difference after the char, tar and water yields have been quantified. Equation 4.4 in Table 4.5 is used to calculate the gas yield (wt.%). However, in this study the gas volume yield was determined and combined with GC compositional data (to identify a set of specified components present in the gaseous phase), in order to determine the mass of the gas produced. Gas produced during pyrolysis experiments were captured in 10L Tedlar gas sampling bags. After completion of a Fischer Assay run and the gas sampling bags removed, the volume of the respective bags is determined via Archimedes's principle. The volume of the empty bags were determined and subtracted from the total gas yield determined in order to determine the yield of the gas content only. The amount of Ar present in each gas bag was measured and subtracted, thus resulting in the quantity of gas produced in each experiment. A schematic of the experimental setup used to determine the volume of each gas sampling bag is displayed in Figure 4.6.

The experimental setup consists of a Radwag PS/750/C/4 balance, a 70L square plastic crate and frame constructed from a combination of mild steel and stainless steel. An adjustable polyvinyl-chloride (PVC) plunger is attached to the metal frame which is used to submerge the gas sampling bag under water as the plastic crate is filled with 42L of water for the volume

determination. The experimental procedure is identical to that of the mercury submersion technique discussed in Chapter 3, Section 3.3.1. Once the volume of a gas sampling bag was determined, a syringe was used to extract gas samples from the bag and injected into the GC to find the compositional data of the derived gas. It was assumed that the gas composition throughout the respective gas bags were constant, therefore the determined volume of the gas was used to calculate the mass of gas produced. A SRI 8610C multiple gas chromatograph was used to analyse the gas samples (Hattingh, 2012; Roets, 2014).

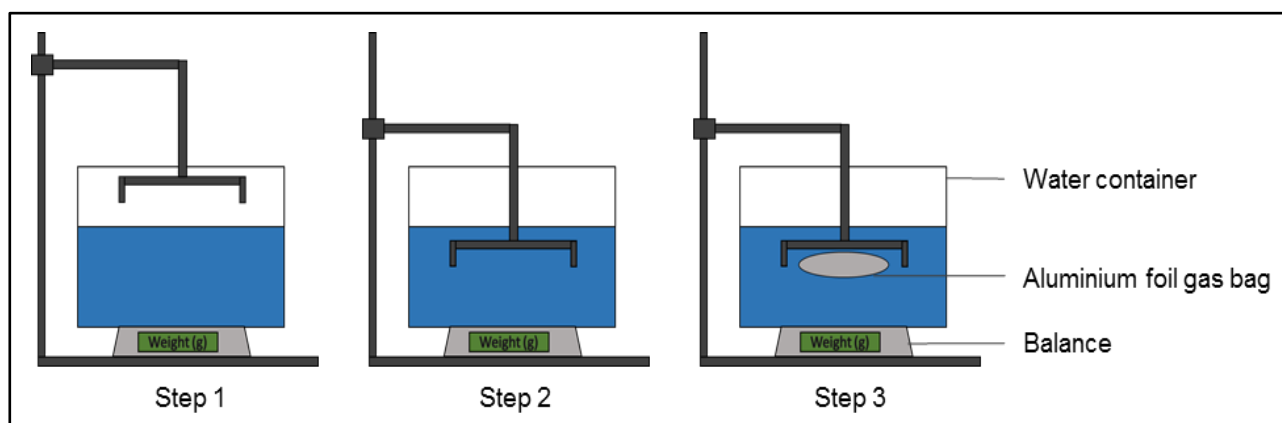


Figure 4.6: Gas bag submersion setup for volume determination.

The GC used in this study separates the gaseous products by means of three packed columns i.e. 6' HayeSep D, 6' 13X molecular sieve and a 3' 5Å molecular sieve all of which have an outer diameter of 1/8". Detectors employed to quantify the products include a flame ionization detector (FID) and two thermal conductivity detectors (TCD1 and TCD2). Peak-382 acquisition software records the compositional data from the manually injected gaseous samples. The equipment was calibrated by injecting a specific refinery gas standard and evaluating the individual elution time frames for the respective components constituting the calibration gas. These components specified include H₂, O₂, N₂, CH₄, CO, CO₂, ethylene, ethane, C₃'s (propylene, propane, propadiene, cyclopropane, methyl-acetylene), C₄s (isobutene, n-butane, isobutylene, 1,3-butadiene, cis-2-butene, trans-2-butene, butane-1), C₅s (isopentane, n-pentane), C₆s (n-hexane, 4-vinyl-1-cyclohexene). Information regarding operating conditions, carrier gas, oven programme and the calibration gas used is listed in Table 4.6.

Table 4.6: Details of gas chromatograph used to analyse evolved gases.

GC conditions	Specification
Inlet temperature	25 °C
Injection volume	0.5 µL
Detector cell temperatures	TCD1: 300 °C TCD2: 150 °C
Carrier gases and flow rates	FID: He (25 psi and 20 mL/min) Methanizer: H ₂ (20 psi and 25 mL/min) and Air (5 psi and 250 mL/min) TCD1: He (25 psi and 20 mL/min) TCD2: Ar (7psi and 10 mL/min)
Oven programme	Hold for 7 min at 60 °C, ramp from 60 °C to 280 °C at 15 °C/min, hold for 20 min at 280 °C.
Calibration standard and unit of measure	Refinery gas standard #1 and mol.%

4.5 Qualitative analysis of Fischer tar and char

The purpose of analysing the Fischer tar product qualitatively is to gain further understanding regarding the composition and characteristics of the tars evolved during pyrolysis of large coal particles. According to Gavalas, (1982), the light oil and tar fractions constitute between 50% and 80% of the mass loss during pyrolysis in the form of volatile matter. Analysis thereof may provide useful information regarding the thermal decomposition of the coal, as well as indicate the compositional presence of high valuable chemicals within the light oil and tar fractions. Dichloromethane is the required solvent for the qualitative analysis of the tar fraction, therefore dichloromethane was also used in the pyrolysis experiments during which the tar samples are formed.

This method necessitates that the water formed during pyrolysis experiments be removed from the Fischer Assay liquid product mixture. In this qualitative study, water removal was achieved via solvent extraction to separate the organic tar fraction from the aqueous layer containing water, which forms as water is not miscible in the organic solvent. Separation is achieved by means of a separation funnel. The liquid product mixture obtained is transferred into the separation funnel and thoroughly mixed. After the two layers have formed they are tapped off separately. After separation, the organic layer was stored in a fridge prior to being analysed. All the tar analyses were performed at Sasol Technology, Research and Development in Sasolburg.

4.5.1 Simulated distillation (Simdis)

Simulated distillation is a standard analysis used to categorise petrochemical products into a manageable number of components based on the respective boiling points of the components

present (Li, *et al.*, 2001; Ukwuoma, 2002). This may provide useful information of the compositional analysis of coal tar in relation to petrochemical refining processes (ASTM, 2008). The Simdis analysis of the coal derived tars were performed according to the ASTM D2887 standard by using a high-temperature GC-FID fitted with an ARX 2887 Restek column with dimensions 10m x 0.53mm x 0.53 μ (Roets *et al.*, 2014). According to the ASTM D2887 method, the Simdis procedure is valid for petrochemical fractions with a boiling range between 55.5°C and 538°C. Each sample injected into the GC column consisted of 0.2 μ L organic liquid mixture (tar dissolved in dichloromethane).

Tar samples used in this analysis were prepared according to the same method as for those used in the GC-MS/FID and SEC-UV analyses. The initial temperature of the GC column was 40°C, followed by a ramp up of 15°C/min until a final temperature of 540°C was reached, where the temperature was held isothermally for 10 minutes.

In order to analyse the results data from the SimDist analyses, the weight average boiling point was calculated for each sample, and the mass loss curves were evaluated (Bakr, *et al.*, 1996; Gray, 1988; Roets *et al.*, 2014). The following equation was used to calculate the weight average boiling point - WABP (Bean, 2013; Gibbins-Matham and Kandyoti, 1988; Hattingh, 2012; Roets *et al.*, 2014):

$$WABP = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5} \quad (\text{Eq. 4.5})$$

With T_{10} , T_{30} , T_{50} , T_{70} and T_{90} being the temperatures at which 10%, 30%, 50%, 70% and 90% of the mass losses occurred.

Further processing of the WABP results were performed, based on dividing the boiling point distributions of the respective samples into crude oil distillation fractions (Rand, 2003; Hattingh, 2012). The boiling point cut fractions as identified from crude oil refining are indicated in Table 4.7.

Table 4.7: Cut fractions of boiling point ranges based on crude oil distillation (Rand, 2003).

Fraction identification	Boiling point range (°C)
Medium naphta	79-121
Heavy naphta	121-191
Kerosene	191-277
Distillate fuel oil	277-343
Light vacuum gas oil	343-455
Heavy vacuum gas oil	455-566

4.5.2 Gas chromatography mass spectrometry (GC-MS) and gas chromatography flame ionisation detection (GC-FID)

Sample preparation for the GC-MS/FID analysis required no further dilution of the tar fraction in an organic solvent, i.e. dichloromethane, after separation of the aqueous phase from the organic phase has been achieved. Dichloromethane was selected as the organic solvent since it was also used as the analysis solvent. For every distinct GC-MS/FID analysis, 1mL of the organic mixture was transferred into a 2mL glass PTFE vial and analysed accordingly (Roets *et al.*, 2014). An Agilent 7890 GC connected to a mass selective detector (MSD) was used for peak identification. The inherent species within the tars were quantified with an Agilent 7890 GC equipped with a FID (Hattingh, 2012). Approximately 1µL of organic liquid was injected into the respective GC systems with a split ratio of 200. Both analyses made use of a HP-PONA (PONA-paraffins, olefins, naphtalenes and aromatics) petrochemical, fused silica column (100% dimethyl polysiloxane) which has an internal diameter of 0.25mm, and able to operate at a maximum temperature of 350°C. Injector and detector temperatures were controlled at 280°C. Helium (He) and Hydrogen (H) were respectively used at a flow rate of 1.2mL/min as the carrier gas through the GC-MS and GC-FID systems (Bean, 2013; Hattingh, 2012; Roets *et al.*, 2014).

The GC column temperature was operated as follows: An initial temperature of 60°C was held for 5 minutes after which the temperature was increased to 240°C at 6°C/min and kept constant for 30 minutes until all the compounds present in the sample have eluted. Quantification of the tar components only took into consideration the components present in quantities higher than 0.005wt.%.

Various components are identified during a GC-MS analysis and comparison thereof may be challenging. In order to achieve the comparison, the species detected were classified into different molecular families and is indicated in Table 4.8. Results obtained from the GC-MS analysis provide useful information regarding components with boiling points below 300°C and above 39.6°C (the boiling point of the organic solvent dichloromethane).

Table 4.8: Compounds identified by GC-MS analysis and classification thereof based on molecular families.

Compound family (Abbreviation)	Standard used
Aliphatic compounds (Aliph.)	Normal- and iso-paraffins, olefins and acetylenes. Acyclic compounds
Alkyl-benzenes (A-B)	Benzene toluene and xylene (BTX) and higher substituted benzenes
Alkyl-phenols (A-P)	Phenol, cresol, xlenol
Aromatic ethers and esters (Arom. E & E)	Dibenzofuran
Alkyl-indenes (A-I)	Indene, Methyl-indene
Alkyl-naphtalenes (A-N)	Naphtalene, methyl-naphtalene and derivatives
Polycyclic aromatic hydrocarbons (PAH's)	Fluorene, anthracene, phenanthrene, fluoranthene and other aromatics
Nitrogen heteroatoms (N-)	Pyridinem methyl-pyridine, benzene-amine etc.
Mixed aliphatic and aromatic compounds (Mixed)	Co-elution of iso-aliphatics and aromatics

4.5.3 Size exclusion chromatography (SEC-UV)

The tar samples for this analysis were prepared in a similar manner to that of the GC-MS/FID, which entailed separation of the aqueous phase from the organic tar fraction dissolved in dichloromethane.

It was found that no further dilution of the organic fraction with 1-methyl-2-pyrrolidinone (NMP) was necessary. Size exclusion chromatography analysis was conducted on the respective tar samples with the intention to estimate the molecular weight distribution of each sample. The apparatus used consisted of an Agilent 1100 high-performance liquid chromatograph (HPLC) equipped with a 300mm PLgel mixed-E (Varian) GPC column with an inner diameter of 7.5mm. This system utilizes two ultra violet visible light (UV-Visible) detectors in series, as well as a refractive index detector (RID). HPLC grade NMP from Merck Chemicals was used as eluent in the SEC-UV analysis at a flow rate of 0.5mL/min (Roets *et al.*, 2014). Each tar analysis required 10µL of tar sample solution to be injected into the column, whilst a total analysis time of 30 minutes was established to be adequate. Quantification of the components required the UV-VIS detectors to be set to multiple wavelengths that consisted of 280nm, 300nm, 350nm and 370nm respectively, of which chromatograms were collected (Bean, 2013; Hatingh, 2012; Roets *et al.*, 2014).

4.5.4 Char analysis

Analysis of the various chars prepared via identical pyrolysis experiments consisted of proximate analysis, ultimate analysis and calorific value. This was done with the intent to compare the properties of the char to that of the original coal.

The analyses were all performed by Bureau Veritas Testing and Inspections South Africa, after sample preparation according to ISO 13909-4, was completed (ISO, 2001). Results of these analyses are discussed in Chapter 5 Section 5.4. The standards on which the respective analyses are based, are listed in Table 4.9.

Table 4.9: Laboratory standards used for char analyses.

Procedure	Standard used
Sample preparation	ISO 13909-4, (2001)
Moisture content (%)	ISO 11722, (1999)
Ash content (%)	ISO 1171, (2010)
Volatile matter content (%)	ISO 562, (2010)
Total sulfur (%)	ISO 19579, (2006)
Gross calorific value (MJ/kg)	ISO 1928, (2009)
Ultimate analysis	ISO 29541, (2010)

4.6 Summary of pyrolysis product analyses

Table 4.10 lists a summary of the analyses performed in the devolatilisation investigation in order to gain a better understanding of quality of the respective pyrolysis products derived under different experimental conditions.

Table 4.10. Summary of the analyses of the respective pyrolysis products.

Product analysed	Analyses	Laboratory responsible
Gas	GC (-TCD and- FID)	North-West University
Tar	GC-MS and GC-FID	Sasol R & D
	SEC-UV	Sasol R & D
	SimDist	Sasol R & D
	Ultimate	North-West University
Char	Proximate	Bureau Veritas
	Ultimate	Bureau Veritas

4.7 Preparation of low-smoke fuel

Low-smoke fuels are produced from coal during the process of pyrolysis/devolatilisation between temperatures of 400°C and 900°C (Ladner, 1988). Chapter 2, Section 2.6 of this study

described the different stages of the thermal decomposition of coal. In essence, a low-smoke fuel is a fuel that emits less pollutants during combustion, therefore resulting in a cleaner airborne environment (Ladner, 1988; Engelbrecht *et al.*, 2001).

4.7.1 Experimental equipment and procedure

The low-smoke fuel in this investigation was prepared through the use of a Lenton Pyrolysis tube furnace at temperatures of 450°C, 550°C, 650°C and 750°C. The temperatures selected in this section of the investigation are identical to those used in the pyrolysis experiments with the Fischer Assay apparatus. The furnace is rated at 18.7 kW over 400 V, and operates according to a pre-programmed heating curve, which was set prior to conducting the experiment.

A 300mm long stainless steel loading boat (into which the coal sample was loaded) was manufactured according to the length of the heating zone of the furnace. The profile of the loading boat is as such that it concurs well with that of the tube it is inserted into. Two tubes were used separately i.e. a Mullite tube; however due to experimental constraints it was replaced with a more robust Kanthal metal tube. Experiments conducted in the Mullite tube were at 450°C and 550°C, whereas the Kanthal tube was used at the two higher temperatures of 650°C and 750°C.

N₂ gas with ultra-high purity grade: 99.999% as supplied by African Oxygen (AFROX) was used to provide the inert atmosphere to prevent combustion of the coal.

The method of devolatilisation necessitated that the coal samples be prepared according to the particle size distribution (PSD) of the coal as obtained from the Kwadela Township, Mpumalanga, South Africa. The top size fraction of the particles (with a diameter of approximately 75mm) were too large for the laboratory scale experimental equipment, and therefore these particles were not included in the experimentation. The rest of the particles were therefore normalised to 100wt.% as presented in Table 4.11.

Table 4.11: Particle size distribution of coal used in char preparation.

Particle size (mm)	Original fraction (%)	Normalised fraction (%)
+75	14	-
-75+53	36	44
-53+37.5	28	34
-37.5+26.5	10	13
-26.5+19	4	5
-19+13.2	2	2
-13.2+9.5	1	1
-9.5	5	-
Total	100	100

It is clear that the -75mm+53mm and -53mm+37.5mm size fractions constituted the largest portion of the coal samples used to prepare the chars. A batch sample size of 1kg was selected for the charring programme, and accordingly the samples constituted the correct weight percentages as per Table 4.11. As soon as the sample preparation was completed, the total sample was weighed, placed into the loading boat and inserted into the tube of the furnace.

The flanges of the tube were coupled and fastened, and the tube outlet was connected to the central ventilation system of the building. Thereafter, the N₂ flow was engaged to purge the system for 5 minutes at a flow rate of 3NL/min. A constant N₂ flow rate of 3NL/min was maintained throughout the duration of the experiment. Once the system purge was completed, the oven was switched on to commence the run. The oven was programmed with a heating rate of 5°C/min up to the specified temperature, at which it would hold the temperature for three hours to ensure complete heating of all the coal particles. After the run was completed, the oven was left to cool down to approximately 50°C before removal and weighing of the char fraction. The char was inserted into sealable plastic bags under N₂ atmosphere, and stored in the fridge prior to further processing. The experimental details of the char preparation are listed in Table 4.12.

Table 4.12: Tube furnace experimental conditions.

Variable	Range specification or composition
Coal feedstock	Kwadela Township coal
Sample weight (g)	1000 ± 0.1
Coal particle size fractions (mm)	+9.5-75
Operating temperatures (°C)	450, 550, 650, 750 (non-isothermal)
Heating rate (°C/min)	5
Holding time (min)	180
Operating pressure	Atmospheric (± 87kPa)
Atmosphere	N ₂

4.7.2 Experimental plan

The experimental plan proposed for the preparation of the chars are listed in Table 4.13.

Table 4.13: Experimental plan for char preparation.

Temperature (°C)	Repeats
45	20
550	20
650	20
750	20
Total	80

A total of 80 experiments were conducted to prepare a sufficient amount of char necessary for a series of combustion performance experiments in which the different combustion behaviours of the raw Kwadela coal, an anthracite and the low-smoke fuels were evaluated.

4.7.3 *Characterisation of low-smoke fuel*

A representative coal sample was pyrolysed at each of the four respective temperatures, of which the chars were characterised according to the proximate and ultimate analyses. Samples were prepared according to ISO 13909-4 (2001) and analysed by Bureau Veritas Testing and Inspections South Africa. Refer to Table 4.9 for the standards and methods used for analyses of the char samples. Refer to Chapter 5, Section 5.4 for the discussion of the char characterisation results.

4.8 Coal, anthracite and char evaluation via combustion tests

4.8.1 *Experimental equipment and process description*

Once preparation of the sufficient amount of low-smoke fuel was accomplished, as described in Section 4.6, the process in which the combustion behaviour of the different fuels was evaluated could commence. This evaluation process consisted of combusting the separate fuels in a typical coal stove, such as those used by the residents in Kwadela Township. The specific stove used in this study was a Union 7, which is currently the most popular appliance wherein coal is combusted to provide energy for cooking and space heating in Kwadela (Nova, 2013). The purpose of utilising a stove typical of that used in Kwadela, was to measure the emissions produced, and performance, obtained during the combustion of raw coal, various coal derived chars and anthracite. The Union 7 coal stove investigated during the combustion performance experiments are displayed in Figure 4.7.



Figure 4.7: Union 7 coal stove investigated during combustion experiments.

Emissions measured throughout the combustion of these fuels consisted of NO_x , SO_2 , CO , CO_2 , total suspended particulate matter (TSP), and volatile organic compounds (VOC's). The particulate matter was measured both quantitatively and qualitatively. From a practical standpoint (performance level), the fuel ignition time, the time it takes to boil 1L of water and the total time heat is provided, was measured in order to present tangible information to the residents of Kwadela Township. Furthermore, the combustion efficiency of each fuel within the stove was determined according to the method developed by Le Roux *et al.*, (2004), of which the definition is provided in Chapter 6, Section 6.4.4. Temperatures measured during the course of each combustion test included the intrinsic temperatures of the fire, flame temperature, and that of the chimney at the point where emissions were measured. The temperature of the water inside the pot was only measured during one experiment per fuel type. Temperatures were all measured with K-type thermocouples connected to a Shinko LMD-100 console/data logger in order to record the respective temperatures. The stove was placed on top of a Sartorius platform scale (CAW1P-4-300LL-I) which enabled the online measurement of weight for the duration of each combustion test.

Liquid Petroleum Gas (Afrox Handigas with approximate propane/butane ratio of 60:40) was selected as the ignition fuel as it could be shut off at a certain time, after which the emissions generated resulted only from the solid fuel in the stove. Being able to shut off LPG at any given stage during a combustion test proved to be advantageous above other ignition fuels such as fire-lighters and wood/paper, hence forming the criteria upon which the decision was based. A bubble flow meter was used to measure the flow of LPG before each experiment was initiated. The LPG bottle was also weighed before and after every combustion test in order to determine the amount of energy injected into the system. A LK's Turbo Gas Lighter was connected to the

LPG bottle and served the purpose of distributing the flames once the LPG is ignited (Refer to Figure B.2.1, Appendix B.2). In Figure 4.8, a schematic is provided detailing the packing of the fuel and placement of the thermocouples at which the different temperatures were measured. A square wire mesh grid was constructed with the purpose of providing a rigid structure within which the fuel could be packed. Consequently it was attempted to keep the fuel packing constant throughout the combustion tests for all fuels. Placement of the thermocouples and the ignition burner were also identical for all experiments in an effort to eliminate as many variables as possible for good reproducibility. The thermocouples were positioned with reference to the grid on top of which the fuel was packed (the thermocouple at the grid being 0cm). Subsequently, the respective heights for the corresponding thermocouples were 0cm, 5cm, 10cm and 20cm above the grid as showed in Figure 4.8. An ash tray was included in the bottom of the stove, (below the grid where combustion took place), on which the ash after each experiment was collected and weighed.

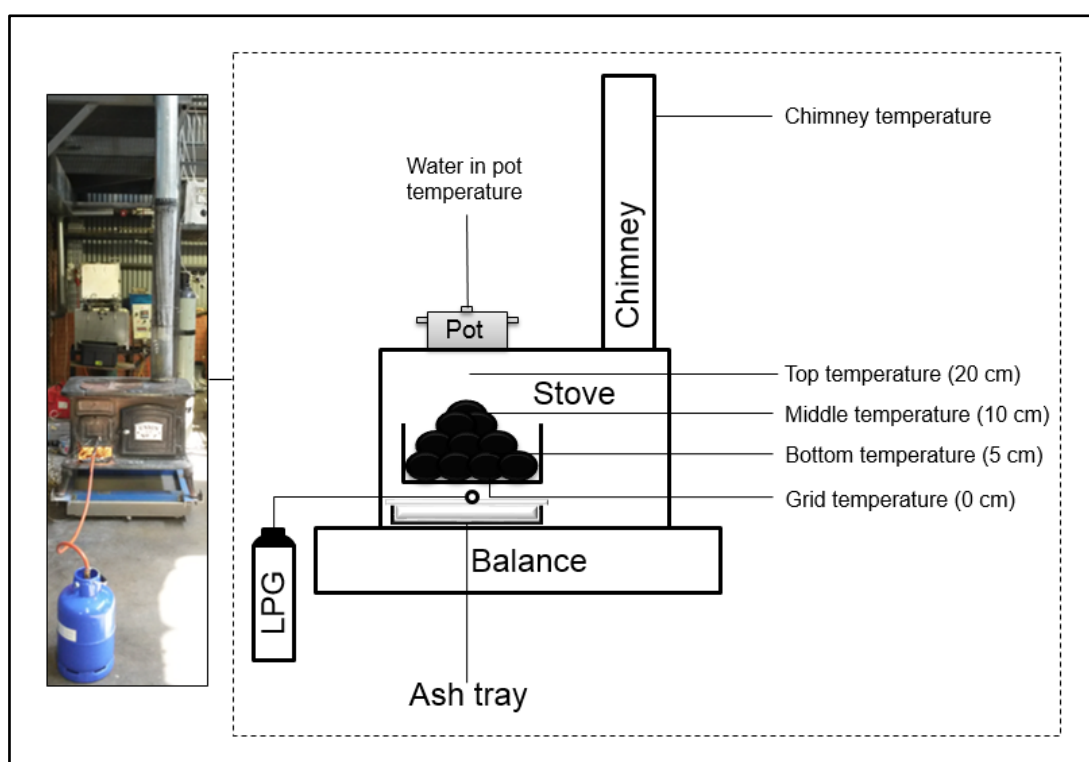


Figure 4.8: Schematic detailing fuel packing and thermocouple placement.

A schematic detailing the experimental equipment is provided in Figure 4.9 and is described in the text to follow. Multiple online analysers, each fulfilling a different purpose, were incorporated to measure the diverse emissions. The charcoal tubes were obtained from Biograde Laboratory Services. The undiluted sample provided gas emission measurements on an undiluted basis. A similar portable gas component analyser (PG-350) was employed to measure the gas components of a stream diluted to some extent with N₂ gas (Nitrogen Technical grade, 99.5%

purity). Refer to Appendix B.1 for details of the calibration gases used to calibrate the PG-250 and PG-350. Both the PG-250 and PG-350 sampled at a volume flow rate of 0.4L/min. The diluted stream was also connected to a TSI Dusttrak II (model no 8530) aerosol monitor that measured the total particulates released during the course of combustion. Dilution was necessary due to a technical limitation of the Dusttrak II instrument only being able to measure particulate concentrations of up to 400mg/m³. Therefore, it was imperative to measure both the undiluted and diluted gas streams in order to calculate the dilution ratio, i.e. the total amount of particulates produced during combustion.

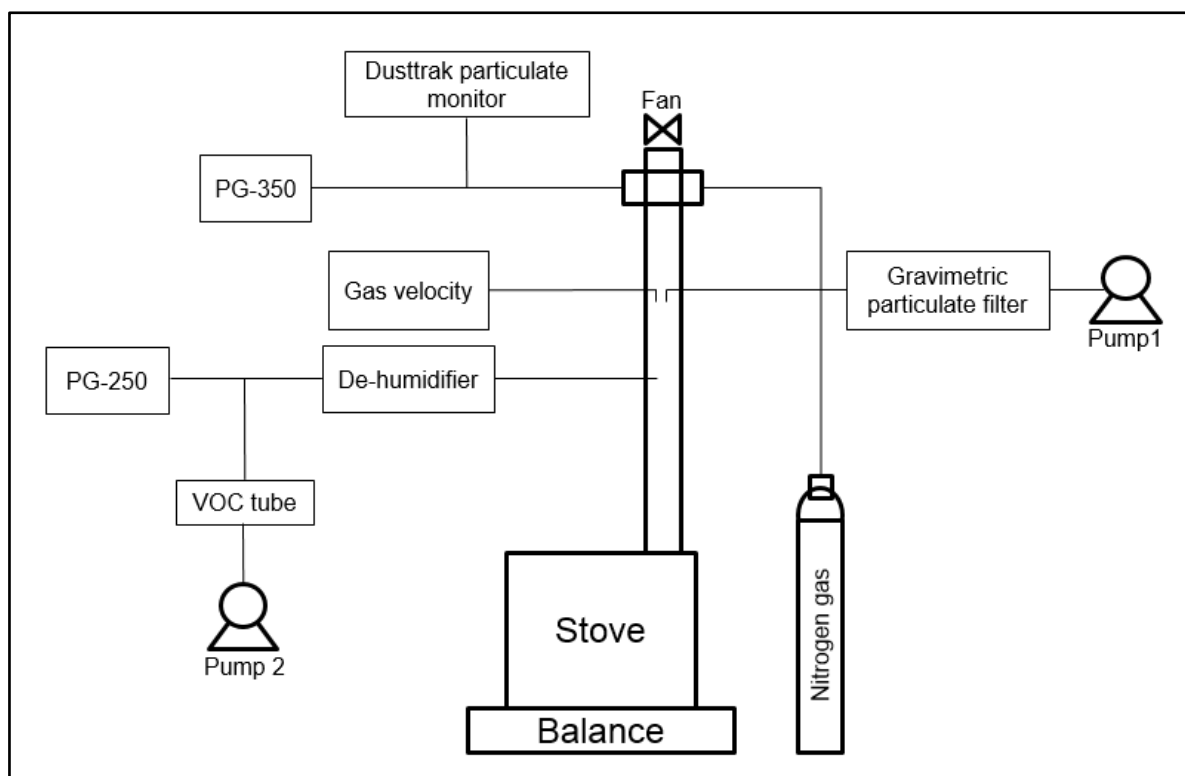


Figure 4.9: Schematic detailing the experimental equipment.

The Dusttrak II is a photometric instrument and was set to sample 3NL/min of which 2NL/min was used as sample flow, while 1NL/min was split off, filtered and used as sheath flow. Sheath flow in this instance is when laminar gas flow inside the instrument is injected back into the sample chamber through which the particles in the remaining sample flow moves, forming a single file. The particles then pass through a sensing chamber where they are illuminated by a sheet of laser light and the scattered light is captured by a spherical mirror which is then focussed on a photo detector.

The gravimetric particulate sampling procedure entailed the withdrawal of particulate matter isokinetically from the source (chimney stack) and collected on a glass fiber filter, from which the total particulate mass was obtained. According to USA EPA Method 5, it is of the utmost importance to sample particulate matter isokinetically, therefore a fan (220V, 25W, 20mm) was

incorporated in an attempt to keep the gas flow rate as constant as possible. A pitot tube connected to a differential pressure gauge was used to measure the flow rate of the gas inside the stack (chimney). A nozzle (elbow design) with an internal diameter of 1.4mm was used. It is compulsory that the sampling velocity at the point of the nozzle where the particulates are sampled is identical to the velocity of the gas flow inside the chimney for isokinetic sampling. The piping from the nozzle is connected to a sample housing that holds a gravimetric filter called a quartz thimble (obtained from Envirocon) onto which the particulate matter was captured for analyses. Downstream from the thimble is a vacuum pump (Aquaria CF 20 Basic high volume dust sampler) supplying the necessary suction at the correct sampling velocity (adjusted every 5 minutes to correct value) for isokinetic particulate matter sampling. The average flow rate of the gas inside the chimney stack throughout all the combustion experiments was approximately 2m/s as a fan was incorporated within the chimney stack with the primary means to supply constant flow to the gravimetric filter. From Figure 4.7 it should be observed that some smoke escaped from time to time through fractures in the heating plate of the stove. Therefore, the secondary purpose of the fan was to improve ventilation throughout the stove setup in an attempt to minimise the amount of smoke escaping through fractures of the stove, which may have an impact on the emissions measured inside the chimney.

4.8.2 Experimental procedure

Calibration of instrumentation is of great importance to ensure reliable measurements and was therefore performed frequently to ensure reliable measurements were taken. Various calibration gases were used to calibrate the two portable gas analysers (PG-250 and PG-350) as it was imperative to measure the gas components accurately due to the fact that a dilution ratio had to be calculated. Refer to Appendix B, Table B.1.1 for properties of the calibration gases used for the two portable gas analysers. The Dusttrak II was purged and zeroed after each combustion experiment to remove any residual particulate matter that may have accumulated within the instrument.

Two core temperatures of the fire (Bottom and Middle) as indicated in Figure 4.8 were monitored and used as the guidelines of when to shut off the LPG. Experimental trials were performed, and the assumption was made that the fire was self-sustaining at the point where both the Middle and Bottom temperatures had respectively reached a temperature of 500°C. Bituminous coal ignites at temperatures ranging between 400°C and 500°C, therefore the temperatures selected at which the LPG was shut off correlated well with that in literature (Arms, 1922).

Once the experimental setup was completed and ready for testing, repeatability experiments were conducted with the use of two Kwadela raw coal samples, each with a weight of 5kg. The

coal samples used in the repeatability testing of the setup were prepared according to the particle size distribution as discussed in Section 4.7. After repeatability of all the measurable variables was established, investigation of the coal derived chars and anthracite could commence.

As soon as the calibrations were completed, and all the analysers as described in Section 4.8.1 had stabilised, preparation for the experiment was initiated by inserting the thermogravimetric filter and VOC tube into the relevant housings. The balance was then zeroed, which meant the fuel (coal/anthracite/char) bed could be packed, and the stove closed and readied for ignition of the LPG. The pumps for the thermogravimetric filter and VOC tube were initiated simultaneously with ignition of the LPG fuel, whilst the gas flow rate inside the stack was constantly monitored and the sampling velocity of the thermogravimetric pump adjusted if required. As soon as the Middle and Bottom temperatures of the fire reached 500°C respectively, the LPG was shut off. Emissions were recorded for two hours after ignition of the LPG. In experiments where the time to boil 1 L of water was determined, the pot was placed on top of the stove at the exact time when LPG was shut off. The temperature of the water inside the pot was constantly monitored until it reached a temperature of approximately 95°C, where it boiled, and was removed from the stove. One experiment for each type of fuel was left to combust naturally until the temperatures returned to room temperature. The ash and residual carbon not combusted were collected and used to determine the combustion efficiency of each fuel inside the stove (Refer to Appendix D.4 for calculations regarding the combustion efficiency).

Combustion of two coal/char/anthracite samples formed the base case from which the combustion results from the other fuels were compared. The goal was to determine the reduction, if any, in emissions produced from combustion of anthracite and coal derived chars, as well as to assess the practical parameters discussed in Section 4.8.1, in comparison to that of raw coal.

4.8.3 *Experimental plan*

The experimental plan for combustion of the six different fuels employed in this study was as follows:

- Repeatability of all the measurable variables such as temperature, mass loss and the emissions emitted (with the exception of the boiling time for 1L of water) was established with combustion of two separate raw coal repeats. Reproducibility of the boiling times was therefore not performed based on the assumption that the boiling time for each fuel would remain relatively constant due to the repeatability determined for the other

variables. It is however proposed that further investigation into the boiling times of the respective fuels be investigated during future studies in order to confirm the assumption.

- Investigation of the emissions and practical parameters of the five other fuels (Anthracite, Char-450, Char-550, Char-650, and Char-750) consisted of two combustion repeats per fuel.
- One experiment per fuel was left to combust naturally after emissions were measured, from which the ash and residual combustible material were collected.
- Therefore a total of 18 combustion experiments were conducted.

4.8.4 Summary of combustion experiments

The combustion performance tests are summarised in Table 4.14, where the different parameters evaluated for the respective fuels during combustion are displayed.

Table 4.14: Summary of combustion experiments.

Property	Description
Fuels combusted	Coal, Anthracite, Char-450, Char-550, Char-650, Char-750
Gaseous emissions	NO _x , CO, CO ₂ , SO ₂
Other emissions	Total suspended particulate matter (TSP), Volatile organic compounds (VOC's)
Practical parameters	Time to boil 1L of water, Total time heat is provided
Scientific parameter	Combustion efficiency
Number of experiments per fuel	3
Total number of experiments	18

CHAPTER 5: EFFECT OF TEMPERATURE AND PARTICLE SIZE ON FISCHER ASSAY PYROLYSIS PRODUCTS

5.1 Introduction

In order to determine the technical viability of a low-smoke fuel (char) that is produced from lump coal, it is necessary to gain a better understanding of the devolatilization behaviour of the coal in a typical thermal decomposition process. This chapter entails the investigation of the effect that both the coal particle size and final pyrolysis temperature have on the respective pyrolysis product yields and composition of the Kwadela coal sample. In order to accomplish this it was necessary to effectively capture the different pyrolysis products which consist of char, water, tar and gas. Compositional analyses of the gases evolved during pyrolysis were performed using a multiple component GC, and tar composition was analysed with the use of Simdis, GC-MS/FID, and SEC-UV. Analyses that provided compositional information of the chars consisted of proximate analyses, ultimate analyses and calorific value analyses. Findings from the TG analysis of the raw coal are reported in Section 5.2. The pyrolysis product yields obtained from experiments conducted using the NWU Fischer Assay setup is discussed in Section 5.3. Char, gas and tar composition results are discussed in Sections 5.4, Section 5.5 and Section 5.6 respectively, and a summary of the most relevant findings is presented in Section 5.7.

5.2 Thermogravimetric analysis

Thermogravimetric analysis was conducted with the purpose of identifying the temperatures at which the Fischer Assay investigation, as well as the bulk char preparation, would be conducted. This part of the study was needed prior to combustion testing of the raw coal, produced chars, as well as an anthracite. The Fischer Assay analysis included the investigation of the effects of final pyrolysis temperature and particle size on the pyrolysis product yields (char, water, tar and gas) for the raw coal obtained in Kwadela. The three particle size fractions selected for the thermogravimetric analysis, as well as the Fischer Assay study, consisted of particles with approximate outer diameters of 20mm, 30mm and 40mm respectively. Therefore, these particles were classified as 20mm, 30mm and 40mm particles. The thermogravimetric analysis provided information regarding the weight loss versus temperature as these experiments were conducted via non-isothermal operation. Consequently, the degree of devolatilisation with respect to temperature could be determined to assist in the temperature selection process. Three duplicate experiments of each particle size were performed in order to assess repeatability. The experimental error on repeatability varied between 2.5wt.% and 5wt.%

throughout the analysis. Figure 5.1 displays the average weight loss versus temperature curves for each particle size fraction.

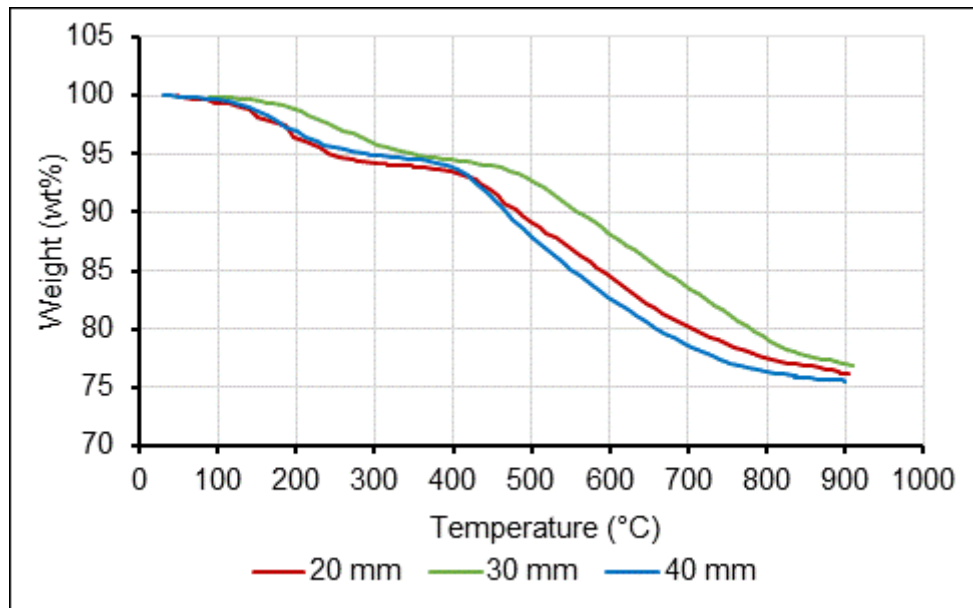


Figure 5.1: Average normalised weight loss for all three particle size fractions.

It is evident from Figure 5.1 that the initial weight loss was slow during the drying phase which occurred between approximately 100°C and 350°C. During this phase all of the moisture was removed resulting in an endothermic process (Bunt and Waanders, 2008). At a temperature of about 400°C the weight loss increased rapidly where the coal particles started to devolatilise in the phase called primary pyrolysis, where hydrocarbon gases, oils and tars are formed. At approximately 700-750°C, the curves started to flatten off which served as an indication that secondary pyrolysis (slow pyrolysis) was occurring. The pyrolysis behaviour of the large coal particles investigated correlates well with that described in literature (Bunt and Waanders, 2008; Kandyoti *et al.*, 2006).

When comparing the devolatilisation behaviour of the three different particle size fractions, it can be observed in Figure 5.1 that the differences were relatively small, however distinguishable. The 40mm particles lost the highest amount of weight (moisture and volatiles) with a value of 24wt.%, followed by the 20mm and 30mm size fractions with respective values of 23.7wt.% and 23.4wt.%. The sum of the moisture and volatiles released by the individual particle size fractions as obtained from the proximate analysis are 25.5wt.%, 29.5wt.% and 24.9wt.% for the 20mm, 30mm and 40mm particles respectively. All three size fractions lost less weight in comparison to the proximate analysis, indicating that not all of the volatiles have yet been driven off. Volatile yields are likely to diminish with an increase in particle size, which is applicable when comparing the 20mm and 30mm particles (Kandiyoti *et al.*, 2006; Anthony *et al.* 1976; Devanathan & Saxena, 1987). Hattingh, (2012), proposed that an increased particle size

inhibits the propagation of heat from the outer surface of a coal particle towards the centre due to the thermal conductivity properties of the coal. However, it was observed that the highest amount of volatiles was released by the 40mm particles in this investigation. This phenomenon can possibly be explained by particle fragmentation, which is an influential factor of the volatile yield with increasing particle size (Kandiyoti *et al.*, 2006; Yang *et al.*, 2013). Particle fragmentation was observed in some instances for the 40mm particles as displayed in Figure 5.2. From Figure 5.2a it is clear that a prominent crack through the length of the particle is visible, whereas minute hairline fractures on the surface of the particle can be noted in both Figure 5.2a and Figure 5.2b, which shows the same particle from different angles. No particle fragmentation was observed for the 20mm and 30mm particle size fractions, which may explain the reason for the low rate of mass loss of the 30mm particles in comparison to the other two fractions. Heat propagates slower through larger particles if fragmentation does not occur during devolatilisation.

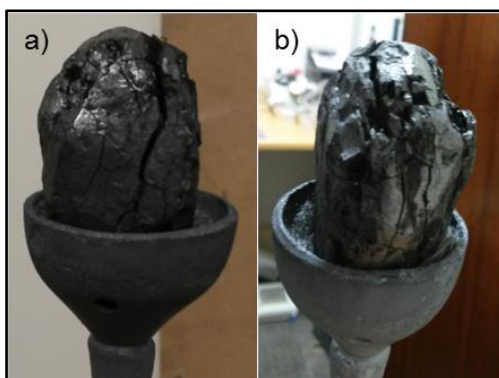


Figure 5.2: Particle fragmentation observed for 40mm coal particle after TG analysis.

The extent to which the coal particles are devolatilised are an important and useful element that can be determined from the results of pyrolysis via thermogravimetric analysis. This element played a key role in the determination of the temperatures at which the Fischer Assay analysis and bulk char preparation would be investigated in the following phases of this study. By combining of the results obtained from the proximate analysis and that of the thermogravimetric analysis, the percentage volatiles driven off from the respective particle size fractions on a dry basis were determined and illustrated in Figure 5.3. It was assumed that all the weight lost up to a temperature of approximately 350-400°C consisted of moisture, and was thus normalised out to indicate the amount of volatiles driven off, excluding moisture.

The curves presented in Figure 5.3 relate directly to those in Figure 5.1 in the sense that the highest amount of volatiles was released from the 40 mm particles, followed by the 20 and 30 mm size fractions respectively. The percentage devolatilised displayed in Figure 5.3 was taken as the mass lost between 350°C and 900°C. The average percentage of devolatilisation was

included, and served as the basis of the temperature selection process for further investigation. From Figure 5.3 it can be observed that the average devolatilisation of 10%, 30%, 50% and 70% of the volatiles occurred at the respective temperatures of approximately 450°C, 550°C, 650°C and 750 °C respectively. Consequently, these temperatures were selected for the Fischer Assay analysis as well as the bulk char preparation phase of the project. These temperatures at which the coal will be investigated correlated well with that of Hatting, (2012), where 20mm particles were devolatilised at 450°C and 750°C.

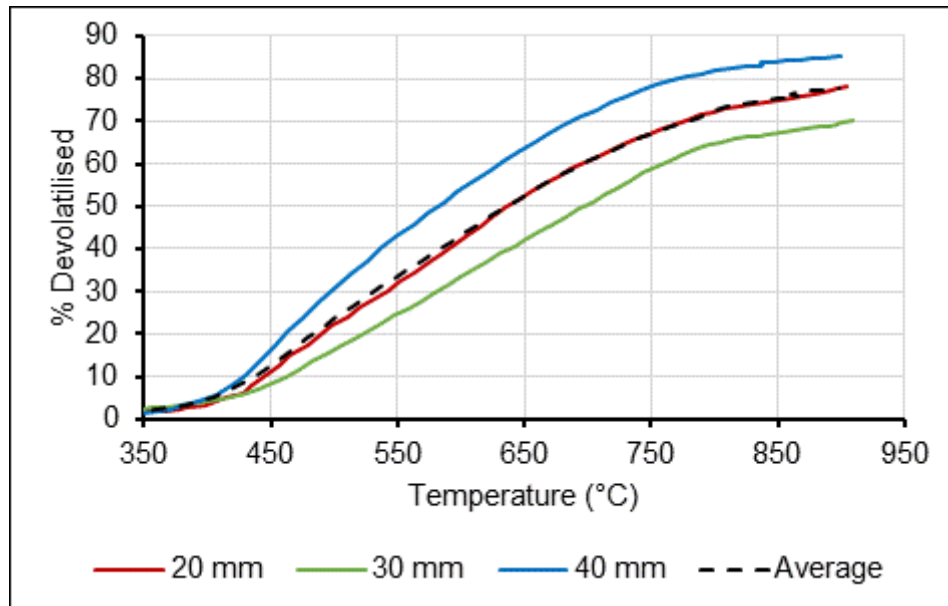


Figure 5.3: Percentage volatiles driven off during pyrolysis (dry-basis).

Yang *et al.*, (2013), studied the effects of pyrolysis temperature and particle size on sub-bituminous coal particles with sizes ranging from 2mm to 14mm at temperatures 500°C, 600°C, 700°C and 800°C, therefore confirming the range of temperatures selected in this study.

5.3 Pyrolysis product yields

Large coal particles, consisting of sizes with approximate diameters of 20mm, 30mm and 40mm, were selected according to the mercury submersion analyses as described in Section 3.5, and thereafter used to construct samples with a weight of $100 \pm 0.05\text{g}$. Prepared samples were subjected to the respective pyrolysis experiments from which the product yields were obtained, as discussed in Section 4.7; the results of which are subsequently discussed in the text to follow.

An overview of the products obtained from the devolatilization of the different particle sizes, each at their respective final temperatures (450°C, 550°C, 650°C and 750°C) is provided in Figure 5.4. It was found that the degree of devolatilization is dependent on the final pyrolysis

temperature, as the char yields decreased with an increase in temperature. Results of the char yields obtained from the Fischer Assay experiments compare well with that of the experiments conducted via thermogravimetric analysis as is visible in Figure 5.1 and Figure 5.3. Char yields from the Fischer Assay operation proved to be slightly lower for the greatest part of the experiments with the average difference being 2.2wt.% (Refer to Table C.1.1, Appendix C.1). The total volatile matter yield was observed to increase as the final pyrolysis temperature increased. Hatting, (2012), compared the devolatilization of coal particles with approximate diameters of 5mm and 20mm at temperatures of 450°C and 750°C and found an identical trend. This is in accordance with the findings of Ladner, (1988) and Yang *et al.*, (2013). According to Kandiyoti *et al.*, (2006); Anthony *et al.*, (1976) and Devanathan & Saxena, (1987), volatile yields are likely to diminish with increasing particle size, however Yang *et al.*, (2013), observed that at temperatures above 500°C that the volatile yields of different particle sizes tend to decrease initially, until a minimum is reached, after which it increased substantially. From Figures 5.1, 5.3 and 5.4 it can be observed that particle size had only minor effects on the degree of devolatilization in the case of this study.

The thermal conductivity of the coal may limit the propagation of heat from the outer surface of the coal particle inwards towards the centre, stressing the difficulty in assessing the effect of particle size on devolatilization (Suuberg, 1977; Hattingh, 2012). Volatiles produced during coal pyrolysis have to escape to the outer surface through the pore structure within each coal particle. This mitigation of volatiles through the particle may result in the cracking, condensing and polymerizing of the volatiles, along with the deposition of some amounts of carbon (Yang *et al.*, 2013). It is expected that these intra-particle secondary reactions might become significant at temperatures higher than 500°C, with an increase in particle size (Yang *et al.*, 2013). Particle fragmentation is an important factor that may also come into effect that influences volatile matter yields (Kandiyoti *et al.*, 2006; Yang *et al.*, 2013).

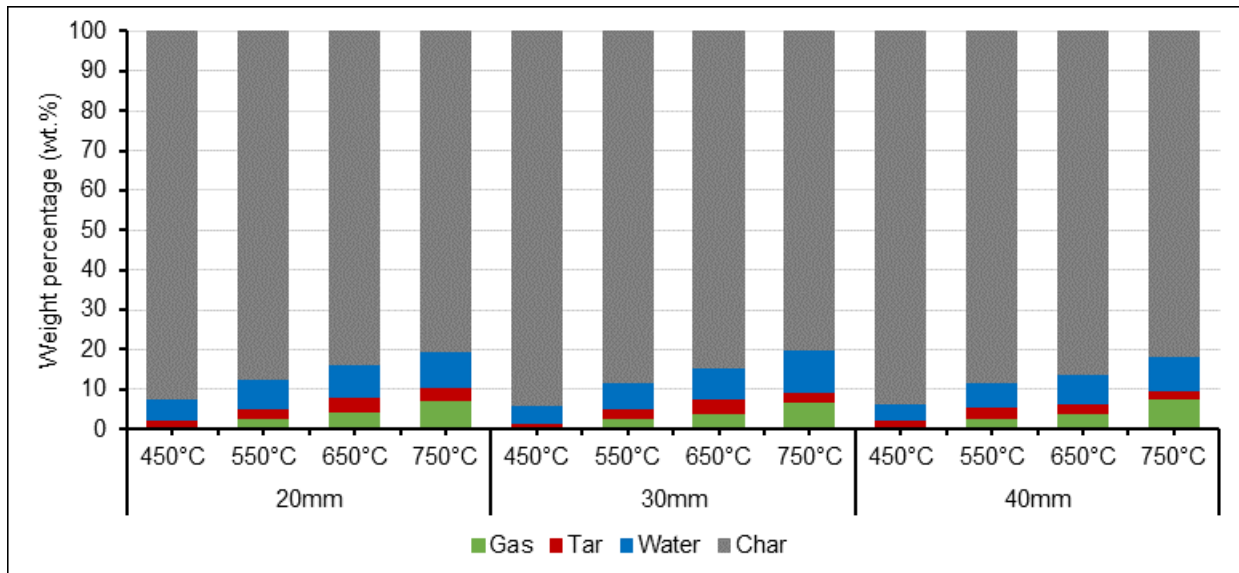


Figure 5.4: Pyrolysis product yields (as determined basis).

A comparison of the yields for the products obtained from pyrolysis experiments was formed in order to observe the trends thereof. The char, tar and gas yields were reported on a dry, mineral matter free basis (d.m.m.f.), while the water yields were reported on a mineral matter free basis (m.m.f.). Mineral matter was calculated using the Parr formula (refer to Appendix C.3 for detailed explanation). A correction factor for the amount of pyrolytic water, originating from the kaolinite present in the coal, was also calculated for the respective particle size fractions and is described in Appendix C.4. An estimation of the amount of pyrolytic water formed during devolatilisation was critical due to the relatively high mineral matter content of the coal investigated. As a result, it was anticipated that the total amount of moisture produced during pyrolysis would be higher than the inherent moisture from the proximate analysis. Large particles may also contain higher amounts of inherent moisture in the lump form due to the heterogeneity of large coal particles. Mineral matter contents for the 20mm, 30mm and 40mm individual particle size fractions were calculated to be approximately 25wt.%, 27wt.% and 26wt.% respectively, whereas the correction for mineral water formed was 1.5wt.% for the 20mm particles and 1.6wt.% for both the 30mm and 40mm particle sizes. Refer to Appendix C2 for all the pyrolysis products with experimental errors reported on an as determined basis (a.d.), as determined normalised (a.d. normalised) basis, dry basis (d.b.), mineral matter free basis (m.m.f.) and dry, mineral matter free basis (d.m.m.f.).

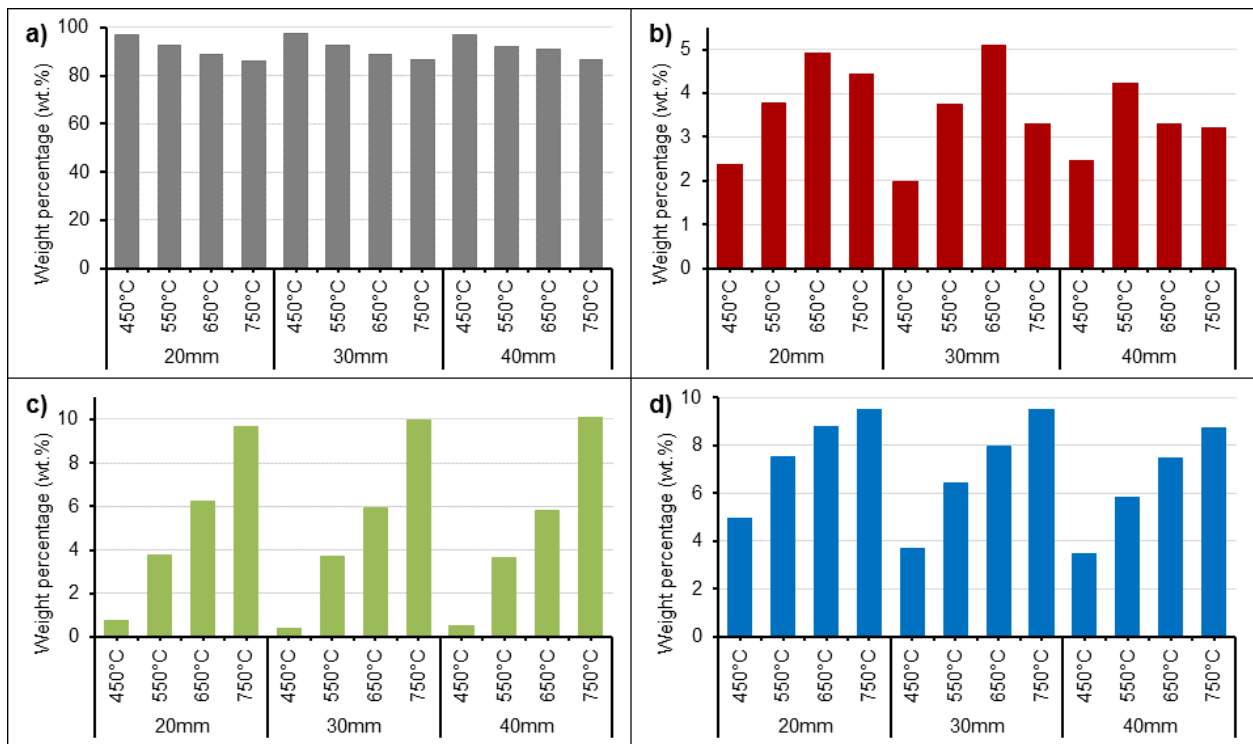


Figure 5.5: a) Char yields (d.m.m.f.); b) Tar yields (d.m.m.f.); c) Gas yields (d.m.m.f.) and d) Water yields (m.m.f.) for the 20 mm, 30 mm and 40 mm particles at 450 °C, 550 °C, 650 °C and 750 °C.

A comparison between the yields of the different pyrolysis products will be discussed in the following section.

5.3.1 Char yield

From Figure 5.5a above, it can be observed that the respective overall trends of the chars for all three particle size fractions are similar, with a decrease in weight percentage as the final pyrolysis temperature increases. This observation compares well with the findings of numerous other authors who also found a reduction in char yield with an increase in final devolatilisation temperature (Fu *et al.*, 1987; Hattingh, 2012; Kandiyoti *et al.*, 2006; Yang *et al.*, 2013). At 450 °C the char yields were 96.9wt.%, 97.7wt.% and 97.1wt.% respectively for the 20mm, 30mm and 40mm particles. A reduction of approximately 5wt% was observed at 550°C for all three particle sizes with the yields being 92.5wt.% for the 20mm and 30mm sizes vs. 92.1wt.% for the 40mm particles. The char yields at 650°C for the 20mm, 30mm and 40mm particle size fractions were 88.9wt.%, 89.0wt.% and 90.9wt.% respectively, and at 750°C the corresponding yields were 85.9wt.% for the 20mm particles vs. 86.7wt.% for the 30mm and 40mm size fractions. No significant differences with regards to variation in particle size were found for the char yields, although it was expected that the char yield would increase as particle size increases. Char yields of the 30mm size fraction were slightly higher than the yields for the 20mm particles at all temperatures, except for 550°C where a yield of 92.5wt.% was reported for both particle sizes.

This increase in char yield corresponds to a decrease in volatile yield with particle size, and may possibly be attributed to the occurrence of intraparticle secondary reactions. During primary pyrolysis, the volatiles produced have to pass through the pore structure within a coal particle to the outer surface, and it is during this movement that the volatiles might undergo cracking. The migrating volatiles may also condense and polymerize after cracking, which is followed by the deposition of some carbon. The extent of fragmentation is dependent on the particle size, the final pyrolysis temperature, as well as the inherent properties of the coal. The maceral/chemical composition of each individual coal particle may also be a factor contributing to the variation in volatile yields (Stubington & Sumaryono, 1984). At higher temperatures such as 700°C and 800°C, a large temperature gradient inside the coal particle is created, which results in a high inner pressure during pyrolysis (Hattingh, 2012, Yang *et al.*, 2013). This pressure gradient may lead to the formation of cracks and fissures, and the breaking of particles into smaller fragments, immediately releasing the inherent volatiles, inhibiting further intra-particle reactions. Even though the observed increase in char yield is only marginal, it correlated well with the work of Hattingh, (2012), who also found slight increases in char yields with increasing particle size of 5mm and 20mm lump coal particles. Yang *et al.* (2013) investigated particles classified as 2mm, 6mm, 10mm and 14mm size fractions, and also found slight increases in char yield with increasing particle size, however fragmentation of the larger particles was observed, which may have resulted in a variation of the trends. In the case of this study, no obvious trends for the 40mm particle size fraction were observed with regards to char yield in comparison to that of the other two size fractions. However at 550°C, the char yield of the 40mm particles was marginally lower (92.1wt.%) when compared to the char yields for the 20mm and 30mm particles (92.5wt.%). In contrast, at 650°C, the 40mm particles yielded approximately 1wt.% more char in comparison to the other two size fractions. Fragmentation of different degrees was observed for the 40mm particles as displayed in Figure 5.6. Therefore, it could be established that the variations in char yields of the 40mm particles could possibly be attributed to fragmentation.

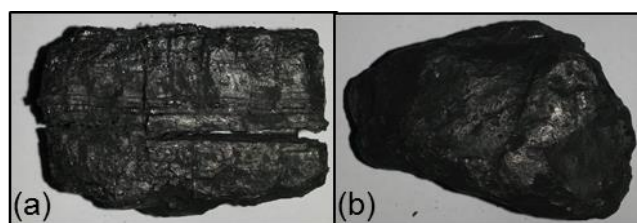


Figure 5.6: Particle fragmentation observed for two 40mm particles.

It is evident from Figure 5.6 that the extent to which the 40 mm lump coal particles fragmented differed greatly from one particle to the next. A great number of cracks and fissures can be observed for the particle in Figure 5.6a (devolatilised up to 750°C) in comparison to the particle displayed in Figure 5.6b (devolatilised up to 550°C). From the devolatilisation experiments, it

was perceived that large coal particles with natural hairline fractures (minute cracks and fissures) on the exterior surface experienced a greater degree of fragmentation than those particles with no external miniscule cracks. Accordingly, another possible factor that may well play a role in the manifestation of fragmentation during thermal decomposition is the natural physical state of the coal particles.

5.3.2 Tar yield

It is well-known that the total amount of volatile matter increases with increasing temperature, regardless of particle size (Kandiyoti *et al.* 2006; Ladner, 1988 and Smith *et al.*, 1994). Consequently, the increase in total volatile matter released in relation to an increase in temperature, (shown in Figure 5.5) agrees well with previous findings. Tar is a liquid product of coal pyrolysis that forms part of the condensable volatile matter that has evolved during pyrolysis. The general trends observed for the tar yields displayed in Figure 5.5b, indicate an increase in yields up to a maximum between temperatures 550-650°C, after which it started to decrease. This finding is analogous to that of previous authors (Cui *et al.*, 2006; Wang *et al.*, 2005) who found the tar yield reached a maximum at around 650°C. A study by Xiong *et al.*, (2010) also showed that the highest liquid tar yield appeared to be at temperatures ranging from 550°C to 650°C. The peak temperature at which the maximum amount of liquid tar is yielded may serve as an indication as to whether the tar has experienced secondary cracking reactions, and the rate thereof. As particle size is increased, the residence time of the primary volatiles within the pore structure of the particle also increases, therefore enhancing their reactivity with coal particle internals, as well as other volatiles. Overall, no significant differences with regards to particle size variation was observed, however at 750°C, the 20mm particles produced respectively 25% and 27% more tar than that for the other two size fractions. Maximum tar yields of 4.9wt% and 5.1wt% were produced at 650°C for the 20mm and 30mm particles respectively, whilst there was a decrease of approximately 16% in the maximum tar yielded (4.2wt.%) at 550°C by the 40mm particles. This observation that tar yields diminish with an increase in particle sizes is in accordance with that found by Hatting, (2012), who investigated two inertinite rich Highveld coals. A similar result was found in a devolatilisation study by Wang *et al.*, (2005). The lower maximum tar yield found for the 40mm particles at 750°C, in comparison to the other two size fractions, may be as a result of secondary reactions occurring during primary pyrolysis within the coal pore structure before the volatiles are able to escape in the event of fragmentation not being of great significance (Yang *et al.*, 2013). Hence the larger extent of fragmentation at higher final pyrolysis temperatures as discussed in Section 5.3.1.

5.3.3 Gas yield

It was apparent from Figure 5.5c, that the gas yields for all three particle size fractions increased monotonically as the final pyrolysis temperature was increased, irrespective of particle size. Similar observations have been made by Hattingh, (2012), Xiong *et al.*, (2010) and Yang *et al.*, (2013). Although it has been established by numerous authors (Devanathan & Saxena, 1987; Kandiyoti *et al.*, 2006), that an increase in particle size is accompanied by a decrease in volatile yield, no substantial decrease in the amount of gas yielded with increasing particle size could be detected. Seebauer *et al.*, (1997) also made a similar finding in a study during which particles ranging between 0.1mm and 2mm were thermally decomposed. This deviation from the consensual trend may be attributed to the limitations posed by the thermal conductivity properties, which limits the propagation of heat towards the core of individual coal particles.

5.3.4 Water yield

By observing the water yield trends displayed on a mineral-matter-free basis in Figure 5.5d, it is evident that the quantity of water produced, increases with an increase in final devolatilisation temperature from 450°C to 750°C. Roets, (2014), found a similar trend at temperatures between 520°C and 900°C in a devolatilisation study using the same experimental setup. When comparing the water yields in terms of the different particle sizes, a gradual decrease was noted as particle size increased, except for the 30mm particles at a temperature of 750°C, which yielded an identical quantity of water to that of the 20mm particles. The fact that a different number of particles were used for each particle size fraction (as the sample mass was constant at 100g) may have contributed to the variances in water yields obtained. The respective particles could have diverse inherent moisture contents due to the heterogenic nature of large coal particles. Another heterogenic aspect that could possibly influence the water quantity, is the amount of mineral matter present in each coal particle. Kaolinite, a large constituent of the mineral matter present in the coal, produces endothermic water upon transformation to form metakaolinite and water between the temperatures of 450°C and 800°C. Therefore it was imperative to calculate a correction factor for the amount of water originating from the kaolinite present in the coal. It should be noted that the correction factor for kaolinite present in the coal is already included in the results presented in Figure 5.5. Refer to Appendix C.4 for a detailed discussion thereof.

5.4 Char composition

The chars produced for all three particle size fractions (20mm, 30mm, 40mm) at the respective temperatures of 450°C, 550°C, 650°C and 750°C were analysed according to the proximate and ultimate analyses with the intent to form a comparative conclusion with regards to the properties

of the raw coal. Results from the analyses performed on the chars provide a better understanding of the effect that final pyrolysis temperature and particle size have on the quality of the remaining char residue.

5.4.1 Proximate- and ultimate analyses

Table 5.1 presents results for the proximate and ultimate analyses of the respective chars, and from which logical trends can be observed. Volatile matter (d.a.f.) decreased, while fixed carbon (d.a.f.) increased for all chars as final pyrolysis temperature was increased from 450°C to 750°C, which is the typical of a pyrolysis process as higher temperatures favour the release of volatile matter (Kandyoti *et al.*, 2006). This finding is consistent with that obtained by numerous authors (Bunt *et al.*, 2012; Chabalala *et al.* 2011; Hattingh, 2012).

The fuel ratio is a useful parameter regarding ignitability, flame quality and how rapidly the fuel will burn out, and is dependent on the quantities of the volatile matter and fixed carbon. The fuel ratio of the raw coal particles are 2.3 for both the 20mm and 40mm particles, while the 30mm size fraction has a slightly lower value of 1.8. As expected, there is an increasing trend for the fuel ratio with increasing temperature for all three particle size fractions. This increase could be attributed to the fact that the devolatilised volatile yield increases with higher temperatures, thus resulting in an increase in fixed carbon content. Higher fuel ratios lead to higher amounts of energy that can be obtained from a carbon conversion process, such as combustion or gasification (Hattingh, 2012), however the fuel may also be more difficult to ignite in comparison to a fuel with a lower fuel ratio- i.e. for 20mm chars produced at 750°C (FR of 9.6) will most likely take longer to ignite than chars produced at 450°C (FR of 3.2), but it will burn for a longer period (Shen *et al.*, 2009; Su *et al.*, 2001). Fuel ratios in Table 5.1 displayed a decreasing trend with increasing particle size, where the values for the 40mm particles were markedly lower than that of the 20mm particles.

The calorific value of coal is the heat produced through the combustion of a unit quantity of coal, via a bomb calorimeter, in the presence of oxygen and under specific conditions (ISO 1928). Trends for the 20mm and 30mm particle size fractions were very similar, where the calorific values increased along with final pyrolysis temperature, whereas that of the 40 mm particles only showed a notable increase at 750°C. The calorific values coincide with the fuel ratios displayed in Table 5.1, which also indicates an increase for both 20mm and 30mm particles, and with only a slight decrease for 40mm chars produced at 550°C, followed by an increase thereafter. In addition the calorific value, volatile matter and fixed carbon may be utilised to classify coal according to rank (ASTM-D388). Classification of the chars was done with the means to indicate the effect that devolatilisation to various extents have on the rank of fuel. Char rank was expected to increase with an increase in final pyrolysis temperature, and from

Table 5.1 it is clear that the char rank increased from the coal being classified as a medium rank C coal up to anthracite.

It is visible from Table 5.1 that the ash content of the respective chars had a positive relationship towards final devolatilisation temperatures, hence the higher ash contents for chars exposed to higher temperatures. This increase in ash content correlated with the findings of Roets *et al.*, (2014) and is a typical behavioural trait of raw coal being devolatilised (Hattingh, 2012). Although not significant, a slight decrease was observed for the 20mm particles at 550°C followed by an increase.

From results of the ultimate analysis presented in Table 5.1 and Figure 5.7, it is clearly visible that the carbon content increases as final pyrolysis temperature is increased, whereas the opposite is observed for the hydrogen and oxygen. The carbon increase is linear to the fixed carbon content, as well as the fuel ratio obtained from proximate analysis of the respective chars. In addition, these changes are also reflected by the atomic H/C and O/C ratios determined from the ultimate analysis that followed a decreasing trend as temperature increased. This observation is in accordance with that of Hattingh, (2012). Jones *et al.*, (1999), Roets *et al.*, (2014) and Wang *et al.*, (2013). For the 20mm and 30mm particles, the oxygen declined relatively gradually between the temperatures of 450°C and 750°C, however oxygen was retained at approximately 11wt.% by the larger size fraction (40mm) up to 650°C, followed by a rapid decrease at 750°C to a weight percentage of 5.7wt.%. Minor differences regarding carbon, hydrogen and oxygen were observed in relation to particle size, where the only notable difference is the oxygen content of the 20mm particles at 750°C, i.e. which is respectively 60% and 54% less than that of the other two particle size fractions at the same temperature. Nitrogen remained relatively constant throughout devolatilisation for all three particle size fractions at approximately 2wt.%, which is similar to that of the raw coal.

Table 5.1: Proximate and ultimate analyses results.

Analyses	Unit	20mm				30mm				40mm			
		450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
Proximate analysis (Dry basis)													
Ash	wt.%	28.7	27.1	31.5	36.4	28.1	27.3	30.4	37.2	23.4	30.5	27.4	31.9
Volatile matter (VM)	wt.%	16.9	13.6	7.1	6.0	16.4	11.8	8.2	6.6	16.5	17.3	12.5	7.6
Fixed carbon (FC)	wt.%	54.5	59.3	61.4	57.6	55.5	60.9	61.4	56.1	60.1	52.2	60.1	60.5
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Fuel ratio (FC/VM)		3.2	4.4	8.7	9.6	3.4	5.1	7.5	8.5	3.6	3.0	4.8	7.9
Proximate analysis (Dry, ash free basis)													
Volatile matter (VM)	wt.%	23.6	18.7	10.3	9.4	22.8	16.3	11.8	10.6	21.5	24.9	17.2	11.2
Fixed carbon (FC)	wt.%	76.4	81.3	89.7	90.6	77.2	83.7	88.2	89.4	78.5	75.1	82.8	88.8
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Coal classification according to ASTM-D388 (Moisture, mineral-matter-free basis)													
Gross calorific value	MJ/kg	31.3	31.6	33.6	34.3	31.1	32.3	33.8	33.8	31.7	31.1	31.7	33.1
Classification		C	C	A	A	C	C	B	A	C	C	C	A
Ultimate analysis (Dry, ash free basis)													
Carbon	wt.%	81.0	83.7	90.5	92.4	80.1	85.0	89.2	89.4	81.9	80.2	84.6	91.1
Hydrogen	wt.%	3.4	2.8	2.3	1.1	3.2	3.0	2.3	0.9	3.1	2.5	1.8	1.1
Nitrogen	wt.%	1.6	1.9	1.9	1.8	1.5	1.5	1.9	1.6	1.9	1.9	1.8	1.7
Oxygen (by difference)	wt.%	12.2	10.9	4.7	2.6	14.3	9.8	5.7	6.6	11.0	12.3	11.2	5.7
Sulfur (IR spectroscopy)	wt.%	1.8	0.7	0.6	2.1	0.8	0.7	0.9	1.4	2.0	3.2	0.6	0.4
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Atomic C/H ratio		2.02	2.56	3.27	6.99	2.08	2.36	3.26	7.98	2.20	2.73	3.90	7.28
Atomic H/C ratio		0.50	0.39	0.31	0.14	0.48	0.42	0.31	0.13	0.45	0.37	0.26	0.14
Atomic O/C ratio		0.11	0.10	0.04	0.02	0.13	0.09	0.05	0.06	0.10	0.11	0.10	0.05

***A** – Anthracite; **B** – Semianthracite; **C** – High volatile A bituminous coal

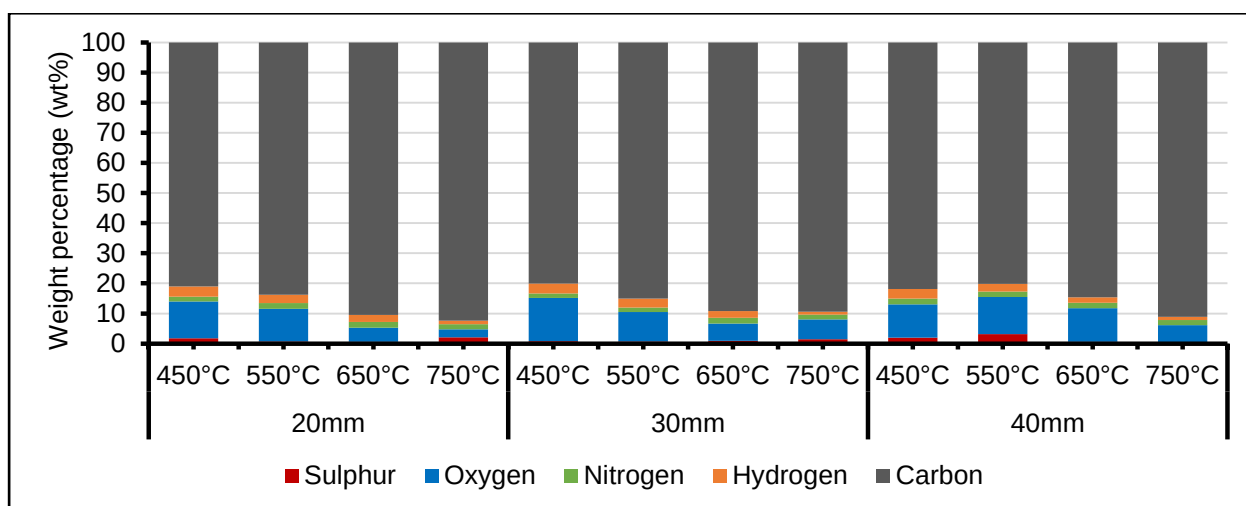


Figure 5.7: Ultimate analyses results for chars (dry, ash free basis).

It is difficult to make conclusive remarks concerning the sulfur content of the respective chars as the trends for the three particle size fractions varied. However, sulfur values of the 20mm and 30mm particles seemed to decrease initially until a minimum was reached, after which an increase was observed. The 40mm particles displayed the exact opposite trend, where sulfur values increased initially followed by a sharp decrease. This discrepancy could be linked to the fact that large coal particles are inherently heterogeneous, leading to inconsistencies in the quantities and composition of inorganic material present in each coal particle. Hattingh, (2012) also reported anomalies regarding the behaviour of sulfur during lump coal pyrolysis. Another factor that could possibly play a role, is that the mineral matter present in the coal structure have the ability to trap sulfur of which calcite and dolomite are examples (Chen *et al.* 1999; Sciazko & Kubica, 2002).

The atomic ratio of H/C may also serve as an indication of the ignitability of a fuel as hydrogen is highly flammable. As the final pyrolysis temperature is increased, higher hydrogen yields are devolatilised, consequently resulting in a reduction in H/C ratio, which coincides with increasing fuel ratio. Henceforth, 20mm chars produced at 450°C with a H/C ratio of 0.5 are expected to ignite easier than those produced at 550°C, 650°C and 750°C with H/C ratios of 0.39, 0.31 and 0.14 respectively, because less hydrogen is present. A lowering of the H/C ratio is indicative of a loss of aliphatic material and the conjoining of aromatic components (Charpenay *et al.*, 1992). The decreasing trend of the O/C ratio may be explained by the increase in quantities of CO and CO₂ (d.m.m.f.) evolved as the final devolatilisation temperature was increased. According to Furimsky & Ripmeester, (1983), and Charpenay *et al.*, (1992), the subsequent decrease in atomic ratios with increasing final pyrolysis temperature suggests that the molecular structure of the respective chars systematically shift to a more aromatic nature.

When compared to the properties of the raw coal, the fixed carbon, ash, fuel ratio and carbon all increased with an increase in final pyrolysis temperature, whilst volatile matter, hydrogen and oxygen reduced. The gross calorific values (d.a.f.) of all the chars produced at the respective temperatures were higher than that for the raw coal, and also increased with temperature.

5.5 Tar composition

Analyses of the coal derived tar produced during this investigation provided useful information regarding the quality of the tar, which has the possibility to be sold to petrochemical companies for further processing. Tar quality may have a financial impact on the low-smoke fuel production process discussed in Chapter 6. Tar composition was evaluated with the assistance of three analyses that consisted of the simulated distillation (Simdis), GC-MS/FID and SEC-UV analyses. Simdis and SEC-UV analyses provided useful information regarding the boiling point and molecular mass distributions of the tars produced, whereas GC-MS/FID analysed the amount of molecular species with boiling points lower than 300°C. The tars derived at all four devolatilisation temperatures (450°C, 550°C, 650°C, 750°C), and from all three particle size fractions of the Kwadela coal sample were analysed and the results are presented in the sections to follow.

5.5.1 Simulated distillation (SimDis)

The boiling point distributions for the tars derived at the respective temperatures for the 20mm, 30mm and 40mm coal particles are displayed in Figure 5.8.

From the boiling point distribution curves in Figure 5.8 it is evident that boiling was initiated at approximately 75°C and terminated at around 520°C. The range within which the tar fractions boiled coincide with the work of Hattingh, (2012), Roets *et al.*, (2014), and Van Niekerk & Coetzer, (2012). Small amounts of material (~3wt.%) was observed at temperatures below 100°C, which was due to removal of an aqueous layer containing water from the tar dissolved in dichloromethane. Separation of the aqueous layer from the organic material was performed prior to analysis via a separation funnel, therefore it is possible that some of the light components such as water in the aqueous layer may not have been completely separated, however the amounts are generally insignificant. Boiling point distributions at all four temperatures appeared to follow similar trends and correlate relatively well with that found for typical fossil fuel and waste-derived tars and oils (Bunger 1976; Hattingh, 2012; Karayildirim *et al.*, 2006; Li *et al.*, 2001; Roets *et al.*, 2014; Shie *et al.*, 2003). The compositions of the tars for the different size fractions derived at temperatures of up to 650°C seemed to be more consistent than that of the tars derived at 750°C, where the 40mm particle size is indicative of components with slightly lower boiling points throughout the distribution curve.

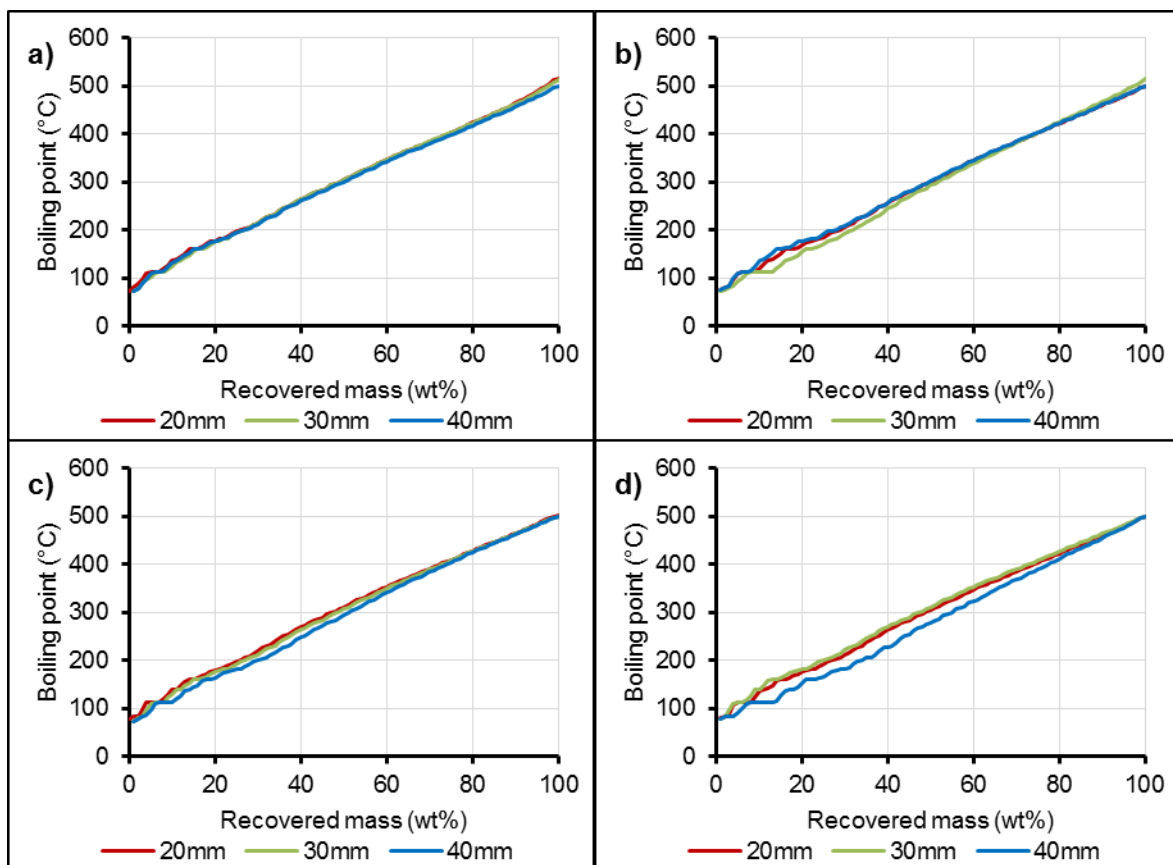


Figure 5.8: Boiling point distribution curves for 20mm, 30mm and 40 mm particles at temperatures a) 450°C, b) 550°C, c) 650°C and d) 750°C.

Further comparison of the tars necessitated an estimation of the weight-average boiling point (WABP) for the respective tars, and in addition the boiling range distributions were fractionated into distinct regions as discussed in Section 4.4.3. The typical cut fraction classification system was developed by Rand, (2003) and may be applied to crude oil refining products (Bakr, *et al.*, 1996; Gibbins-Matham & Kandiyoti, 1988; Rafenomanantsoa *et al.*, 1998). It is evident from Table 5.2 that, for all cases, that light vacuum gas oil (boiling point range of 343-455°C) was the most prominent fraction being approximately 10wt% higher than the fraction with the second highest presence, which was kerosene. Distribution of the boiling constituents between heavy naphta, kerosene and distillate fuel oil was relatively similar for each tar analysed, and variation with temperature showed little differences. However, for the 40mm particles, a slight shift towards the lighter boiling fractions was observed as final pyrolysis temperature increased (650°C and 750°C), which is in accordance with the findings of Roets *et al.*, (2014) and Hattingh, (2012). In this instance, where the recovery of lighter boiling constituents are favoured, may be as a result of thermal cracking at the higher temperatures, hence the increase in lower distillation fractions (Bunger, 1976; King *et al.*, 1978). Little variation was also noted with regards to particle size, with, once again, only the 40mm size fraction showing a minor shift towards the lower boiling range at 650°C and 750°C. Tar produced for the 30mm particles

displayed similar behaviour at a devolatilisation temperature of 550°C in comparison to the 20mm size fraction. From Table 5.2 it can be observed that the amount of tar contained in each cut fraction was calculated per 100g coal on a dry, mineral-matter-free basis. This was done with the intent to provide further insight concerning the compositional properties of the coal.

Throughout the investigation, the WABP ranged consistently between the temperatures of 290°C and 310°C, except for the 40mm particles devolatilised at 750°C, which was estimated slightly lower at 282°C. The WABP has been noted to be reliant upon the trend of the boiling point distribution as it was found to decrease in the event of a shift towards the lighter boiling range (Hattingh, 2012; Roets *et al.*, 2014). Consequently, the WABP was observed to be greatly influenced by heavy vacuum gas oil, light vacuum gas oil and distillate fuel oil, where the greatest reductions were observed for the 40mm particles at 750°C. The 30mm particles devolatilised at 550°C once again displayed a similar trend.

Table 5.2: Boiling point distributions for derived tars based on crude oil fractions.

Boiling point range (°C)			g/100 g coal		g/100 g coal		g/100 g coal		g/100 g coal
		wt.%/°C	(d.m.m.f.)	wt.%/°C	(d.m.m.f.)	wt.%/°C	(d.m.m.f.)	wt.%/°C	(d.m.m.f.)
		450°C		550°C		650°C		750°C	
20mm									
Medium naphta	79-121	7	0.16	8	0.29	7	0.33	7	0.30
Heavy naphta	121-191	16	0.38	17	0.62	16	0.75	16	0.68
Kerosene	191-277	19	0.45	18	0.66	18	0.85	18	0.76
Distillate fuel oil	277-343	17	0.40	15	0.55	16	0.75	16	0.68
Light vacuum gas oil	343-455	28	0.66	29	1.06	30	1.41	30	1.27
Heavy vacuum gas oil	455-566	13	0.31	13	0.48	13	0.61	13	0.55
IBP (°C)		73		75		76.8		80.6	
WABP (°C)	100-550	301		299		300		304	
FBP (°C)		516		501		502		502	
30mm									
Medium naphta	79-121	8	0.16	12	0.45	7	0.35	6	0.19
Heavy naphta	121-191	15	0.29	16	0.59	16	0.79	15	0.47
Kerosene	191-277	18	0.35	17	0.63	18	0.89	19	0.59
Distillate fuel oil	277-343	17	0.33	15	0.56	16	0.79	16	0.50
Light vacuum gas oil	343-455	29	0.57	26	0.97	29	1.44	30	0.94
Heavy vacuum gas oil	455-566	13	0.25	14	0.52	14	0.69	14	0.44
IBP (°C)		73		73		73		78.6	
WABP (°C)	100-550	304		293		306		310	
FBP (°C)		517		518		500		500	
40mm									
Medium naphta	79-121	7	0.17	7	0.29	9	0.29	13	0.48
Heavy naphta	121-191	16	0.39	16	0.67	17	0.54	17	0.62
Kerosene	191-277	19	0.47	19	0.80	18	0.58	18	0.66
Distillate fuel oil	277-343	17	0.42	16	0.67	15	0.48	15	0.55
Light vacuum gas oil	343-455	29	0.71	29	1.22	28	0.90	26	0.95
Heavy vacuum gas oil	455-566	12	0.29	13	0.55	13	0.42	11	0.40
IBP (°C)		73		75		73		76.8	
WABP (°C)	100-550	301		302		295		282	
FBP (°C)		501		502		502		501	

5.5.2 Gas chromatography-mass spectrometry and-flame ionization detection (GC-MS and GC-FID)

As discussed in Section 4.5.2, the GC-MS/FID analyses are expected to provide useful information regarding the low molecular weight hydrocarbon species present in the tar fractions. Only the species with boiling points lower than 300°C (~50%) will however be identified, hence the confinement to lower molecular weight compounds. In order to form a comparison between all the derived tars, it was necessary to classify the detected species into different molecular families as presented in Table 4.8. Data obtained from the GC-MS/FID analysis are semi-quantitative, and results were normalised on a solvent-free basis to a 100wt.% of the sample analysed. Accordingly the results were classified into molecular families based on those provided in Table 4.8, Section 4.4.2.

From the results presented in Table C.5.1, Appendix C.5, it is clearly visible that the largest constituents of molecular families for all the tars analysed were mixed aliphatic and aromatic compounds, alkyl-phenols and aliphatic compounds. This finding correlates well with the work of Van Niekerk & Coetzer, (2012), where tars were derived through pyrolysis of Permian-aged South African coal (particle sizes ranging between 1.7mm and 19mm) with high inertinite content. For tars derived from the Kwadela coal (also inertinite rich) of different sizes, the mixed aliphatic and aromatic compounds was the largest, except for the tar captured from the devolatilisation of the 40mm particles at 450°C, where the alkyl-phenols were the most predominant molecular family. It has been said that the predominance of aromatics and their oxygenated compounds such as phenols and cresols are typical for tars derived from high-rank coals, while tars from lower rank coals will display a distinguishable series of n-alkane homologues ranging between C₁₁ and C₂₈ (Casal *et al.*, 2008). No clearly visible trends for the mixed aliphatic and aromatic compounds with variation in particle size and temperature could be observed, which may be attributed to co-elution. Therefore, it is suggested that GC-GC-MS analysis is used in future investigations in order to prevent co-elution.

5.5.3 Size exclusion chromatography (SEC-UV)

Size exclusion chromatography is a useful analytical technique that has been widely used to estimate the molecular weight distributions of coal derived liquids over a wide molecular size range (Herod *et al.*, 1996). Results obtained from the SEC analysis are presented in Figure 5.9 and Table 5.3. Refer to Figure C.5.1 and Figure C.5.2, Appendix C.5 for elution time and molecular weight distribution curves for all of the generated tars.

Figure 5.9 and Table 5.3 portrays a comparison of the heavy vs. light components detected by the SEC analysis for the tars related to the different particle sizes derived at the four temperatures investigated. The molecular weight remained relatively constant for all instances with only minor differences being observed with reference to final pyrolysis temperature and particle size. Molecular weight increased slightly for the 20mm and 30mm fractions up to a maximum after which a small decrease was noted, whereas tar molecular weight derived from the 40mm particles decreased with an increase in final pyrolysis temperature.

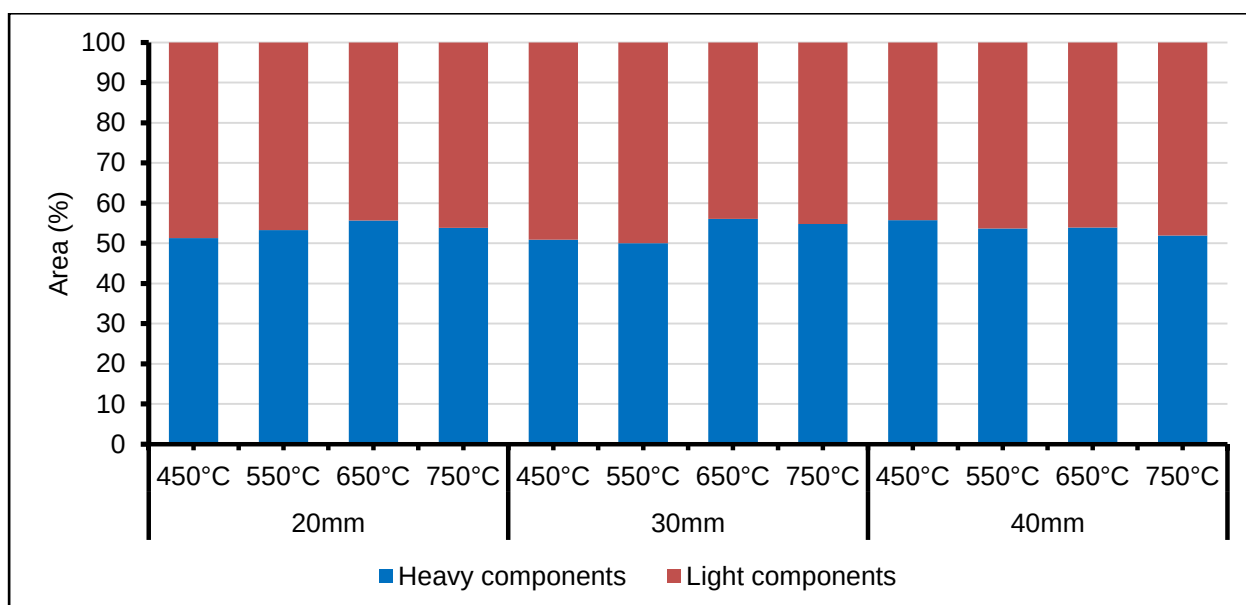


Figure 5.9: Heavy- and light component distribution of tars according to the SEC analysis.

It is clear from Figure 5.9 that the heavy components constituted slightly larger portions (~53%) of the respective tar samples analysed, resulting in higher overall molecular weights. This is in accordance with the findings of Van Niekerk and Coetzer, (2012), and is in agreement with results from the Simdis analysis which indicated that the tars consisted largely of higher boiling point fractions. As final pyrolysis temperature is increased, secondary tar cracking reactions become more apparent, thus resulting in a reduction in molecular weight at the higher temperatures, and is especially noted for the 40mm size fraction (Adegoroye *et al.*, 2004). In relation to particle size variation, an increase in molecular weight was observed for the tars derived at 450°C and 550°C. The higher temperature tars (650°C and 750°C), in contrary, experienced a reduction in molecular weight. The increase in molecular weight observed for the two lower temperature tars suggests that secondary tar cracking reactions were not highly favoured, although the differences are relatively small. At the higher devolatilisation temperatures (650°C and 750°C), the possibility exists that tar decomposition was controlled by an increased rate of cracking. It is important, however to note that NMP was used as eluent, and as a result thereof, aliphatic species could not be detected due to their low solubility in NMP (Herod *et al.*, 2007). From the results tabulated in Table 5.3, it is clearly visible that all the tars generated, consisted of components within the molecular size range of 25Da to 5564Da, and is in accordance with the observations made by numerous other authors (Adegoroye *et al.*, 2004; Hattingh, 2012; Lázaro, *et al.*, 1997; Millan *et al.*, 2005).

Table 5.3: Summary of SEC results for tars derived from Kwadela coal.

Component property	450°C			550°C		
	20mm	30mm	40mm	20mm	30mm	40mm
Molecular mass range (Da)	25-5564					
Heavy component peak max. (Da)	420	424	427	437	428	432
Light component peak max. (Da)	219	219	219	229	227	226
Light components (Area%)	48.7	49.1	44.2	46.7	50.0	46.3
Heavy components (Area%)	51.3	50.9	55.8	53.3	50.0	53.7
	650°C			750°C		
Molecular mass range (Da)	25-5564					
Heavy component peak max. (Da)	443	430	430	426	431	428
Light component peak max. (Da)	231	227	229	228	228	226
Light components (Area%)	44.3	43.9	46.1	46.2	45.2	48.1
Heavy components (Area%)	55.7	56.1	53.9	53.8	54.8	51.9

Heavy and light component peak maxima for all tars were relatively constant for all tars at ~430Da and ~225Da respectively. Similar findings from previous investigations have been made where coal tar was also derived via pyrolysis at relatively analogous temperatures (Hattingh, 2012; Li *et al.*, 1993; Roets, 2014). The heavy component peak maximum for the 20mm and 40mm fractions shifted up with an increase in temperature up to 650°C, followed by a slight decrease. The 30mm particle size derived tar displayed a positive monotonic increase with pyrolysis temperature, however the changes are of little significance. Results from previous studies investigating tars derived from gasification and devolatilisation indicated similar increases in heavy component maxima (Adegoroye *et al.*, 2004; Mokoena *et al.*, 2008). Similar trends were observed for the light component peak maxima.

5.6 Gas composition

As outlined in Section 4.4.4, the gas composition of the various gas products captured during pyrolysis experiments was determined with the help of quantitative gas chromatography (GC) analyses. Calibration of the apparatus was conducted with two calibration gas standards; a refinery gas standard with compositional properties typical of gaseous components evolved during coal pyrolysis, and another standard consisting of approximately 20mol.% CO and CO₂ respectively with N₂ as the balance. Refer to Figure C.6.1, Appendix C.6 for calibration curves generated for the GC used in chromatography analyses of the evolved gases. Results obtained from the GC analysis were reported on a N₂, Ar and O₂ free basis. According to previous studies, the most predominant gas species evolved during coal pyrolysis include H₂, CO, CO₂

and CH₄, however other gaseous components such as C₂H₄, C₂H₆, C₃H₆, C₃H₈ are also commonly found in coal derived gas (Fuentes-Cano *et al.*, 2013; Gómez-Barea *et al.*, 2010; Reichel *et al.*, 2013; Zhang *et al.*, 2010). In some cases C₄ hydrocarbon gases have been detected that includes species such as butane, iso-butane and n-butane, however in this study C₄s were rarely identified throughout the pyrolysis of lump coal. SO₂ was not measured by the GC during compositional analysis of the pyrolysis gas captured in the gas bags due to an equipment constraint at the time.

Table 5.4: Molar composition of gas formed during pyrolysis.

Molar composition of evolved gas (mol.%)				
20mm				
Component	450°C	550°C	650°C	750°C
H ₂	8.8	23.2	35.1	43.7
CH ₄	31.6	28.5	28.9	23.0
CO	15.1	13.9	13.1	15.6
CO ₂	37.6	28.6	18.2	14.6
30mm				
H ₂	10.4	24.2	34.6	45.1
CH ₄	28.3	31.3	30.2	19.7
CO	14.4	12.0	13.1	17.0
CO ₂	41.7	25.9	17.1	16.2
40mm				
H ₂	9.8	22.8	36.1	44.3
CH ₄	30.4	40.0	29.3	24.2
CO	14.8	10.9	12.4	13.9
CO ₂	37.8	17.4	17.9	13.9

Evidently (from Table 5.4), the main gas species identified via GC analysis during the investigation of the Kwadela coal sample consisting of various size fractions were H₂, CO, CO₂ and CH₄ (Table 5.4), and consistent with the findings of other authors (Fuentes-Cano *et al.*, 2013; Gómez-Barea *et al.*, 2010; Reichel *et al.*, 2013; Yang *et al.*, 2013; Zhang *et al.*, 2010; Zhang *et al.*, 2015). A considerable shift in gaseous compositional yields was noted for the main gas components as the final devolatilisation temperature increased, while effects from particle size were relatively insignificant. The only irregularity observed with variation in coal particle size was that of the 40 mm particles pyrolysed at a temperature of 750°C. Quantities observed of the dominant gases present in the order of decreasing amounts were established to be CO₂>CH₄>CO>H₂, for experiments conducted at 450°C, H₂>CH₄>CO₂>CO for devolatilisation at 650°C, and H₂>CH₄>CO>CO₂ for experiments conducted at 750°C. At 550°C, gas amounts captured from the 20mm and 30mm fractions were in the order of CH₄>CO₂>H₂>CO as opposed to

$\text{CH}_4 > \text{H}_2 > \text{CO}_2 > \text{CO}$ for the 40mm particles. From Figure 5.10 it is clear that the yields of the four main gas components all increased as final pyrolysis temperature was increased, while other gas species reported in Figure 5.10, showed minor differences only; all of which will be discussed in the following sections. Refer to Appendix C.6 for the molar and weight compositional data as well as the relevant experimental errors on repeatability as the detailed discussion in this chapter is based on molar yields as well as gram gas species produced per gram coal (d.m.m.f.).

5.6.1 Hydrogen (H_2) yield

It is apparent from both Table 5.4 and Figure 5.10a that minimal hydrogen evolution occurred at the lowest devolatilisation temperature of 450°C, after which a sharp increase was observed as the temperature increased. At 750°C, H_2 constituted the largest portion of the molar composition (~45mol%) irrespective of particle size, stating its significance at higher pyrolysis temperatures. Previous authors made similar findings with regards to an increase in final pyrolysis temperature (Chen *et al.*, 2010; Fuentes-Cano *et al.*, 2013; Khan, 1989, Xiong *et al.*, 2010; Yang *et al.*, 2013). The H_2 evolved at the lower temperatures (450°C and 550°C) is thought to be as a result of dehydrogenation through the scission of weak aliphatic (C-H or O-H) bonds (Smith *et al.*, 1994; Zhang *et al.*, 2010). In addition, the significant increase in H_2 yield observed during higher temperature pyrolysis can be ascribed to the cracking of C_4 and long-chain hydrocarbons in which H_2 is released, particularly above 725°C where CH_4 becomes inherently unstable (Khan, 1989; Yang *et al.*, 2013). The re-arrangement and condensing of aromatic structures of the formed chars may also contribute to the formation of H_2 (Cypress & Bettens, 1989; Siva *et al.*, 2013; Uzun *et al.*, 2007). No conclusive remarks could be made with regards to variances in particle size as H_2 yields were relatively consistent throughout.

5.6.2 Methane (CH_4) yield

The CH_4 yields reported in Figure 5.10b appeared to increase by substantial amounts with increasing pyrolysis temperature, consistent with the work of Fuentes-Cano *et al.*, (2013), Hatting, (2012) and Roets, (2014). Once again little variation regarding particle size was found at all four devolatilisation temperatures. According to Charpenay *et al.*, (1996), the presence of CH_4 during thermal decomposition may be indicative of hydro-aromatic and/or aryl methyl group putrefaction. Although only low quantities of CH_4 are present at the lower temperatures (450°C and 550°C), it points to the decomposition and/or hydrogenation of methyl groups on the raw coal or evolved tars (Cui *et al.*, 2006). CH_4 yielded at high pyrolysis temperatures, can be associated with the cross-linking reactions of coal macromolecules and/or the cracking of saturated hydrocarbons (Cui *et al.*, 2006). From Figure 5.5 the tar yields were observed to increase up to a maximum temperature of between 550°C and 650°C followed by a decrease at

750°C. This reduction in tar yield has also been observed by previous authors who suggested it could be as a result of de-alkylation reactions linked to the possible decomposition of primary tars (during which CH₄ is formed) at devolatilisation temperatures higher than 600°C Fuentes-Cano *et al.*, 2013).

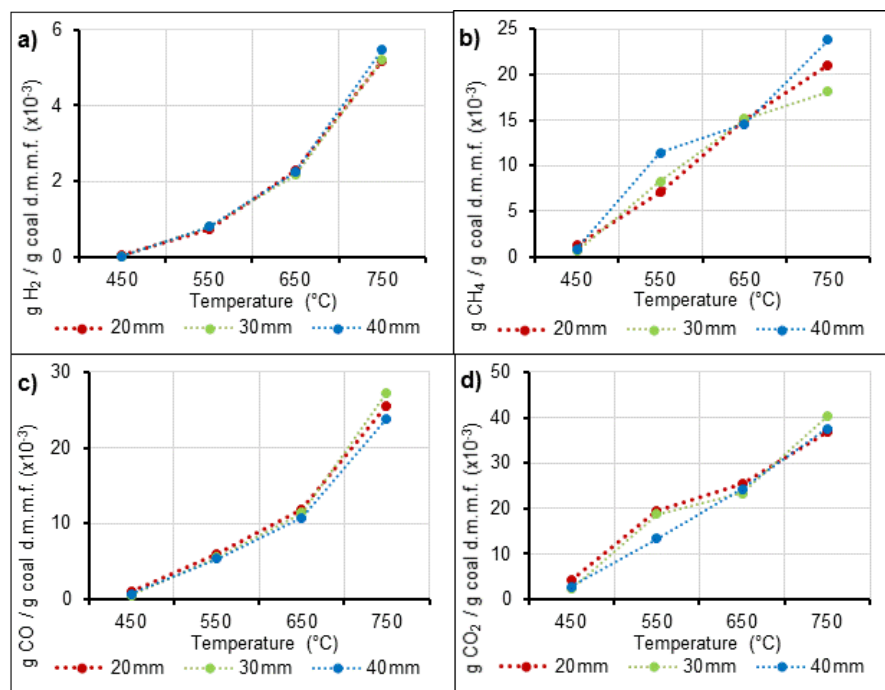


Figure 5.10: Main gas component yields with a) H₂, b) CH₄, c) CO and d) CO₂.

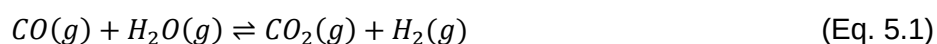
5.6.3 Carbon Monoxide (CO) yield

Increasing and almost identical tendencies can be observed for the CO yields of all three particle size fractions investigated with an increase in pyrolysis temperature. CO formation during the process of devolatilisation at different temperatures may occur as a result of numerous contributing factors that include: the decomposition of carbonyl groups at sub 400°C temperatures, and the oxygen heterocycles have been noted to rupture at temperatures in excess of 500°C (Zhu *et al.*, 1998). De-hydrogenation of hydroxyl groups and the initiation of CO₂ gasification at temperatures above 700°C (Smith *et al.*, 1994; Wang *et al.*, 2005; Zhu *et al.*, 2000). The quantity of CO expressed on a molar compositional basis remained relatively consistent with variations in both temperature and particle size.

5.6.4 Carbon Dioxide (CO₂) yield

CO₂ was the most predominant species (on wt.% basis) as displayed in Table C.6.2, Appendix C.6 for all instances in this investigation, and is in agreement with the findings of Yang *et al.*, (2013), who performed a similar devolatilisation study in which coal consisting of multiple particle sizes were investigated. According to Yang *et al.*, (2013) and numerous other authors,

the formation of CO₂ is mainly dependent upon the quantity and decomposition of carboxyl groups present in the coal (Cui *et al.*, 2006; Murakami *et al.*, 1997; Zhu *et al.*, 2000). Carboxyl groups are commonly converted to CO₂ during pyrolysis at low temperatures such as 450°C, and the decomposition of minerals such as carbonates (calcite and dolomite). The extensive increase in CO₂ yields with pyrolysis temperature may be indicative of carboxyl groups being present in large quantities in the coal, however the possibility that the water-gas shift reaction occurred also exists and is shown in Equation 5.1 below:



The presence of kaolinite in the coal may also come into play as water formed during the transformation process of kaolinite to form metakaolinite, therefore increasing the possibility of the water-gas shift reaction. Refer to Appendix C.2 for detailed explanation on the pyrolysis behaviour of kaolinite clay.

5.6.5 Other gas species

The gas species that constituted only small fractions of the total gas yields are reported in this section and include C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄s. Of these, displayed in Figure 5.11, it can be observed that the saturated alkane, C₂H₆, is present in the largest quantities for all the particle sizes (Roets, 2014). Although very small increases are noticeable for all three particle sizes with increasing pyrolysis temperature, the trend of the 40mm fraction varies from that of the 20mm and 30 mm particles which are relatively similar. For the C₂H₄, C₂H₆, C₃H₆, C₃H₈ species the 20mm and 30 mm increased almost linearly up to 650°C, after which it started to stabilise, and even minor decreases were noticed in the case of the 30mm particles. For the 40mm particles, however, the minor gaseous species increased up to 550°C, followed by a slight decrease/stabilisation up to 650°C from where a second increase was observed. Trends for the 20mm and 40mm fractions compared rather well for the C₄s, where the only obvious increase occurred between 650°C and 750°C. The 30mm particles displayed a similar trend to that of the 20mm and 30mm particles for the other four species. Dealkylation of substituted aromatic compounds, and the cracking of long-chain tars result in the formation of saturated hydrocarbons such as ethane and C₃s. In addition, the formation of unsaturated hydrocarbon gas species (alkenes) may be attributed to dehydrogenation reactions of relatively small saturated hydrocarbons as well as the decomposition of primary tars at elevated temperatures (Fuentes-Cano *et al.*, 2013; Hayashi *et al.*, 1992). According to Cui *et al.*, (2006), and Gavalas, (1982), alkenes and H₂ are products of alkane decomposition reactions as olefins are thermally stable at the higher temperatures. The slight increase of C₄ compounds between the temperatures of 650°C and 750°C could possibly be linked to an increase in the occurrence/rate

of secondary cracking reactions of the primary tars formed (Cui *et al.*, 2006; Fuentes-Cano *et al.*, 2013 Gavalas, 1982).

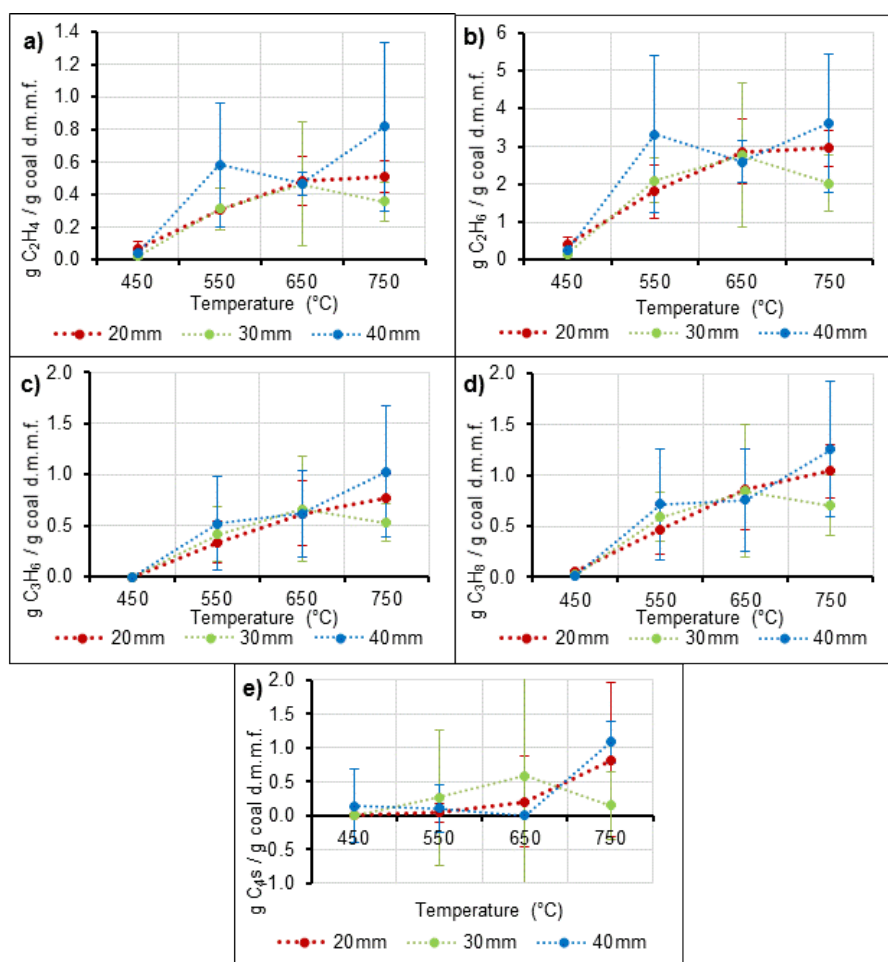


Figure 5.11: Other gas species with a) C_2H_4 , b) C_2H_6 , c) C_3H_6 , d) C_3H_8 and e) C_4S .

5.7 Summary

An in depth investigation into the pyrolysis behaviour of large coal particles was conducted in order to provide useful information regarding both the quantity and quality of the respective products resulting from low-smoke fuel production (devolatilisation). The extensive knowledge gained in this chapter in relation to the products resulting from a low-smoke fuel production process will be applied in the selection process of the ideal low-smoke fuel that may possibly replace coal as a household fuel. This ideal low-smoke fuel should lead to a reduction in air pollution during combustion, while still producing sufficient energy to fulfil the requirements of residents in Kwadela Township. The investigation performed in this chapter employed the NWU Fischer Assay experimental setup. Large coal particles of sizes 20mm, 30mm and 40mm were each devolatilised from room temperature up to four different final temperatures (450°C, 550°C, 650°C and 750°C). The char product obtained constitutes the largest portion of the products resulting from coal pyrolysis and is the low-smoke fuel desired in the study. Other products of

pyrolysis that include water, tar and gas were also investigated with the intent to possibly increase the economic viability of the low-smoke fuel production process.

Throughout this investigation it was found that final pyrolysis temperature was the predominant factor dictating the yield and quality of the respective products, whereas variance in particle size had only minor effects. Low-smoke fuel (char) yields decreased with increasing pyrolysis temperature, therefore indicating an increase in the degree of devolatilisation with temperature. Average char yields for all three sizes devolatilised at 450°C, 550°C, 650°C and 750°C were approximately 97wt.%, 93wt.%, 90wt.% and 87wt.% respectively, indicating a 10wt.% difference in char yield between the highest and lowest devolatilisation temperature. Fragmentation was observed for the 40mm particles at the higher devolatilisation temperatures (650°C and 750°C), however not consistently. As the char product quantity decreased with temperature, the volatile matter increased which is typical of a pyrolysis process. In general, the tar (d.m.m.f.) yields increased with temperature up to a maximum at temperatures between 550°C and 650°C, followed by a slight decrease. Gas (d.m.m.f.) and water (m.m.f.) yields both increased monotonically with increasing devolatilisation temperature.

Proximate analysis of the respective chars correlated well with the pyrolysis yields as the fuel ratio serves as a good relationship, taking into account the amount of fixed carbon and volatile matter. The fuel ratio therefore increased with increasing temperature, indicating that the coal devolatilised at higher temperatures may contain larger amounts of energy, however could be more difficult to ignite in comparison to fuels with a lower fuel ratio. Classification, based on coal rank, of the different low-smoke fuels was done via the ASTM-D388 method. Consequently the rank of the fuels was found to increase with temperature. Characteristics obtained from the ultimate analysis of the chars indicated that the atomic C/H ratio increased, while the O/C ratio decreased with increasing temperature. Inconsistencies in sulfur yields may possibly be attributed to particle variation as large particles are inherently heterogeneous.

Further analyses of the tar samples consisted of the Simdis, GC-MS and SEC-UV analyses, and it was found that both final pyrolysis temperature and particle size variation had only minor effects on the results thereof. From the Simdis analysis it was found that the weight average boiling point averaged at approximately 300°C, with the largest constituent of the tar being light vacuum gas oil, which is a high boiling point fraction. Results from the GC-MS analysis were used to classify the compounds in the tars according to molecular families, and indicated that the largest group was mostly represented by mixed aliphatic and aromatic compounds, followed by alkyl-phenols and aliphatic compounds. SEC analyses of the tars differentiated between heavy and light components, and found that the heavy components constituted a slightly larger fraction which resulted in higher overall molecular weights. Findings from the SEC and Simdis

are in agreement, as both are respectively indicative of heavier components and higher boiling point fractions being present in the largest quantities

Compositional analysis of the gases evolved during pyrolysis found that H_2 , CO , CO_2 and CH_4 was the four major components present throughout the investigation, with CO_2 being the largest constituent. Devolatilisation temperature seemed to have considerable effects on the H_2 and CO_2 yields produced, while particle size proved to be relatively trivial. The H_2 fractions increased significantly with increasing pyrolysis temperature, whereas the opposite trend was found for CO_2 present in the gas. The lower amounts of H_2 present in the chars produced at higher temperatures could lead to increased difficulty when these fuels are ignited during combustion, therefore the coal devolatilised at 450°C and 550°C (that still contain considerable amounts of H_2) may ignite with more ease.

CHAPTER 6: LOW-SMOKE FUEL CHARACTERISATION AND EVALUATION

6.1 Introduction

A crucial part of this study was to examine whether the devolatilised coal or so called “low-smoke fuels” (LSF/Char) do, in fact, result in less air pollution during combustion in comparison to raw coal. The chars combusted in this chapter were prepared according to the process described in Section 4.7, which is different from the chars discussed in Chapter 5 (Fischer Assay chars). The Fischer Assay experimental setup has a capacity of approximately 200g whereas the tube furnace used to prepare the chars used in combustion experiments has a capacity of 1000g. Due to time constraints and the fact that approximately 80kg of char was required for the combustion tests over and above that required for the Fischer Assay experiments, it necessitated that the tube furnace setup be used. Consequently, this chapter contains the results of an investigation to determine the viability of low-smoke fuel production, and the use thereof as a fuel on residential level. Anthracite has an inherently low volatile content, similar to that of the chars produced in this study and was therefore included in this section of the investigation. The raw coal, and anthracite, along with the low-smoke fuels produced are characterised in Section 6.2 according to proximate and ultimate analysis, as well as classified according to rank. Section 6.3 provides in depth information regarding emissions evolved during combustion of the different fuels evaluated, whereas practical parameters with which residents in Kwadela can associate with are discussed in Section 6.4, such as ignition time and the time to boil 1L of water. The findings of Sections 6.2-6.4 will form the basis of a selection process (provided in Section 6.5) in which one of the produced chars will be selected for further investigation in a techno-economic feasibility study to be presented in Chapter 7. It should be noted that anthracite fuel was used for comparative purposes only in this chapter, and will not be considered as a viable option to replace coal as a household fuel as it was not within the scope of this project. A summary is also included in Section 6.5, which forms part of the low-smoke fuel selection process.

6.2 Characterisation of fuels evaluated

Results obtained from the proximate and ultimate analyses of the various fuels evaluated in the combustion experiments are reported in Table 6.1. The fuels were also classified based on rank according to ASTM-D388 (similar to the classification in Section 5.4.1). It should be noted that the fuel labelled as “Anthracite” was classified as a semi-anthracite according to the ASTM-D388 method, which is evident from the high fixed carbon (86.8wt.% d.a.f.), calorific value (35.3MJ/kg m.m.m.f.) and low volatile matter content (13.2wt.% d.a.f.) reported for this fuel. The

anthracite relates reasonably well with the char produced at a pyrolysis temperature of 550°C with regards to volatile matter, however, the anthracite contains significantly less ash in comparison the other fuels. The sulfur content of the anthracite and char produced at 550°C is above the acceptable limits of South African coals which is normally less than 1.0wt.% (Milne, 2004; Thomas, 2002; Gönenç *et al.*, 1990). The exact origin of the anthracite sample is however unknown due to it being acquired locally in the town of Vanderbijlpark, situated approximately 100km south of Johannesburg. Organic sulfur clearly forms the largest constituent (1.24wt.%) of the total sulphur present in the anthracite sample, while pyritic sulfur was the predominant sulfur species present in the raw coal. Similar observations to that of the chars presented in Table 5.1, Section 5.4.1 were made for the devolatilised coal in relation to the trends of the fixed carbon (d.a.f.), volatile matter (d.a.f.) and fuel ratio; all increasing as final pyrolysis temperature increased.

Examining the ultimate analyses of the respective fuels, an increasing trend with temperature can be observed for the carbon, whereas the opposite occurred for both the hydrogen and oxygen. This is in accordance with the findings in Table 5.1, Section 5.4.1 as well as that of previous investigations (Hattingh, 2012; Jones *et al.*, 1999; Wang *et al.*, 2013). The atomic H/C and O/C ratios both decreased with increasing pyrolysis temperature which may indicate a slight increase in aromaticity of the chars (Furimsky and Ripmeester, 1983). Refer to Figure D.1.1, Appendix D.1 where the trends of the different components of the respective fuels obtained from the results of the ultimate analysis can be observed. The nitrogen content of the anthracite was respectively 0.9wt.% and 0.7wt.% higher than that present in the coal, and all the chars, except the char produced at 750°C which contains the same amount as present the coal.

The fuel ratio of the respective fuels was expected to increase as the pyrolysis temperature increased according to the in depth investigation of which the results indicated an increase in fuel ratio (refer to Table 5.1, Section 5.4.1). Given that the fuel ratio is the ratio of fixed carbon to volatile matter present in a fuel, it may be indicative of a fuel's ability to ignite, and therefore it is a good practical parameter when the behaviour of a fuel during combustion is being predicted. It has been said that fuels with a higher fuel ratio possibly have a larger quantity of energy that can be obtained during combustion, however the fuel may have a reduced ability to ignite (Shen *et al.*, 2009; Su *et al.*, 2001). According to the fuel ratios reported in Table 6.1, the order in which the fuels would ignite is Coal→Char-450→Char-550→Anthracite→Char-650→Char-750. The coal samples analysed in Chapter 5 were selected according to the density of the respective particles present in each sample, whereas that in Chapter 6 were only selected based on size and no separation process was employed. Consequently, variations in large particles may have resulted in the discrepancies regarding the fuel ratios.

Table 6.1: Proximate and ultimate analyses results.

Analyses	Unit	Anthracite	Coal	Char-450	Char-550	Char-650	Char-750
Proximate analysis (Air-dry basis)							
Inherent moisture	wt.%	0.9	2.8	1.3	1.3	1.1	1.0
Ash	wt.%	11.9	36.6	30.4	33.0	41.6	37.7
Volatile matter (VM)	wt.%	11.5	20.2	14.9	11.7	4.5	2.4
Fixed Carbon (FC)	wt.%	75.8	40.4	53.4	54.0	52.8	58.9
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0
Fuel ratio (FC/VM)		6.6	2.0	3.6	4.6	11.8	24.6
Total sulfur	wt%	1.47	0.82	0.72	2.00	0.57	0.64
Forms of sulfur (Air-dry basis)							
Pyritical sulfur	wt.%	0.22	0.490	-	-	-	-
Sulphatic sulfur	wt.%	0.01	0.077	-	-	-	-
Organic sulfur	wt.%	1.24	0.253	-	-	-	-
Proximate analysis (Dry basis)							
Ash	wt.%	12.0	37.7	30.8	33.4	42.0	38.1
Volatile matter (VM)	wt.%	11.6	20.8	15.1	11.9	4.5	2.4
Fixed Carbon (FC)	wt.%	76.4	41.6	54.1	54.7	53.4	59.5
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0
Proximate analysis (Dry, ash free basis)							
Volatile matter (VM)	wt.%	13.2	33.3	21.8	17.9	7.8	3.9
Fixed Carbon (FC)	wt.%	86.8	66.7	78.2	82.1	92.2	96.1
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate analysis (Dry, ash free basis)							
Carbon	wt.%	88.8	76.4	81.4	84.0	90.5	93.2
Hydrogen	wt.%	3.5	3.9	3.3	2.4	1.4	0.5
Nitrogen	wt.%	2.6	1.7	1.9	1.9	1.9	1.7
Oxygen (by difference)	wt.%	3.4	16.5	12.3	8.7	5.2	3.6
Sulfur	wt.%	1.7	1.4	1.1	3.0	1.0	1.0
Total	wt.%	100.0	100.0	100.0	100.0	100.0	100.0
Atomic H/C ratio		0.47	0.62	0.49	0.34	0.19	0.07
Atomic O/C ratio		0.03	0.16	0.11	0.08	0.04	0.03
Coal classification according to ASTM-D388 (Moisture, mineral-matter-free basis)							
Gross calorific value	MJ/kg	35.3	29.5	31.5	32.8	34.9	35.0
Classification		B	E	D	C	A	A

***A** – Meta-anthracite; **B** – Semi-anthracite; **C** – High volatile A bituminous coal; **D** – High volatile B bituminous coal; **E** – High volatile C bituminous coal

Consequently, the coal devolatilised at 450°C and 550°C respectively may serve as viable options to replace coal as both fuel ratios are relatively close to that of the coal. The order of ignition was an important factor taken into consideration during the selection process provided in Section 6.6. In order to assist with the selection process, it was necessary to conduct combustion experiments (results presented in Section 6.3) that will be used in conjunction with the fuel characteristics provided in this section to improve the accuracy of the selection.

6.3 Combustion results

As the main purpose of this study is to produce a fuel which not only results in less air pollution produced during combustion, but that is also practically viable for the residents of Kwadela

Township, it was necessary to perform a series of combustion experiments. As described in Chapter 4, Section 4.8, a Union 7 household coal stove was the appliance wherein combustion experiments of the fuels were conducted. The results regarding the emissions measured (NO_x , CO , CO_2 , SO_2 , TSP and VOC's) during the experiments obtained from the combustion of each individual fuel are discussed in this section. In principal, the combustion of coal consists of three basic stages: (1) Volatile matter is released as a result of heat being applied to the coal, (2) Released volatile matter is burned, and (3) Residual solid (char) remaining is combusted (Merrick 1984; Ralph and Bertrand, 1963). The burning process of volatile matter and coal char may occur simultaneously, sequentially or with overlapping depending on the combustion conditions (Merrick 1984; Ralph and Bertrand, 1963). The combustion process for the anthracite and coal derived chars (low-smoke fuels) investigated in this study are identical to that of the coal. Repeatability of the experimental setup was first established and will be discussed in the following section.

6.3.1 Repeatability

Repeatability of the combustion experimental setup was established by performing three identical experiments using the raw Kwadela coal as fuel. The emissions measured during repeatability experiments included NO_x , CO , CO_2 , SO_2 , TSP and VOC's, and a series of temperatures were also recorded over time to provide information regarding the temperatures within the combustion chamber as well as in the chimney. The experimental errors were determined within an 80% confidence interval (consistent with the method used to calculate the errors on repeatability of the in depth devolatilisation investigation in Chapter 5 of this study). Table 6.2 presents the experimental errors found during the repeatability experiments for combustion of coal in the Union 7 coal stove.

Table 6.2: Experimental error on repeatability for combustion experimental setup.

Emission measured	Error (% of average for three repeats)
NO_x	19
SO_2	27
CO	7
CO_2	29
TSP	12
VOC's	23

From Table 6.2, it can be observed that the experimental errors found for the coal combustion experiments were all below 30%, which is acceptable when taking into consideration the heterogeneous nature of lump coal. Although an attempt was made to keep the fuel packing

constant, it is still possible that inconsistencies could prevail as large coal particles are geometrically indifferent, which may have resulted in different combustion behaviours. The temperatures displayed in Figure 6.1 are indicative of relatively good repeatability being achieved after approximately 40 minutes since initiation of the respective experiments. The temperatures, however, fluctuated to a somewhat great extent which brings to mind the fact that ignition of the individual coal/fuel particles may play a significant role in the temperatures indicated by the respective thermocouples. It is possible that the flames from the gas burner followed a different pathway through the packed bed each time, thus resulting in the fuel bed igniting differently, and may possibly explain the anomalies observed for the temperatures recorded in Figure 6.1b and Figure 6.1c. However, the temperatures observed in Figure 6.1a and Figure 6.1d displayed relatively good repeatability. These two temperatures were respectively measured just below the top of the stove on top of which the pot containing 1L of water was placed, and that of the chamber approximately 5cm above the grid on top of which the fuel was packed.

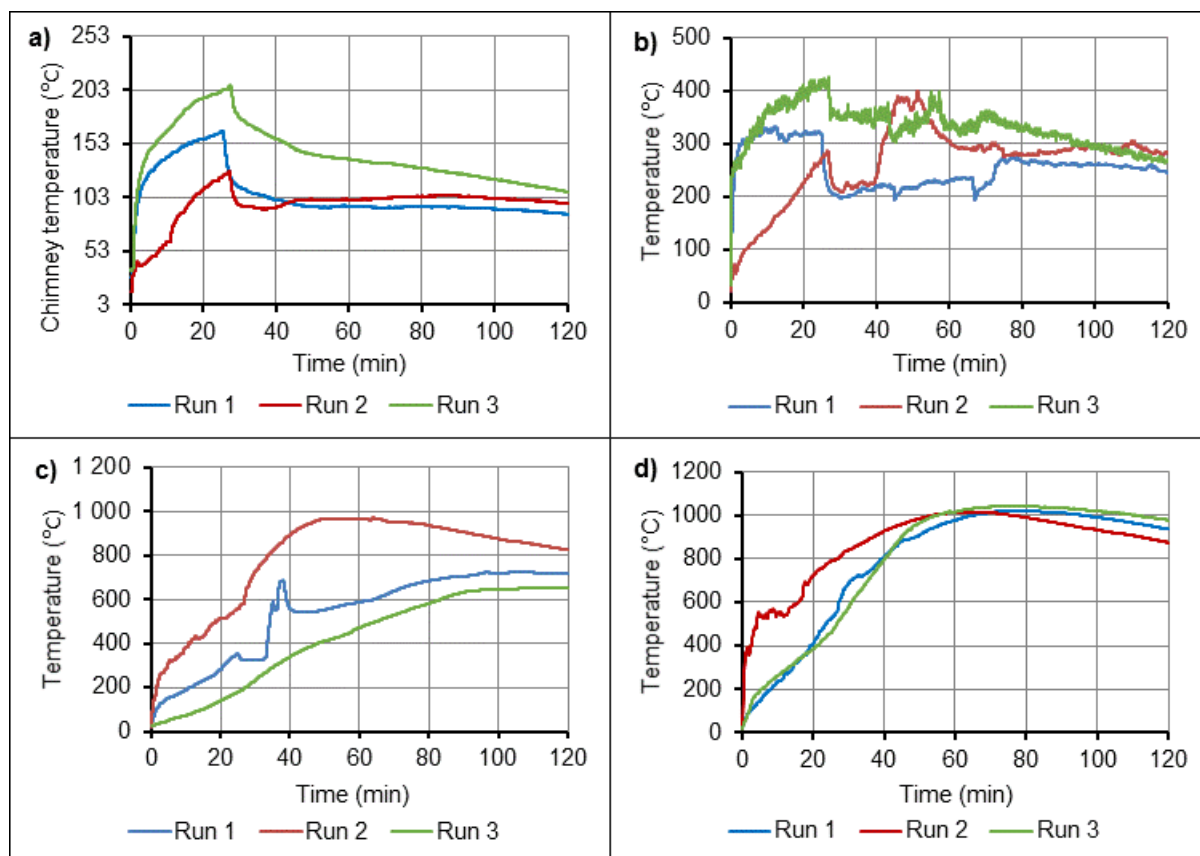


Figure 6.1: Coal combustion temperatures for repeatability with a) chimney temperature, b) top chamber temperature (20cm above grid), c) middle chamber temperature (10 cm above grid) and d) bottom chamber temperature (5cm above grid)

A summary of all the emissions quantified (mg/MJ) during combustion of the respective fuels are reported in Table 6.3.

Table 6.3: Summary of emissions measured during combustion tests.

Fuel	NO _x	SO ₂	CO	CO ₂	TSP (x10 ³)	VOC's (x10 ³)
Emission quantity (mg/MJ)						
Coal	12	98	746	6129	349	28
Anthracite	11	44	476	6012	84	4
Char/LSF-450	8	113	808	6281	85	6
Char/LSF-550	11	88	935	7507	75	3
Char/LSF-650	9	62	981	7593	89	3
Char/LSF-750	4	58	780	4724	65	2

The most notable reductions can be observed in terms of the TSP and VOC's produced for the anthracite and all four low-smoke fuels evaluated. CO₂ is clearly the largest constituent produced during combustion of all the fuels. In addition, Table D.4.1, Appendix D.4 provides the emissions quantified on a mg/kg_{fuel} basis. A detail discussion regarding the emissions produced during the combustion tests are provided in the text to follow. The graphs constructed in the sections to follow were done so with the use of the emissions produced on a mg/MJ basis as reported in Table 6.3.

6.3.2 Gas emissions

The gaseous components classified as gas emissions include NO_x, CO, CO₂, SO₂. Although CO₂ is a greenhouse gas, and associated with complete combustion, it is still included as part of the emissions. Due to the fact that LPG was used as the ignition fuel, it was necessary to measure the emissions resulting from LPG combustion in order to report the emissions resulting from the respective fuels on a LPG free basis. Refer to Table D.6.1, Appendix D.6 for exact quantities of emissions resulting from LPG combustion. All of the emissions discussed in this chapter are reported as a percentage of the emissions produced during coal combustion (LPG free) as reported in Table 6.3 and illustrated in Figure 6.2. CO₂ constituted the largest fraction of the gases evolved during combustion followed by CO, SO₂ and NO_x respectively. Results of the gaseous emissions obtained from Table 6.3 were normalised to coal, thus the quantities are expressed as a percentage of coal in Figure 6.1.

6.3.2.1 Nitrogen oxides (NO_x)

The emissions classified as oxides of nitrogen that are formed during coal combustion consist primarily of nitrogen oxide (NO), with nitrogen dioxide (NO₂) only contributing a small percentage per volume. Nitrous oxide (N₂O) constitutes the smallest fraction (few parts per million) of the NO₂ emissions during combustion of coal (US EPA, 1978; Acurex Environmental Corp. *et al.*, 1993). NO_x emissions produced during combustion of the anthracite and LSF-550 were similar to that of coal. Similar quantities were detected (~23% reduction) for both of the

chars produced at 450°C and 650°C respectively, while the amount of NO_x reduced significantly during combustion of LSF-750.

NO_x emissions are formed via three mechanisms: i.e. thermal NO_x, prompt NO_x and fuel NO_x, of which the thermal and fuel NO_x mechanisms are more significant in coal combustion. (Baukal, 2005). The formation of thermal NO_x is affected by four factors that include the peak temperature, N₂ concentration, O₂ concentration (or flame stoichiometry), and the time the fuel is exposed to the peak temperature (US EPA, 1978; US EPA, 1979). Consequently an increase in the peak temperature, O₂ availability and/or residence time at high temperatures will lead to increased NO_x presence in the evolved gas. From Figure 6.8c it is seen that the temperatures measured during combustion of the anthracitic fuel peaked at the highest values, and that the residence time at the high temperatures was relatively long in comparison to some of the other fuels. This observation may serve as an explanation for the extreme increase in NO_x emission produced during combustion of the anthracite. The formation of fuel NO_x is a result of the direct oxidation of inherent organic N₂ compounds within the fuel, and although insignificant for high-quality fuels such as natural gas or propane, the mechanism might become important during coal combustion as coal possibly contains large amounts of organic N₂. Refer to Appendix D.5 for a discussion on the three reaction mechanisms responsible for NO_x formation. With reference to the NO_x emissions it seems that all the chars produced may be viable options to replace coal as a household fuel.

6.3.2.2 Sulfur dioxide (SO₂)

Emissions in the form of oxides of sulfur (SO_x) are formed during coal combustion from the oxidation of sulfur within the fuel and are primarily converted into SO₂. It has been found that uncontrolled SO_x emissions largely depend on the sulfur content of the fuel combusted (Peer *et al.*, 1995). From Figure 6.2 it can be observed that the SO₂ from the anthracite was significantly less (~60%) than for coal, while the SO₂ produced by the char devolatilised at 450°C was approximately 20% higher in comparison to coal. The amount of SO₂ detected for coal devolatilised at 550°C was relatively similar to that of coal (~10% lower), and a reduction of approximately 40% was observed for the chars produced at 650°C and 750°C. The high SO₂ detected for Char-450 does not correlate with reference to the sulfur content from the proximate analyses reported in Table 6.1 (highest sulfur value is reported for Char-550), however it should be noted that large coal particles were investigated in this study and that particle variation (heterogeneity) may play an influential role. In support of this claim, Berkowitz, (1979) stated that the heterogenous nature of the macroscopic coal structure results in the term “coal” being broadly defined and that the solid material to which it is applied are mostly dissimilar than identical.

Pyrite (FeS_2) is often the main constituent of inorganic sulfur found in coal and decomposes according to the following reaction during pyrolysis (Attar & Hendrickson, 1982):



It was found that the rate of this reaction is fast between temperatures of 550°C and 600 C. This suggests that the highest amount of sulfur could possibly be detected from the char produced at 550°C (Attar, 1978) since elemental sulfur is also formed during the decomposition between 550°C and 600°C. This agrees with results for the total sulfur displayed in Table 6.1 that indicates the high SO_2 value detected for Char-550 in comparison to the other fuels.

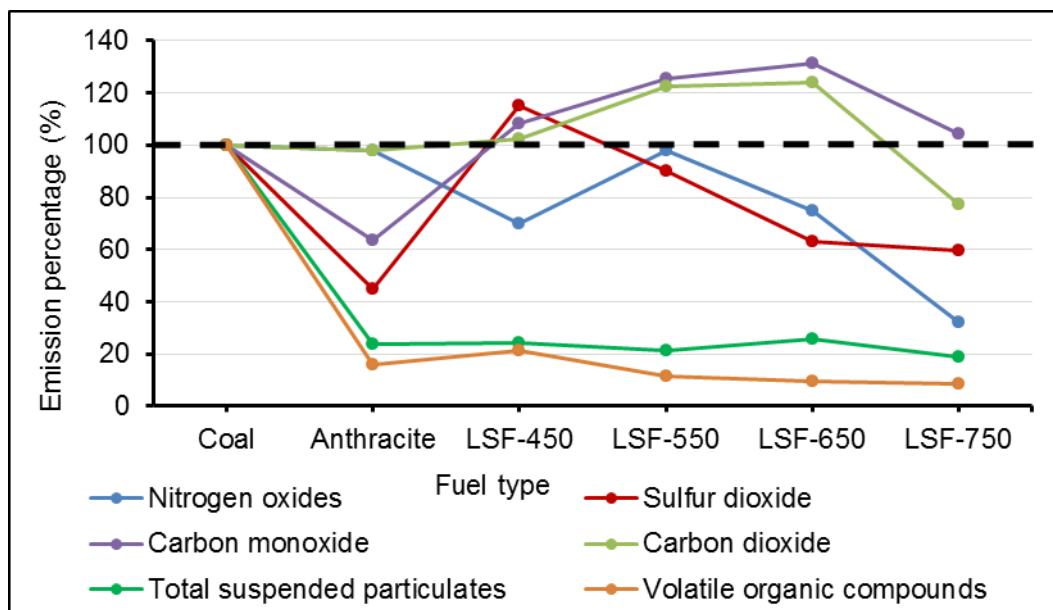


Figure 6.2: Gas emissions measured during combustion of various fuels (Ant – Anthracite, -450, 550, 650, 750 – Char/LSF produced at respective temperatures.

6.3.2.3 Carbon monoxide (CO) and carbon dioxide (CO_2)

The quantities of CO and CO_2 measured during combustion displayed similar trends for all four chars produced. Approximately 40% less CO was measured for the anthracite, while CO_2 emissions thereof were similar to that produced during coal combustion. The amount of CO measured during combustion of LSF-750 was slightly higher than for coal and CO_2 emissions reduced by approximately 20%. LSF-450 produced relatively similar quantities of CO and CO_2 than coal with only slight increases as observed in Figure 6.2. Furthermore, the CO and CO_2 emissions produced during combustion of LSF-550 and LSF-650 were relatively high (20-40% higher) in comparison to that of coal. The increase in CO and CO_2 may be attributed to the higher amounts of carbon present in the fuels other than coal as the primary reactions of coal-

char combustion include the following as reported in Table 6.4 (Merrick 1984; Ralph and Bertrand, 1963):

Table 6.4: Primary coal-char combustion reactions.

Reactions	Heat of reaction	Equation
$C + O_2 = CO_2$	-392.9	Eq. 6.1
$C + 1/2O_2 = CO$	-111.2	Eq. 6.2
$CO + 1/2O_2$	-281.7	Eq. 6.3
$C + CO_2 = 2CO$	+170.5	Eq. 6.4

From Table 6.1 it is clear that the carbon content present in the fuel is of great importance, and has to be considered when combustion behaviour is evaluated. Consequently, the quantity of carbon, as observed from the ultimate analyses (Table 6.1) for the different fuels, are higher than that within the raw coal. According to NRC, (2010), and U.S. Department of State, (2007), CO₂ is the primary greenhouse gas emitted through human activities, and although it is naturally present in the earth's carbon cycle, human activities largely contribute to the increase thereof. It is a well-known fact that CO is associated with incomplete combustion, while CO₂ is the main product of complete combustion and according to Acurex Environmental Corp. *et al.*, (1993), the rate of CO emissions that result from combustion greatly depends on the oxidation efficiency of the fuel (WCA, 2009). Therefore, if a combustion unit is not operated and/or maintained properly, the possibility exists that the subsequent formation of CO as well as organic compounds may increase, especially in small furnaces such as the Union 7 stove investigated in this study (US Acurex Environmental Corp. *et al.*, 1993). The increased CO and organic emissions from small coal fired units may be ascribed to the disability of the units to maintain high-temperature residence times, hence resulting in less time available to achieve complete combustion. The temperatures measured within the respective fires are presented in Figure 6.8, where it can be observed that the anthracite reached the highest maximum temperature at two of the measured temperatures. The residence time thereof at high temperatures displayed in Figure 6.8d seemed to be greatest, which may indicate that complete combustion occurred to a larger extent in comparison to the other fuels. This observation agrees with that of the significant decrease in CO produced by the anthracite as reported in Figure 6.2. The relationship of CO and CO₂ with regards to the combustion efficiency of the respective fuels will be discussed in Section 6.4.4. The decrease in CO and CO₂ detected for LSF-750 in comparison to LSF-550 and LSF-650 may be attributed to the low combustion efficiency observed for LSF-750. Although a low combustion efficiency would likely result in an increase in CO production, it was noted that some of the LSF-750 fuel particles did not ignite and were unburnt, and the residual organic carbonaceous material obtained after combustion was greater than that of any of the other fuels. This may have resulted in reduced CO and CO₂ emissions

released during combustion of LSF-750. Refer to Table D.7.1, Appendix D.7 for the loss on ignition determined for the respective fuels. Due to the fact that no significant reduction in the CO and CO₂ emissions was found for any of the chars, it could be concluded that none of the chars qualified as a viable option to replace coal in terms of CO and CO₂ emissions.

6.3.3 Total suspended particulate matter (TSP)

Combustion of coal on a residential level has been identified as one of the primary source contributors to elevated ambient particulate matter quantities present in the industrialised areas of South Africa (Engelbrecht *et al.*, 2001). Therefore (in this study), low-smoke fuels with different characteristic traits were produced of which the combustion behaviours were evaluated against that of coal and anthracite. The percentage reduction in total particulate matter for the fuels in comparison to coal is presented in Figure 6.3.

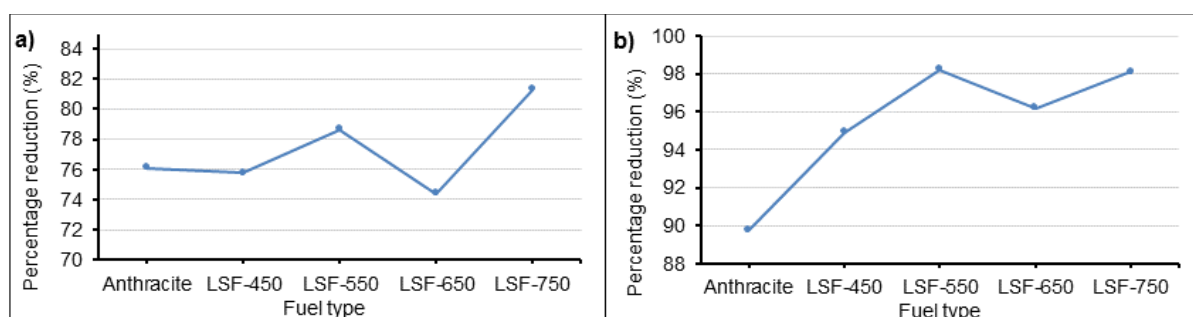


Figure 6.3: Total suspended particulate matter from a) gravimetric sampling and b) continuous sampling via a TSI Dusttrak II.

It is clear that significant reductions in particulate matter resulted from the combustion of anthracite and all of the chars produced during the devolatilisation phase of this study. A notable difference can be observed between the two methods of sampling, of which the respective results are displayed in Figure 6.3a and Figure 6.3b. This difference may be attributed to the fact that gravimetric sampling (Figure 6.3a) was conducted isokintetically according to US EPA Method 5, whilst continuous sampling (Figure 6.3b) via the TSI Dusttrak II was not conducted isokinetically. Therefore, results obtained from continuous sampling may not have indicated the correct quantities of particulate matter sampled, however, the trends obtained may be useful for comparative purposes to that of the gravimetric sampling. Accordingly, the trends obtained from the two distinct sampling methods are relatively similar for the respective fuels, indicating a larger reduction in total particulates detected as the final pyrolysis temperature increased. The char produced at a devolatilisation temperature of 650°C behaved slightly different to the overall trend (a small increase in particulate matter in relation to char produced at 550°C), however the total reduction in particulate matter is still significantly high. This observation is in agreement with the findings of previous authors who also

investigated the particulate matter released by different fuels during combustion on a residential level (Engelbrecht *et al.*, 2001; Le Roux *et al.*, 2004). It can be concluded that final devolatilisation temperature has little effect regarding the percentage reduction of particulate matter as a maximum difference of only 8% was observed. Therefore, any one of the chars may be a suitable household fuel to replace coal when only particulate matter emissions are considered.

6.3.4 Volatile organic compounds (VOC)

Volatile organic compounds have been defined as any organic compound, with the exception of CO, CO₂, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions (US EPA, 2015). Compounds deemed to have a negligible photochemical reactivity, and therefore exempt from the definition of VOC's, include methane, ethane, methyl chloroform, methylene chloride and most chlorinated-fluorinated compounds (commonly known as CFC's). Accordingly, VOC's can be characterised as a pollutant class that form as a result of unburned vapour phase hydrocarbons, and include essentially all vapour phase organic compounds emitted during coal combustion (Interpoll Laboratories, 1990). Such emissions predominantly consist of aliphatic, oxygenated and low molecular weight aromatic compounds of which all exist in the vapour phase at flue gas temperatures, and consist of alkanes, alkenes, aldehydes, carboxylic acids and substituted benzenes such as benzene toluene and xylene (Interpoll Laboratories, 1990; Radian Corporation, 1992). According to the US EPA, (2015), tropospheric ozone, commonly referred to as smog, is formed when oxides of N₂ and VOC's react in the atmosphere in the presence of sunlight. Figure 6.4 displays the reduction VOC's of the anthracite and low-smoke fuels in relation to that produced during coal combustion. It is clear that the quantity of VOC's reduce by a great extent for all the fuels investigated. Approximate reductions of 80%, 85% were found for LSF-450 and anthracite respectively, whereas the amount of VOC's detected for LSF-550, LSF-650 and LSF-750 were approximately 90% lower than that for coal. Further investigation is, however, recommended to determine the VOC's emitted during low-smoke fuel production. According to the results obtained for combustion of the low-smoke fuels, it is suggested that any of the low-smoke fuels may be a suitable replacement for coal to be used in household burning activities.

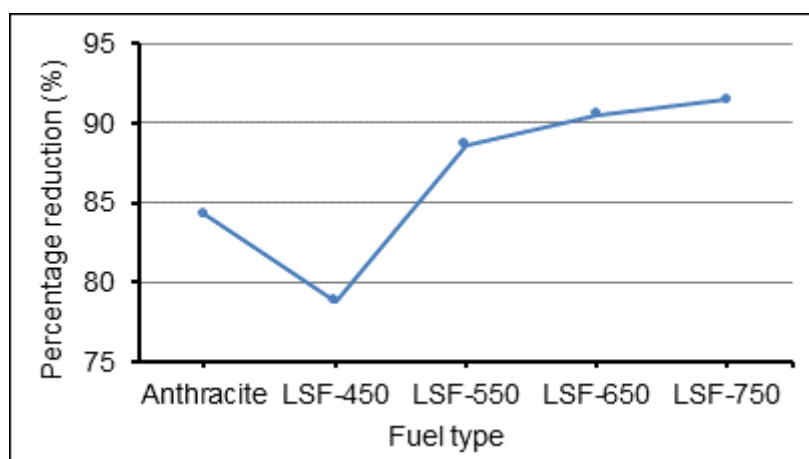


Figure 6.4: Volatile organic compounds detected during combustion.

6.4 Practical parameters

In order to compare the combustion performance of the respective fuels on a concrete basis that would serve as part of the criteria according to which the low-smoke fuels will be evaluated, it was necessary to develop a set of practically implementable parameters. Accordingly the parameters developed consisted of: (1) Ignition time (of the fuel), (2) Time to boil 1L of water, (3) Total time space heat is provided (in relation to amount of fuel used, and (4) Combustion efficiency. The time to boil 1L of water and total time space heat is provided were measured in order to provide tangible evidence to the residents of Kwadela.

6.4.1 Ignition time

In this study, the ignition time was defined as the period of time for which LPG fuel was used during the initial stages of combustion. As discussed in Section 4.7.1, four thermocouples were used to measure the temperature of each fire and were described with reference to the grid (as level 0 cm) on top of which the fuel was stacked. Two temperature measurements (thermocouples placed approximately 5cm and 10cm above grid) were utilised with the means to determine the ignition temperature of the respective fuels. Gas flow of the LPG fuel was shut off at the instance where both thermocouples indicated a minimum temperature of 500°C, or the first of the temperatures 5cm and 10cm above the grid to reach 700°C and/or 500°C respectively depending on which. This decision was based on trials and agrees with the work of Merrick, (1984) and Ralph and Bertrand, (1963). It should be noted that emission sampling was conducted for 120 minutes since ignition of the LPG fuel. The two respective temperatures measured during combustion of the various fuels are presented in Figure 6.5.

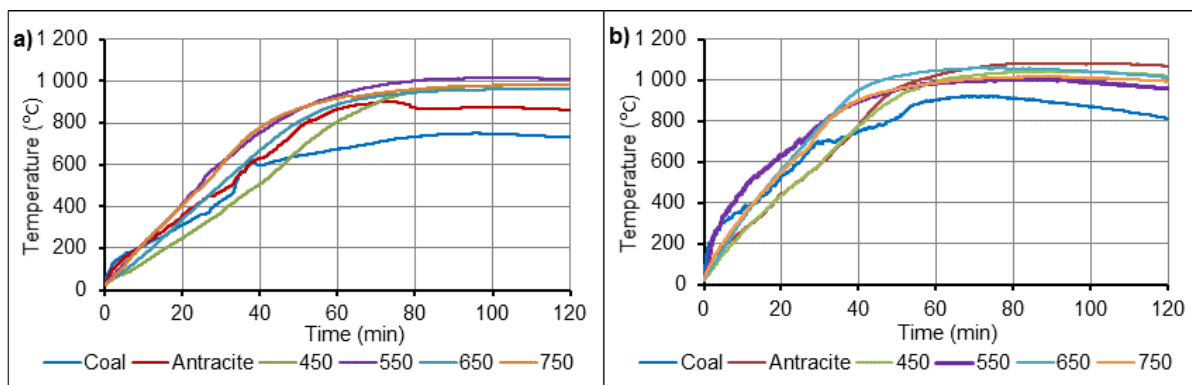


Figure 6.5: Temperatures in the core of the fires with a) +5cm above grid and b) +10cm above grid.

It is clear from Figure 6.5 and Figure 6.5 that all the fuels ignited after approximately 25 minutes to 35 minutes after ignition of the LPG fuel. The fuel ratios in Table 6.1 displayed an increasing trend as devolatilisation temperature was increased, and that of the raw coal was the lowest. Thus it was expected that the amount of energy in increasing order required for the fuels to ignite would be Coal<Char-450<Char-550<Anthracite<Char-650<Char-750. Although the anthracite and chars ignited over a longer period of time in comparison to coal, no conclusive trends could be observed for the sequential times at which the respective thermocouples reached the desired temperatures specified as the ignition temperature. Refer to Appendix D.6 for the exact ignition times, quantities of energy (MJ) used during ignition of the respective fuels. The amount of LPG used and the ignition times are presented in Figure 6.6 from which the ignition times of the low-smoke fuels can be compared to that of coal. From Figure 6.6 it can be observed that the least amount of LPG was used for ignition of Char-550, and that the ignition time thereof is similar to that of coal, however the amount of LPG used to ignite coal was approximately 8g more. The amount of fuel used can be observed to increase as the ignition time of the respective fuels increase.

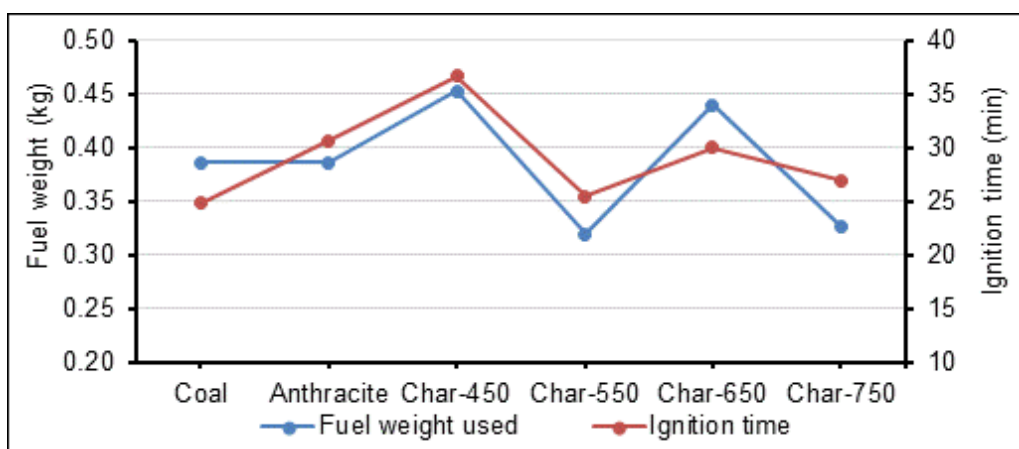


Figure 6.6: LPG fuel weight used for ignition and ignition times.

It is important to note that although it was attempted to keep the packing of the fuel bed, as well as placement of the thermocouples and LPG burner, constant throughout the experiments, the possibility exists that these factors fluctuated as large particles of different shapes and sizes were used. Therefore the route followed by the flames of the LPG burner through the fuel bed may have varied for each experiment resulting in dissimilar thermal conductivity behaviour of the fuels. This may have contributed to the anomalies found regarding the amounts of energy used. Another element that possibly influenced the ignition times, was the fact that a Handigas (10kg) cylinder with no regulator was used, therefore the flow of LPG could not be regulated. However an attempt to regulate the flow through time was made by measuring the LPG flow rate from the gas cylinder with a bubble flow meter prior to each experiment as discussed in Appendix D.6.

6.4.2 Time to boil 1L of water

The temperatures just below the top of the stove where the pot was placed are presented in Figure 6.7a, whilst the respective temperatures of the water inside the pot are displayed in Figure 6.7b.

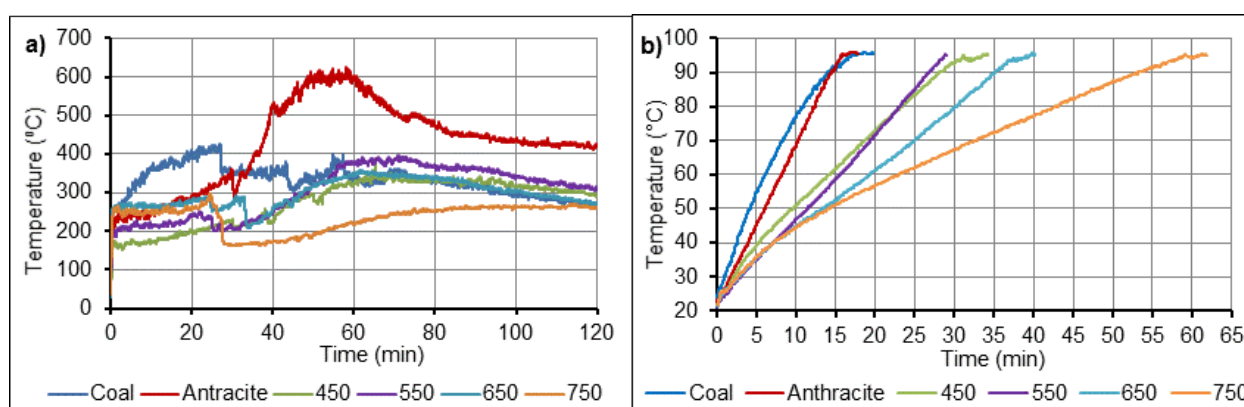


Figure 6.7: Temperatures associated with boiling of 1L of water with a) +20cm above grid (stove) and b) temperature of water in pot.

In general, the boiling time seemed to increase as the devolatilisation temperature increased with anthracite and coal showing the shortest boiling times, as seen in Figure 6.7b. This observation agrees relatively well with the temperature profiles displayed in Figure 6.7a, where the coal and anthracite displayed high temperatures (especially the coal during the initial 30 minutes of combustion after which it reduced slightly). Boiling times for Char-450 and Char-550 were similar with a moderate difference to that of Char-650, while the water only boiled after approximately 60 minutes during combustion of Char-750. An observation was made during the course of the combustion tests that the coal and anthracite produced significantly larger amounts of visible flames, along with red hot coals, once the LPG fuel was shut off in comparison to the chars (only red hot coals were observed), hence the shorter boiling times of

coal and anthracite. The heat transfer caused by the flames may have resulted in a higher heating rate of the top platform of the stove on top of which the pot containing the water was placed. The presence of flames can be attributed to the combustion of volatiles contained within the fuels, therefore it can be expected that the presence of flames diminish as the amount of volatiles in the fuel decrease. Refer to Table 6.1 for volatile matter of the fuels. The presence of flames observed, in decreasing order, was as follows: Anthracite>Coal>Char-450>Char-550>Char-650>Char-750. Although anthracite does not contain a large amount of volatile matter (similar amount to Char-550), the ash content thereof is very low, whereas the fixed carbon content is high in comparison to the char on an air dry basis. The amount of H₂ reported in Table 6.1 for the ultimate analyses of the respective fuels also indicates that the anthracite has a relatively high quantity of H₂. As the ultimate analysis is reported on an ash free basis and the ash content of the anthracite is low in comparison to the other fuels, the H₂ yield is automatically the highest per weight of fuel sample. Accordingly it is suggested that coal be replaced by Char-450 or Char-550 when taking the boiling time for 1L of water into account.

6.4.3 *Total time space heat is provided*

As discussed in Section 6.4.2, the observation regarding the presence of flames after the LPG gas flow was closed off seemed to play an important part initially, however the residence times at the high temperatures proved to be useful when space heating was considered. Therefore, the results in this section will be discussed in terms of the time interval after which the temperature of the fires returned to 100°C. With reference to Figure 6.8c and Figure 6.8d, which are the two temperatures representative of the core of the fires, clear differences in residence times at high temperatures can be observed over the total period of combustion. From Figure 6.5c the heat provided, in decreasing order was as follows: Char-750>Char-650>Char-450>Anthracite>Char-550>Coal, whereas in Figure 6.8d the order was Char-750>Anthracite, Char-650, Char-450>Coal>Char-550. Similar trends can be observed for the residence times at high temperatures for the different fuels in Figure 6.5c and Figure 6.5d. However these two temperatures are only representative of the fire and not the area surrounding the fire, therefore the temperatures displayed in Figure 6.8a and Figure 6.8b, may serve as a better indication of the space heating as the temperature in (a) is the temperature in the chimney just above the stove, and the temperature in (b) is the temperature just below the top platform of the stove. The period of time heat was provided as presented in Figure 6.8a, in decreasing order, is as follows: Anthracite>Char-450>Char-750/Char-650>Char-550 >Coal, while that in Figure 6.8b is Anthracite>Char-750/Char-650>Char-550>Char-450>Coal. The maximum temperatures should also be considered as the char produced at 750°C was approximately 100°C lower than that of coal after LPG was shut off. Minor differences could be noted between the chars and the coal, therefore any one of the chars may be a suitable fuel to replace coal in terms of space heating,

although the chars produced at 650°C and 750°C may provide heat for a slightly longer period of time.

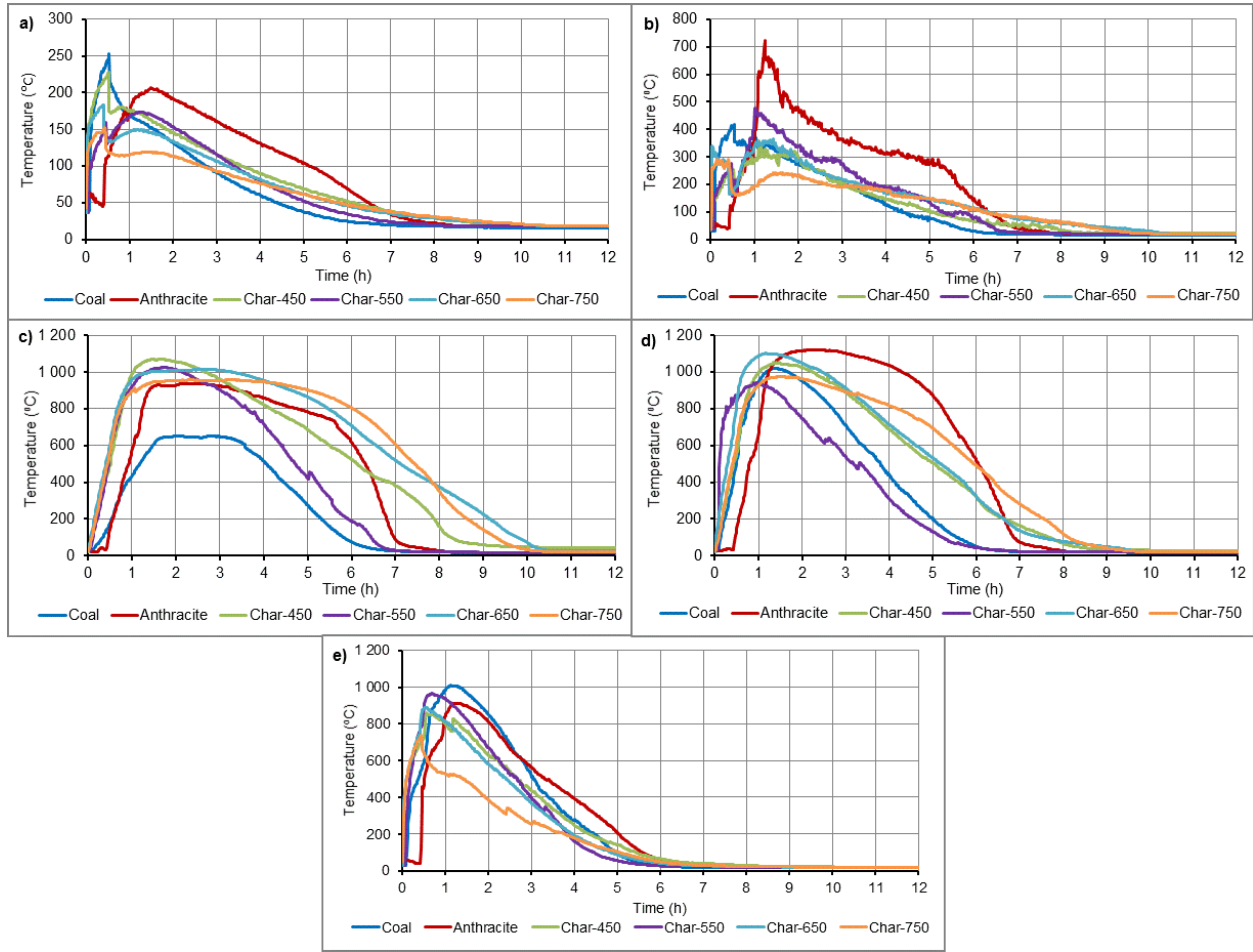


Figure 6.8: Temperatures measured within fires with grid as level zero: a) +100cm (chimney), b) +20cm (stove), c) +10cm (stove), d) +5cm (stove), e) +2cm (stove).

6.4.4 Combustion efficiency

In this study, the combustion efficiency of the respective fuels was defined as the amount of combustible material residue obtained once the combustion procedure was completed, as described in Equation 6.5:

$$\text{Combustion efficiency (\%)} = \left[1 - \frac{(\text{Carbon in residual ash}) \times 32.8}{\text{Batch start mass} \times G_{CV}} \right] \times 100 \quad \text{Eq. 6.5}$$

with:

- Carbon in residual ash (kg) = (Total mass of residual ash after combustion) × (%LOI/100).
- G_{CV} = Gross calorific value of carbon (32.8 MJ/kg).
- % Loss on ignition/combustibles (LOI) in residual ash.

- % Loss on ignition/combustibles (LOI) in fly ash were assumed to be negligible.

The percentage combustibles present in the residual ash after combustion was determined by preparing representative samples for each of the respective fuels, which were treated in a furnace in the presence of air at a temperature of 950°C for 4 hours to ensure heating throughout the sample. The residual carbon remaining may contribute to the anomalies of the CO and CO₂ detected for char-750 as it was observed that some of the lump particles did not seem to ignite. The higher amount of unburnt carbon present after combustion observed for the char-750 in comparison to the other low-smoke fuels may possibly explain the lower combustion efficiency and the decreased CO₂ and CO emissions detected for char-750 as less of the fuel combusted per mass in comparison to the other fuels.

According to literature, it is generally acknowledged that the combustion efficiency of a fire is directly related to the quantities of CO and CO₂ produced, as these are respectively associated with incomplete and complete combustion (Acurex Environmental Corp. *et al.*, 1993; WCA, 2009) The CO and CO₂ trends displayed in Figure 6.2 correlate well with the combustion efficiency presented in Figure 6.9b for the anthracite (80%) which is indicative of a high CO₂ to CO ratio. From Figure 6.2, it can be observed that the CO₂ for the anthracite is approximately similar to that of coal, whereas the CO for the anthracite is 40% less, hence a high CO₂ to CO ratio. The CO₂ to CO ratio for the low-smoke fuels follow a similar trend than that of the CO₂ and CO observed in Figure 6.2, and the combustion efficiency seemed to decrease with a decrease in CO₂ to CO ratio. Char-550 is an exception however as the CO₂ to CO ratio is slightly higher than that of Char-450, but the combustion efficiency is lower. An efficiency of 69% can be observed for the coal, while that of the chars were approximately 79%, 77%, 67% and 62%. Hence the order of efficiency in increasing order for the fuels is Char-750<Char-650<Coal<Char-550<Char-450<Anthracite. The maximum temperature recorded for the respective fuels may be dependent on the combustion efficiency as the highest maximum temperature was noted for the anthracite having the highest combustion efficiency. From a combustion efficiency point of view it is suggested that the chars produced at 450°C and 550°C may be utilised as a suitable fuel to replace coal that will still fulfil the household needs of residents in Kwadela. Refer to Appendix D.5 for a discussion regarding the method of calculation of the combustion efficiency.

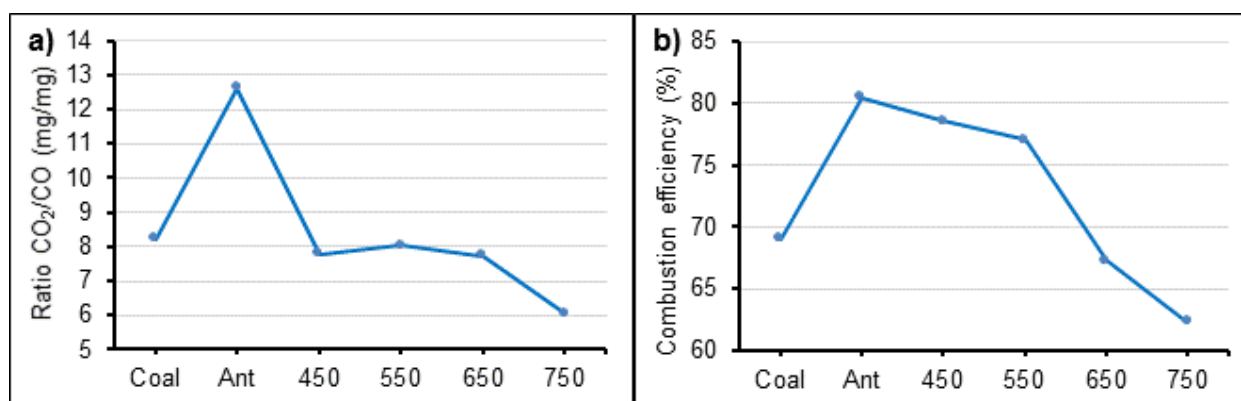


Figure 6.9: Carbon dioxide to carbon monoxide (CO_2/CO) ratio in a), and combustion efficiency in b).

The higher amount of unburnt carbon present after combustion observed for the Char-750 in comparison to the other low-smoke fuels may possibly explain the lower combustion efficiency and the decreased CO_2 and CO emissions detected for Char-750.

6.5 Ideal low-smoke fuel selection process and summary

The selection process entailed the development, and implementation, of specific criteria in order to not only classify the different fuels according to their emissions, but also their practical aspects. Anthracite was included in the process and will also be considered as an option in the selection of a viable fuel to replace coal. The criteria, classification of the different fuels and outcome thereof are clearly visible in Table 6.5.

Table 6.5: Ideal low-smoke fuel selection process.

Fuel	Emission criteria						Practical criteria				Total
	NO _x	SO ₂	CO	CO ₂	TSP	VOC	Time to boil 1L of water	Total time space heat provided	Combustion efficiency	Ignition time	
Anthracite	↓ 5	↓ 1	↓ 1	↓ 2	↓ 5	↓ 5	↓ 1	↑ 4	↑ 1	↑ 5	30
Coal	6	6	2	3	6	6	2	6	4	1	42
LSF-450	↓ 2	↑ 5	↑ 4	↑ 4	↓ 2	↓ 4	↑ 4	↑ 3	↑ 2	↑ 6	36
LSF-550	↓ 4	↑ 4	↑ 5	↑ 5	↓ 3	↓ 3	↑ 3	↑ 5	↑ 3	↑ 2	37
LSF-650	↓ 3	↓ 3	↑ 6	↑ 6	↓ 4	↓ 2	↑ 5	↑ 2	↓ 5	↑ 4	40
LSF-750	↓ 1	↓ 2	↑ 3	↓ 1	↓ 1	↓ 1	↑ 6	↑ 1	↓ 6	↑ 3	25

*Classification according to numbers 1-5 with 1=best and 5=worst.

During performance evaluation of the respective fuels it should be noted that two distinct perspectives are regarded, i.e. the practical and emissions perspective. It is of the utmost importance that the fuel that would replace coal as a source of energy in low-income households delivers an equal, or better, performance in terms of the practical aspects investigated in this study. The two practical aspects regarded as the most important included

the ignition time and the time to boil 1L of water. If the fuel does not perform adequately, the possibility exists that it may not be accepted on a societal level by the residents of low-income households. Therefore, the practical parameters evaluated were regarded as more important than those of the emissions, as the product first had to be accepted by the residents of low-income households. With regards to the emissions produced, the TSP and VOC's were regarded as the most influential and the highest reductions were observed thereof during combustion of the low-smoke fuels in comparison to that of coal. According to Fullerton *et al.*, (2008), the particulate matter released into the atmosphere during coal combustion is of great significance with respect to respiratory illnesses.

When considering the total column included in the selection process provided in Table 6.5, it should be noted that the lowest number will be representative of the most ideal fuel to replace coal, however it should also be remembered that the practical aspects outweigh that of the emissions. Consequently the fuels were classified from best to worst, and the order was found to be: LSF-750→Anthracite→LSF-450→LSF-550→LSF-650.

In terms of the time to boil 1L of water, the anthracite performed the best of all the fuels with approximately 18 minutes. The char produced at 450°C and 550°C both displayed boiling times of approximately 30 minutes, which is significantly shorter in comparison to the chars produced at the two higher temperatures especially Char-750, that took almost one hour. No significant differences were observed for the total time space heat (between 5.5h and 8h) was provided rendering all the fuels (other than coal) equal according to this parameter. The combustion efficiencies however, differed greatly and were found to be (in decreasing order): Anthracite→LSF-450→Char-550→Coal→LSF-650→LSF-750. Assessment of the ignition times, LSF-550 ignited at approximately the same time (25 minutes) as coal, whereas all the other low-smoke fuels and anthracite only ignited over longer periods. Anthracite ignited in approximately 30 minutes, about 5 minutes longer than LSF-550. Thus, according to the practical aspects considered, the anthracite and low-smoke fuel produced at 550°C would be the best two suitable fuels to replace coal.

In the case of considering the gas emissions criteria it is suggested that the anthracite fuel be selected followed by LSF-750, LSF-450, Coal, LSF-650 and LSF-550, respectively. All of the emissions (NO_x , SO_2 , CO_2 , CO, TSP and VOC's) of the Char-750 were the lowest for all of the low-smoke fuels investigated, and CO_2 was the most predominant species throughout. The TSP and VOC's were relatively similar for all of the low-smoke fuels, with decreases observed ranging between 76%-82% and 79%-91% respectively, rendering any of the fuels investigated viable to replace coal in terms of the TSP and VOC's. Consequently, from an emissions perspective, the most suitable fuel is the LSF-750 and anthracite are the best two options.

It could therefore be concluded that the overall behaviour of Char/LSF-550 seemed to be the most representative of an ideal low-smoke fuel when both the criteria for the emissions and practical aspects were considered. In addition, the char produced at 450°C performed well in terms of TSP and VOC emissions and the time to boil 1L of water. Anthracite would also be an ideal fuel as it performed well in both the emissions and practical categories, however further investigation is necessary to determine the economic potential of the fuels. Therefore a techno-economic feasibility study was performed of which the outcomes are provided in Chapter 7.

The benefits of using low-smoke fuels of which anthracite forms part, are listed below:

- Heat is provided for a longer time by all the low-smoke fuels
- The ignition time of the suggested LSF-550 is similar to that of coal
- Acceptable time to boil 1L of water with anthracite, LSF-450 and LSF-550
- Increased combustion efficiencies for anthracite, LSF-450 and LSF-550
- Total suspended particulate emissions are reduced by approximately 80% with LSF-550
- Volatile organic compound emissions are reduced by approximately 90% with LSF-550

Thus it can be concluded that low-smoke fuels may serve as a viable fuel to replace coal as fuel to adequately fulfil the energy requirements of low-income households, while simultaneously resulting in less air pollution being produced as a result of the combustion thereof.

CHAPTER 7: TECHNO ECONOMIC EVALUATION

Two options regarding the provision of low-smoke fuels were evaluated in this chapter i.e. the cost to acquire and distribute anthracite to Secunda versus the economic feasibility of a low-smoke fuels production facility that produce low-smoke fuels locally in Secunda from coal obtained within close proximity of Secunda. A techno-economic feasibility study was performed so as to provide some indication with regards to the economic feasibility of a low-smoke fuel production process, however it was not the primary purpose of this investigation. It should therefore be noted that the design of the plant was not based on the conceptual design principles as proposed by Douglas, (1988). Furthermore, specific process conditions and detailed design of equipment were not included in this study. The fundamentals of the process investigated was based on that designed by Larsen and Stutz, (1932), which is a low-smoke fuel production process designed to produce a fuel that would result in less emissions during household combustion. The assumptions made are clearly stated in Section 7.1, whereas the costs regarding anthracite is discussed in Section 7.2. The location of the plant is discussed in Section 7.3 and a process flow diagram of the process is provided and briefly discussed in Section 7.4.

A comprehensive cost estimate is provided and consists of three primary components:

- Estimation of the total capital investment (Section 7.5)
- Estimation of the revenue generated (Section 7.6)
- Estimation of the total production cost (Section 7.7)

Details regarding these three components will be discussed in detail in this chapter. In addition to the cost estimate, a cash flow analysis (Section 7.8), profitability (Section 7.9) and optimum design and sensitivity analysis of the plant (Section 7.10) will be analysed and applied, after which the findings will be summarised in Section 7.11.

7.1 Assumptions and fixed variables

The assumptions made during this investigation are as follows:

1. The cost price of an anthracite fuel was taken as R1.00/kg (Anon, 2015d).
2. The transportation cost of anthracite was obtained from and taken as R0.50/kg (Anon, 2015e).
3. Residents in Kwadela Township buy coal at approximately R1.00/kg, therefore the price of the low-smoke fuel should be within that range. A value of 1.00R/kg was therefore selected as the selling price for the low-smoke fuel to be produced at 550°C (Nova, 2013).

4. The base year was selected as 2015.
5. The plant capacity (10000 tonne/year of coal treated) with an availability of 75% (ETSAP, 2010). The downtime allowed for maintenance is allowed for in the 25% fraction of the capacity which would not be available. The capacity of 10000 tonne/year was selected as Kwadela Township has a population of approximately 1,200 residents with a total annual coal use of 62 ton (Nova, 2013; Statistics South Africa, 2011). Embalenhle is a significantly larger township within a 100km proximity. Embalenhle Township houses approximately 120,000 occupants and a projected annual coal use of 6,200 tonne (Statistics South Africa, 2011). Accordingly, 21 tonne of coal was treated daily.
6. The plant will be operating 345 days annually and 24 hours a day, allowing for 20 days of downtime.
7. Cost estimation of the primary process equipment was calculated according to the process designed by Holt & De Jager, (2012), which is a similar plant. Inflation was added from 2012 to 2015 for equipment costs.
8. Steam (superheated and saturated) was bought from Sasol, Secunda Plant at R108/tonne and the cost thereof was calculated via the cost index provided in Peters *et al.*, (2004). A sensitivity analysis of the variable production costs was performed to allow for changes regarding the steam price.
9. Superheated steam usage was taken as 1kg steam per kg coal (used for heating) (Larsen and Stutz, 1932).
10. Saturated steam usage was taken as 0.5kg steam per kg coal (used for cooling) (Larsen and Stutz, 1932).
11. The cost for cooling water was taken as R2.75/m³ according to Randwater, (2015).
12. Cost of raw coal to be treated was taken as R226/tonne (Sasol, 2014).
13. Labour cost was taken as the minimum wage of R6,400 per operator monthly (International Labour Organisation, 2014). Inflation for one year was added to the wage as the base year is 2015.
14. The value of the crude oil pyrolysis product obtained was based on that of the current Brent crude oil, 50 USD/barrel (Anon, 2015a).
15. Product yields were based on that found for the LSF-550 in Chapter 5, and displayed in Table C.2.3, Appendix C.2.
16. A tax rate of 28% was assumed (Anon, 2015b).
17. An inflation rate of 5% was assumed (Statistics South Africa, 2015).
18. A discount rate of 15% was assumed.
19. The ZAR/USD exchange rate is taken as the average for 2015 from June 2015 to November 2015 at R13/USD (Anon, 2015c).

20. For higher accuracy in estimations, no downtime was taken into account in the labour cost calculations.
21. It was assumed that the plant has a lifetime of 25 years.
22. Design and commissioning was assumed to be 3 years.
23. The expenses of FCI will be equally divided between year 1 and 2 and WC will be supplied in year 3.
24. Depreciation was calculated according to the method provided in the PKF Africa Tax Guide, (2015).

7.2 Cost of anthracite

As stated in Section 7.1, the anthracite would cost approximately R1.50/kg to deliver in Secunda and in order for the fuel to be affordable to the local residents of low-income communities, it should be sold at a lower price of R1.00/kg. Thus, R0.50/kg anthracite would have to be subsidised externally in order to sell the anthracite at an affordable rate to the low-income communities. The anthracite would be acquired from the Nkomati Anthracite mine in Komatipoort, Mpumalanga, South Africa (Anon, 2015d). The techno economic evaluation of a facility that produce low-smoke fuels from coal, in Secunda are discussed in Section 7.3-Section 7.10, to follow.

7.3 Location of the plant

As this study was based on the coal obtained in Kwadela Township situated approximately 50 km east of Secunda, it is proposed that the plant be located within a 150 km radius of Kwadela. Therefore, the plant would be able to supply not only Kwadela with LSF, but also other nearby townships such as Embalenhle Township, which has a vast population in comparison to Kwadela Township. As the location of the plant is situated in close proximity to the Sasol Secunda Operations, the possibility of collaboration in terms of a local social development initiative should be further investigated. An example is that of Sasol ChemCity, which offers assistance to entrepreneurs that are operating within the energy and chemical industry. If a low-smoke fuel plant could be situated in close proximity of the Sasol Plant, Secunda, it may prove ideal as excess steam could be bought from Sasol resulting in a reduction in fixed capital required. The by-products of pyrolysis (crude oil, tar) may be sold to Sasol, therefore establishing a market for the products other than the low-smoke fuels.

7.4 Process flow diagram (PFD)

A concise description of the low-smoke fuel production process is provided in this section. It should, however be noted that the process was not designed in detail and that the product yields were assumed to be that of the LSF-550. A process flow diagram of the low-smoke fuel

production process is provided in Figure 7.1. The proposed process is a continuous coal pyrolysis process that utilises retort type reactors to produce devolatilised coal (low-smoke fuel) at 550°C. The raw coal is transported from Sasol's Secunda Plant via a conveyor to the screening section, where the particles smaller than 15mm are removed. The coarse coal fraction, i.e. the +15mm size fraction, is loaded into the hopper bunker feeding the reactor via another conveyor. Superheated steam is injected into the reactor, moves through the coal packed bed and provides the necessary energy to heat the coal up to the required 550°C. Before the low-smoke fuel product is removed at the bottom of the reactor, saturated steam is injected into the bottom section with the purpose of quenching the solid char product. The low-smoke fuel lumps are removed at the bottom of the reactor, whereas the volatile products along with the steam exit the reactor section at the top, from the side. The gaseous product first passes through an electrostatic precipitator, which removes the particulate matter, while the tar and water fractions condense and are fed into a water/tar separator to obtain the respective products. The water may be recycled back to the steam generation unit or used to quench the low-smoke fuel product, however that was not investigated in this study.

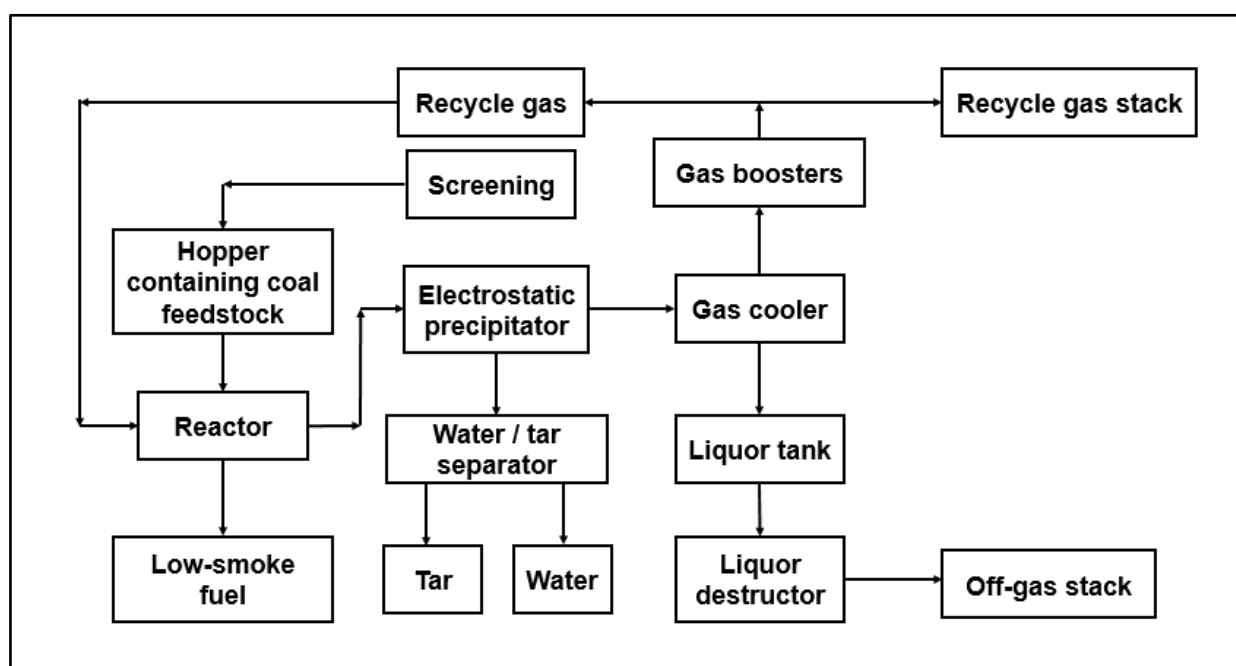


Figure 7.1: Process flow diagram of low-smoke fuel production process.

The remaining coal off-gas exiting the electrostatic precipitator is separated in a cyclone separator and cooled in a shell and tube heat exchanger with cooling water. The gas product exiting the cooler can be sold, flared, used to combust liquor or recycled back to the retort to provide additional heat. The latter case was employed in this study, where the recycle gas was burned with a gas burner to provide additional heat within the walls of the retort. Evaporative cooling is used to precipitate water containing hydrocarbon oils, phenols and sulfur, which is

termed “liquor”, and is stored in a liquor tank. Water condensing from the gas boosters are also collected as liquor. This liquor is a waste product resulting from the pyrolysis process, and is destroyed via a liquor destroyer by burning it with coal gas generated during devolatilisation inside the retort.

7.5 Total capital investment (TCI)

Capital, and capital investment, can be defined as the amount of money used to acquire and install equipment, land and service facilities. In addition, all costs related to erecting the plant must be covered, and it is necessary to provide an amount of money to cover some of the running expenses during commissioning and start-up of the plant (Peters *et al.*, 1991). Consequently, the total capital investment of a plant can be divided into two sections i.e. fixed capital (FCI) and working capital (WCI^b). Fixed capital primarily entails the capital required for plant facility setup, equipment and construction, and can be subdivided into direct costs (manufacturing FCI) and indirect costs (non-manufacturing FCI) (Peters *et al.*, 2004). Working capital can be described as the reserves, other than FCI and start-up monies, necessary to cover expenses until payment for produced and sold goods that are received from external parties (Seider *et al.*, 2010). It can therefore be interpreted as the current assets minus the current liabilities, and as it is completely recoverable; depreciation is not taken into account for the WCI^b.

According to Peters *et al.*, (2004), the study/factored estimate type, as used in this investigation, is estimated according to information of major items of equipment and provides an accuracy of $\pm 30\%$. This type of estimation was considered as the most appropriate as a result of the amount and type of information available. The Percentage of Delivered Equipment Cost (DEC) method was selected to estimate the TCI. This method is commonly employed in introductory and study estimations, and is therefore adequate for the basic economic feasibility study performed in this thesis. The cost of the delivered equipment was obtained from the study by Larsen and Stutz, (1932), which was used to determine the TCI. The rest of the direct and indirect costs were determined as a percentage of the TCI according to Peters *et al.*, (2004). The basic calculation of the TCI is given by the following equation (Peters *et al.*, 2004):

$$C_n = E \sum (1 + f_1 + f_2 + \dots + f_n) \quad \text{Eq. 7.1}$$

Where C_n the new capital investment calculated, E the cost of delivered purchased equipment and $1 + f_1 + f_2 + \dots + f_n$ the multiplying factors for installation, piping, buildings etc. According to Peters *et al.*, (2004), an accuracy of between 20% and 30% can be expected when this method is applied. The cost of the equipment delivered was calculated to be R1.48 million from which the remainder of the costs were determined. Estimation of the TCI consisting of the direct and

indirect costs are reported in Table 7.1. The fixed capital investment determined for the low-smoke fuel process was R6.25 million, and as the working capital investment was taken as 75% of the purchased delivered, equipment, the TCI amounted to R7.36 million as reported in Table 7.1. Refer to Table E.1.1, Appendix E.1 for a detailed cost estimation of the equipment involved in the proposed low-smoke fuel production process.

It should be noted that the initial capital expenditure was calculated with the inclusion of a coal fired steam boiler and superheater to produce the necessary steam for the process. The capital expenditure was however, too high and the production costs would also increase as an additional 7.5 tonne of coal per day would be required for steam production. Thus, it was assumed that the possibility exists that steam may be bought from Sasol, Secunda Plant and a boiler system was excluded from the capital expenditure provided in Appendix E.1.

Table 7.1: Estimation of total capital investment (TCI)

Direct costs	Factor*	Estimated cost (million)
Purchased equipment		R 1.48
Purchased-equipment installation	0.39	R 0.58
Instrumentation and controls (installed)	0.26	R 0.38
Piping (installed)	0.31	R 0.46
Electrical systems (installed)	0.10	R 0.15
Buildings (installed)	0.29	R 0.43
Yard improvements	0.12	R 0.18
Service facilities (installed)	0.55	R 0.81
Land (fraction of TCI)	0.01	R 0.07
Total direct cost, D (manufacturing costs)		R 4.54
Indirect costs		
Engineering and supervision	0.32	R 0.47
Construction expenses	0.34	R 0.50
Legal expenses	0.04	R 0.06
Contractor's fee	0.09	R 0.13
Contingency	0.37	R 0.55
Total indirect cost, I (non-manufacturing costs)		R 1.72
Fixed capital investment, D+I		R 6.25
Working capital (WCI)	0.75	R 1.11
Total capital investment (TCI), D+I+WCI		R 7.36

* Factor values used for cost estimation of a solid-fluid processing plant as given by Peters *et al.*, (2004).

7.6 Revenue

The revenue generated can be described as the income earned from the selling of products produced by the process plant (Towler *et al.*, 2008). The annual capacity was assumed to be the same as the actual annual production of the process plant for estimation purposes, hence the assumption that all products are sold. Downtime was included in the 25% of the annual production that would not be available (ETSAP, 2010). Equation 7.2 was used to calculate the sales revenue generated (Peters *et al.*, 2004):

$$\begin{aligned} \text{Annual sales revenue } \left(\frac{R}{yr} \right) & \quad \text{Eq. 7.2} \\ &= \sum \left(\text{sales of product, } \frac{kg, m^3}{yr} \right) \times \left(\text{product sale price, } \frac{R}{kg} \right) \end{aligned}$$

The annual revenue calculated is presented in Table 7.2, where the respective values of the products sold are shown.

Table 7.2: Annual revenue of low-smoke fuel production plant.

Product	Cost	Unit
Low-smoke fuel	R 1.00	per kg
Crude oil	R 4 147.25	per m ³
Operation time	365	days/yr
Availability	75%	
Daily production capacity	21	ton/day of coal treated
Annual production capacity	7500	ton/year of coal treated
Annual revenue (million)	R 7.63	per year

The annual revenue estimated was approximately R7.63 million as reported in Table 7.2.

7.7 Total production cost (TPC)

The total production cost consists of all the costs associated with plant operation, sales, corporate divisions like future endeavour developments, and the recovery of invested capital. TPC can be divided into two categories that include manufacturing costs and general expenditures (Peters *et al.*, 2004). Manufacturing expenses originate from operations and equipment directly responsible for manufacturing, and consist of variable, fixed- and overhead

plant operation expenses, whereas the general expenses include general costs for plant operation that comprise of administrative, research, marketing, etc. expenses. The variable expenses may fluctuate as it includes the costs of raw materials, maintenance and labour costs etc., while the fixed plant expenses would be relatively constant irrespective of the production rate and consists of depreciation, taxes, insurance etc. Some of the expenses classified as overhead plant expenses include storage services, packaging, additional buildings and equipment that was not intended for direct use in manufacturing (Peters *et al.*, 2004). The estimation of the production costs are reported in Table 7.3, where the TPC was estimated to be R5.32 million annually. Furthermore, it is clear that the variable production costs constitute the largest fraction (~60%) of the total production costs. Operating labour was based on the minimum wage of R6,400 per operator according to International Labour Organisation, (2014). The number of operators was selected based on the information provided in Peters *et al.*, (2004), thus two operators per shift with five shift crews totalling ten operators (Seider *et al.*, 2010). Peters *et al.*, (2004) stated that respectively 0.5 and 0.2-0.5 workers/unit/shift would be required for continuous reactors and process vessels (including pumps and exchangers).

Table 7.3: Production cost estimation of low-smoke fuel production plant.

Cost component	Suggested factor	Base	Per/year (million)
Raw/feed materials			
Coal treated			R 1.70
Operating labour			R 0.77
Operating supervision	0.15	of operating labour	R 0.12
Utilities			
Cooling water			R 0.03
Maintenance and repairs (including labour)	0.07	of FCI	R 0.44
Operating supplies	0.15	of maintenance	R 0.07
Total variable production costs			R 3.11
Insurance	0.01	of FCI	R 0.06
Total fixed production costs			R 0.06
Plant overhead	0.5	of operating labour, supervision and maintenance	R 0.66
Manufacturing costs			R 5.10
Administrative	0.15		R 0.12
Distributing and marketing expense	0.02	of TPC (to this point)	R 0.10
General expenses			R 0.22
TOTAL PRODUCTION COSTS (WITHOUT DEPRECIATION)			R 5.32

7.8 Cash flow analysis

Cash flow is defined as the funds that flow into the capital reserves owing to project achievements and is summarised in Figure 7.2, where the logical flow of funds can be observed. It can be observed that TCI flows from the capital source and contains the funds for manufacturing and non-manufacturing FCI as well as the working capital. The funds available for working capital flow to the project operations and vice versa, thus ensuring satisfactory funds in the working capital for effective operations. Revenue generated from sales are considered as income, whereas the TPC is regarded as an expense flowing out of the operations for the complete project. The difference between revenue and TPC is the gross profit before depreciation (GPBD), and once depreciation is deducted, the residual value is called gross profit after depreciation (GPAD). After deducting income taxes from the GPAD, the net profit is obtained, and the annual cash flow can be estimated by adding the depreciation charge to the net profit (Peters *et al.*, 2004).

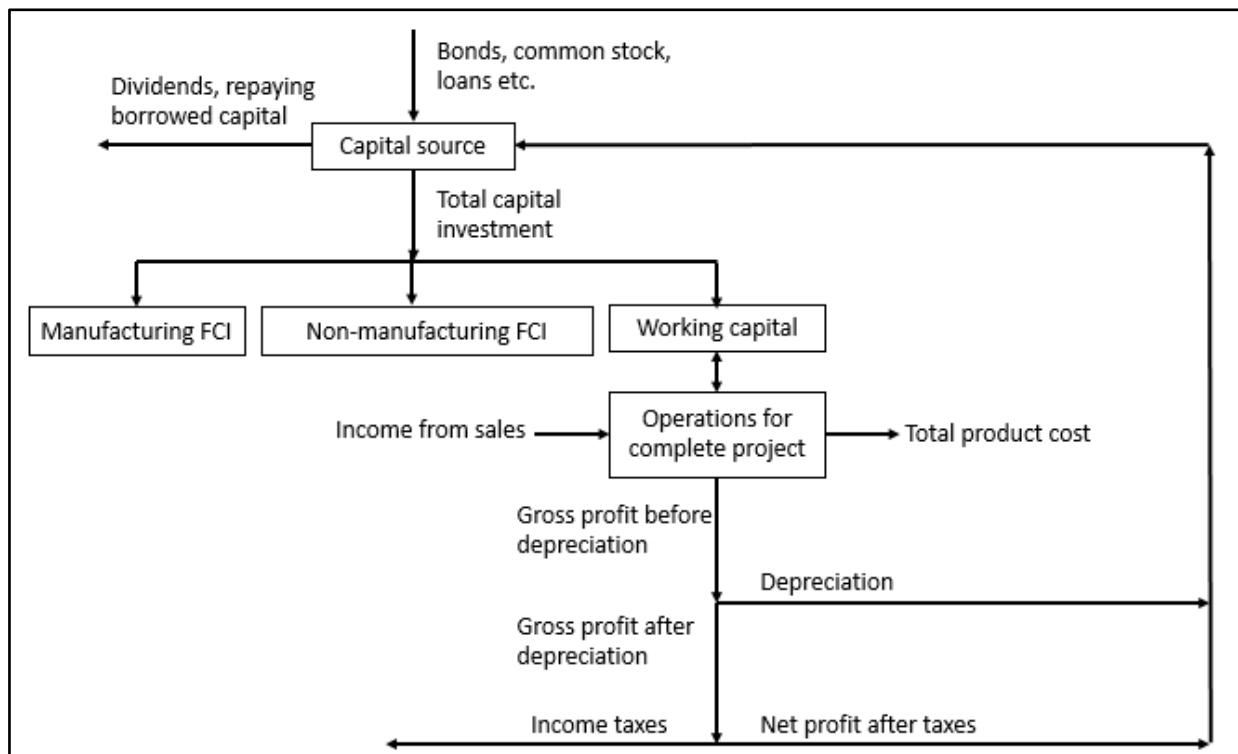


Figure 7.2: Outline of cash flow operations (adapted from Peters *et al.*, (2004)).

7.8.1 Gross profits, net profits and tax deductions

The GPBD is obtained by deducting TPC from the revenue obtained from sales. Depreciation is deducted from the GPBD, and results in the GPAD from which income taxes are calculated and deducted to determine the net profit. The annual cash flow can then be determined by adding depreciation to the net profit and subtracting the capital payments (when applicable).

Depreciation implies that the value of assets decrease over time and has a substantial influence on the cash flow position of a project. Depreciation can be of physical nature or functional nature. The physical nature of depreciation leads to a reduction in the serviceability of the property due to changes in its physical appearance that may include corrosion, plant upgrades, deterioration etc. which in turn results in the loss of financial value of the property. Functional depreciation entails the loss of value owing to novel technological developments, drop in product demand, unsatisfactory plant capacity, etc. The guidelines provided by the PKF Africa Tax Guide, (2015), was employed to determine the depreciation. Depreciation charges were therefore charged as follows: 40% of FCI (excluding land cost) in the first year of production, and 20% after the first year for the next three consecutive years. Thus depreciation was only charged over a period of four years during the initial stages of operation, which improved the annual cash flow position significantly.

The total amount depreciable was R6.18 million, with R2.47 million in the first year and R1.24 million in the three consecutive years after the first year.

The relationship between depreciation and taxable profits is important due to the fact that although depreciation is regarded as an expense, it is considered to be a payment into the company capital reserve. The depreciation charge is therefore not taxable (Peters *et al.*, 2004).

7.8.2 Cumulative cash flow analysis

The cumulative cash flow of a project is of great importance in order to assess the growth thereof over the project lifetime, as well as to predict the profitability and risks. It represents the rates of cash flow, takes into account the time value of money, and indicates when capital investments are expected to be paid back. Figure 7.3 illustrates the cumulative and cumulative discounted cash flow over the 28 year period, as detailed design, construction and commissioning was assumed to take 3 years and a plant lifetime of 25 years was assumed.

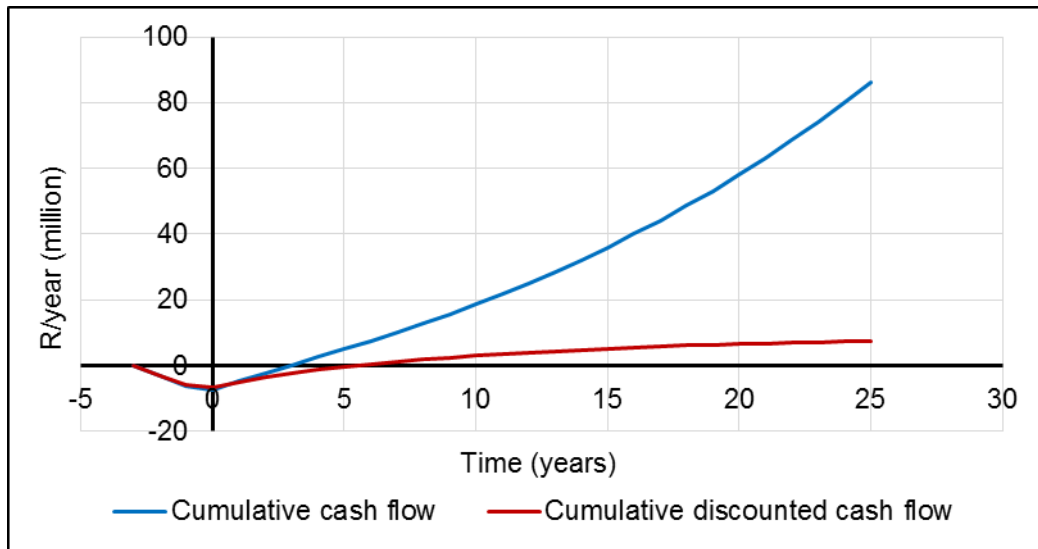


Figure 7.3: Accumulated cash and -discounted cash position over 30 years.

The zero point on the time coordinate represents the point at which construction has been completed and start-up has commenced. The initial negative cash position is attributed to the total capital investment at zero time. Thereafter, the cash flow to the company treasury (in the form of net profit after taxes plus depreciation) starts to accumulate with time and gradually repays the total capital investment. From Figure 7.3, it can be observed that the capital investment is paid back at approximately 5-6 years. A positive cumulative cash flow indicates that profits are accumulating (Peters *et al.*, 2004). The discounted cash flow employs future, free cash flow (cash a company generates after laying out the money essential to maintain or expand its asset base) projections, and discounts them to arrive at a present value estimate. This estimate is used to evaluate the potential for investment (Peters *et al.*, 2004). A salvage value at the end of the project lifetime was not taken into account in this instance, but would normally include the land value, working capital and the value at which the plant equipment was sold (if possible) (Peters *et al.*, 2004). Calculations of the cumulative cash flow analysis are provided in Appendix E.3, which include that of the gross profits, net profits, tax deductions, depreciation, cash flow and discounted cash flow as well as the cumulative cash flow and discounted cash flow.

7.8.3 Breakeven point

The breakeven point is the production rate at which the income from sales are equal to the production costs, therefore if production rate is increased from this point on, a profit will be made, whereas a reduction in the production rate will result in a loss. The components taken into consideration during calculation of the breakeven point is shown in Table 7.4, where a breakeven point of 2173 tonne/year of coal treated can be observed.

Table 7.4: Breakeven point.

Component	Value
Annual variable production cost (million)	R 4.38
Remaining TPC (million)	R 0.94
Fixed charges (million)	R 0.06
Overhead costs (million)	R 0.66
General expenses (million)	R 0.22
Revenue (million)	R 7.63
Sales price (per ton of coal treated)	R 1 018
Sales of product (ton/yr of coal treated)	7500
Direct product cost (per ton)	R 584
Breakeven point (ton/yr of coal treated)	2173

A breakeven chart is a useful presentation of the ideal operation conditions and shows the rate of production. The influence of production rate on production costs and revenue is displayed in Figure 7.4. The breakeven point observed in Figure 7.4 agrees with that reported in Table 7.4. It is clear that a higher production rate is favourable when revenue and production costs are taken into account.

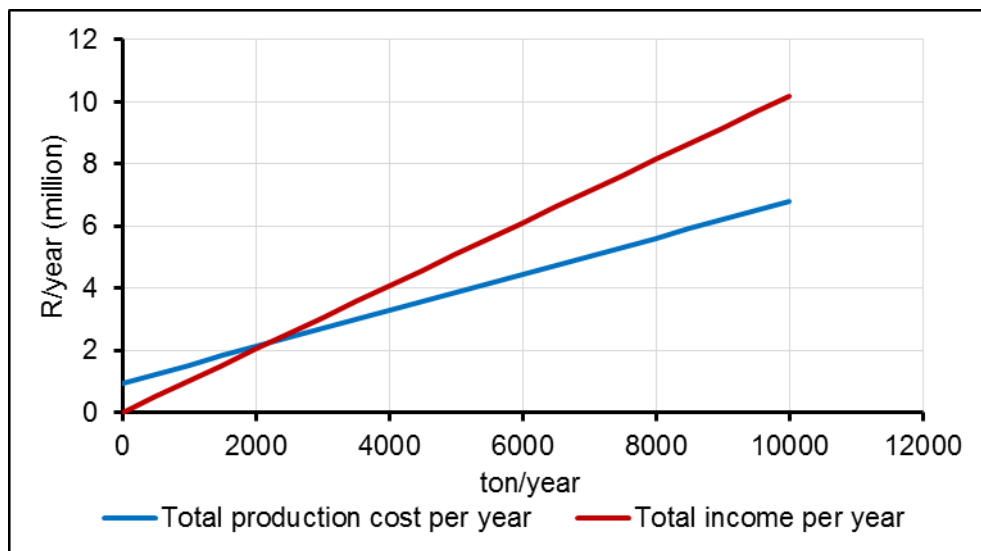


Figure 7.4: Breakeven chart.

7.9 Profitability

The profitability of a proposed project plays a key role in assisting with investment decisions, and it is important that the profit accumulated throughout the plant lifetime exceeds that of the total initial capital investment. Hence, the need to determine a series of profitability measures

that will compare the implications of the project, project options, and the initial investment, and are discussed in this section (Seider *et al.*, 2010).

7.9.1 Capital cost and rate of return

During assessment of the profitability and feasibility of a project it is important to take into consideration the amount of money that has to be paid back to the sources of capital as incentive for supplying these funds. The TCI supplied by the source serves as the basis from which these amounts are established. Such capital costs include bond dividends, stock and interest on loans.

The minimum acceptable rate of return (m_{ar}) or hurdle rate specifies the minimum rate of earning required by the involved investors supplying the TCI. This standard is expressed as a fraction per annum, and is usually based on the maximum achievable earning rate (Peters *et al.*, 2004). Although the process of coal pyrolysis is well established, the use of low-smoke fuels to fulfil household energy requirements is not yet an established market in South Africa. Therefore, Peters *et al.*, (2004), suggests a m_{ar} ranging between 24% and 32% is applicable, however as this project is strategically driven (low-income community upliftment, while air pollution is reduced) rather than economically, a hurdle rate of 15% was selected.

7.9.2 Profitability measures

The profitability directories can be determined without/with taking into consideration the time value of money. Measures that do not consider the time value of money include return on investment (ROI), payback period (PBP) and the net return (R_n), whereas net present worth (NPW) and discounted cash flow rate of return (IRR/DCFR) do consider the time value of money. The equations utilised to estimate these parameters are provided in Appendix E.2. The net return is the cash flow over and above that necessary to satisfy the minimum acceptable rate of return and recover the capital investment (Peters *et al.*, 2004). NPW is the total of the present worth of all cash flows minus the present worth of all capital investments, whereas DCFR is the return attained in which all investments and cash flows are discounted. The estimated profitability measures with interpretations thereof are reported in Table 7.5.

Table 7.5: Profitability measures.

Measure	Value	Interpretation
ROI (%)	23	Greater than hurdle rate m_{ar} (15%)
Reference PBP (yr)	4.6	Reference according to Peters <i>et al.</i> , (2004)
Actual PBP (yr)	4.3	2 Years greater than reference
R_n (million)	R 45	Positive value (Positive investment)
NPW (million)	R 7.4	Positive value (Positive investment)
IRR/DCFR (%)	26	Greater than hurdle rate m_{ar} (15%)

The hurdle rate of 15% selected is representative of a moderate degree of risk as low-smoke fuels for household coal usage are yet to be implemented, however there is a significant need for such a fuel in South Africa. A ROI of 24% was determined for the project, which was 1% lower than the minimum specified for such ventures according to Seider, *et al.*, (2003). There is, however, a possibility to decrease the production costs of the project such as the possibility of acquiring the coal feedstock at discounted prices, and in the event of using excess steam from nearby power plants or petrochemical industries such as Sasol, may also reduce the production costs of the plant. This would increase the return on investment for the project, and an evaluation of the effect of production cost on the ROI, PBP and NPW is provided in Section 7.8. The positive NPW of R7.6 million is indicative of the project providing a return at a rate greater than the discount (earning) rate used throughout the calculations, therefore the larger the NPW, the more favourable the investment. The NPW value was taken as the final cumulative discounted cash flow value reported in Table E.3.7, Appendix E.3. The actual earning rate represented by the IRR/DCFR was estimated at 27%, which is 12% higher than the minimum acceptable rate of return selected. A positive net return (R_n) value indicated that the cash flow to the project is in fact greater than the amount necessary to repay the capital investment, while the minimum acceptable rate of return is achieved. The reference and actual payback periods estimated are relatively similar at 4.6 and 4.3 years respectively, after start-up was initiated which agrees relatively well with the 5-6 years found by the cash flow analysis, indicated in Figure 7.3.

7.9.3 Effect of inflation

Inflation can be defined as the gradual increase in costs of resources and services over time and is expressed as an annual percentage of costs. It is therefore of utmost importance to take the effect inflation on production costs and revenue into account when estimations for plant operations over many years are made (Peters *et al.*, 2004).

The effect of inflation is provided by Equation 7.3 (Peters *et al.*, 2004):

$$Cost_{year} = (Cost_{0,years}) \times (1 + i')^j \quad \text{Eq. 7.3}$$

here i' is the annual inflation rate and j the number of years for which inflation is charged (Peters *et al.*, 2004).

7.10 Optimum design and sensitivity analysis

Optimum design conditions are specified with the intent to ensure desirable financial results, therefore it is imperative to firstly define the optimization measures followed by defining all the factors with an influence on the respective measures. The relationship between measures and influential factors are frequently of mathematical nature. By clearly defining these components it becomes possible to determine which factors have both positive and negative impacts on the profitability measures. Such an analysis is referred to as a sensitivity analysis (Peters *et al.*, 2004).

A sensitivity analysis was conducted in order to determine the effect of a specified set of parameters on the profitability measures investigated in this chapter. These values were varied from -40% to 40% and include the following:

- Minimum acceptable rate of return (m_{ar})
- Fixed capital investment (FCI)
- Variable production cost per year
- Total revenue

The profitability measures evaluated consisted of:

- Return on investment (ROI)
- Payback period (PBP)
- Net present worth (NPW)

Results of the sensitivity analysis are displayed in Figure 7.5, Figure 7.6 and Figure 7.7, and the respective calculations thereof are provided in Appendix. E.4.

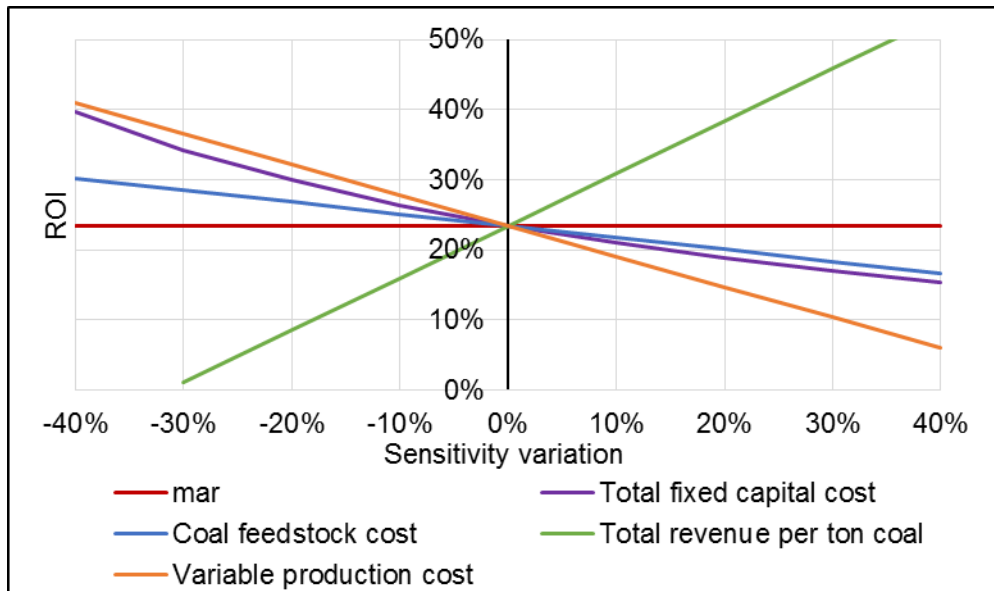


Figure 7.5: Sensitivity analysis of the return on investment (ROI).

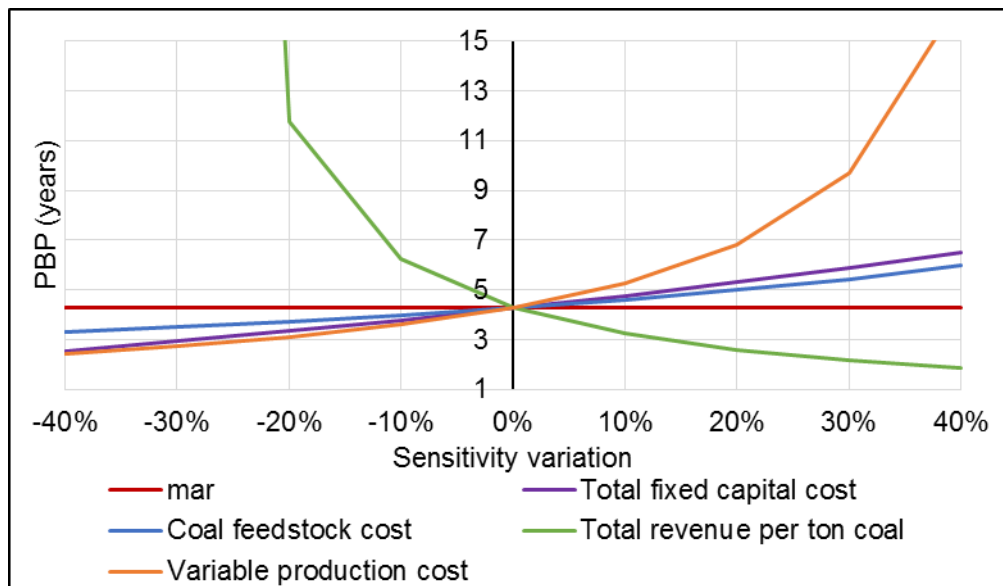


Figure 7.6: Sensitivity analysis of the payback period (PBP).

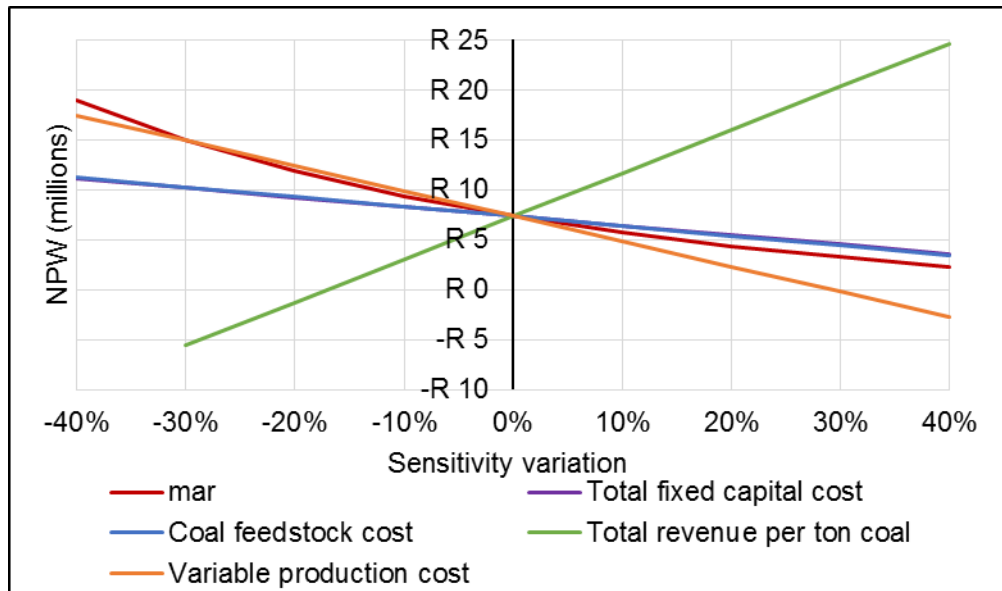


Figure 7.7: Sensitivity analysis of the net present worth (NPW).

During interpretation of the sensitivity analyses' results, the effect of each variable on the profitability measures (ROI, PBP and NPW) is observed. It should be noted that the lines for the total revenue did not continue throughout the total sensitivity variation in the event of negative values reported for the ROI and NPW. The vertical axis of Figure 7.6 was limited to 15 years, however exponential increases in PBP with regards to the total revenue per tonne of coal treated and the variable production cost was observed, and the actual values can be found in Table E.4.1 - Table E.4.5, Appendix E.4. From the results it is clear that the revenue and variable production cost have the greatest influences on the profitability of the project, and the effect thereof on the ROI and NPW is linear. As revenue increases the ROI and NPW also increase linearly and vice versa. Although the PBP increases exponentially with a decrease in revenue, a relatively linear decrease in PBP can be observed for an increase in revenue. The ROI and NPW decrease with increasing production costs and vice versa, and it is clear that the PBP increases exponentially with increasing production costs. Similar to the trend of the revenue, the PBP decreases relatively linear with decreasing production costs. The fixed capital cost and coal feedstock cost posed to have a similar influence, with a relatively strong linear correlation with all of the profitability parameters. As fixed capital cost and coal feedstock cost increases the m_{ar} and NPW decreases linearly and vice versa, whereas the opposite can be observed for the PBP. The m_{ar} only seemed to have a notable influence on the NPW as the NPW increases with decreasing m_{ar} and vice versa.

7.11 Summary

It should be noted that this section of the investigation was performed with the intent to provide a high level indication of the economic feasibility of a low-smoke fuel production plant. Therefore

it is acceptable that estimates with an accuracy of $\pm 30\%$ were made. It is however, recommended that further detailed designs of such a process be conducted, with the possible assistance of industries that are interested in low-income community upliftment.

A total capital investment of R7.36 million was estimated for the project with the annual total production costs and revenue being R5.32 million and R7.63 million respectively. With regards to the profitability measures, a ROI of 24% was found, and the PBP was estimated to be around 5 years, which is one year longer than the acceptable time frame of four years according to Seider *et al.*, 2003). Therefore, additional funding would possibly be required for successful implementation of a low-smoke fuel production facility. A positive net return and NPW of R46 million and R7.6 million respectively are indicative of a good investment. An IRR of 26%, which is 11% higher than the hurdle rate selected for this investigation, also point towards a relatively positive investment. A breakeven point of 2173 tonne of coal to be treated yearly was found, which represented approximately 29% of the project's capacity; and after production increases past this point, profits and positive cash flow would be realised. From the sensitivity analyses, it was found that the annual revenue and total production costs have significant effects on the profitability of the project. Coal feedstock cost and the fixed capital cost effect the profitability to a lesser extent, whereas the hurdle rate has a strong linear effect on the NPW, but not on the ROI and PBP. Furthermore, a significant number of jobs would be created during the three year construction period (50-80 jobs), and ten permanent operational jobs since operation of the plant. These jobs could be sourced locally, and potentially as part of a social development project from a major company to develop skills within the local community.

It was, however found that a low-smoke fuel production facility may in fact have a higher feasibility in comparison to acquiring anthracite to be sold to low-income communities. As it costs approximately R1.50 to deliver the anthracite to Secunda from Nkomati Anthracite mine in Komatipoort and the fuel is to be sold at R1.00/kg to the residents, would require that R0.50/kg be subsidised via external funding. The low-smoke fuel production facility, however, has the potential to produce low-smoke fuels at a lower cost, being able to sell low-smoke fuels at the desired R1.00/kg. It is however crucial that the by-products obtained from the pyrolysis process are sold in order for the campaign to become viable. Consequently, the low-smoke fuel production process is the more viable option to consider.

It should be remembered that steam utilised in the process was bought from Sasol, (Secunda Plant) and therefore, no capital costs were accounted for with regards to a boiler system to produce the necessary steam, resulting in lower fixed capital investment. A gas fired burner may be an alternative option to steam use, which would result in less water condensing downstream of the reactor section, however capital and production costs thereof would have to be investigated first. With the ROI being slightly low, it points towards a high risk investment. The

sole purpose of a low-smoke fuel production plant would be to provide low-smoke fuels to low-income households throughout South Africa, while less air pollution is produced. Furthermore, a low-smoke fuel production facility would not necessarily be economically driven to make a profit, therefore the project could be feasible in this specific case. A secondary purpose of a low-smoke fuel production plant would be to create jobs in low-income areas which, together with the reduction in air pollution, contribute to community upliftment.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

The topic of this investigation was the production of technically viable low-smoke fuels with the means to replace coal as a household fuel that will also fulfil the energy requirements of low-income households, while the amount of air pollution is simultaneously reduced. This chapter concludes the findings of this thesis based on the objectives set out in Chapter 1 (Section 7.2), the contribution made to the existing field of knowledge in Section 7.3, and recommendations for future work are suggested in Section 7.4.

8.2 Conclusions regarding project objectives:

8.2.1 *Characterisation of the parent coal sample obtained from Kwadela, a typical South African anthracite and the low-smoke fuels produced through chemical, mineralogical and petrographic analyses as to form a basis with which low-smoke fuels can be compared.*

Various samples of the Kwadela coal were characterised consisting of a representative composite sample as well as three respective particle size fractions (20 mm, 30 mm and 40mm particles). Kwadela coal was classified as a medium rank C inertinite rich bituminous coal with a mean random reflectance of 0.83, and consisted of 82vol.% inertinite, 11vol% vitrinite and 7vol.% liptinite, all of which were reported on a mineral matter free basis. The chemical characteristics of the three particle size fractions investigated were relatively similar to that of the representative Kwadela coal sample with only minor differences observed. The representative composite sample contained approximately 6wt.% (a.d.) more ash in comparison to the 20mm (23.5wt.% (a.d.)), 30mm (24.9wt.% (a.d.)) and 40mm (24.3wt.% (a.d.)) particles. Whereas, a relatively constant fuel ratio (FC/VM) of approximately 2 was observed in all cases. The gross calorific values of the respective coal samples were fairly similar ranging from 20.5 MJ/kg to 22.5MJ/kg (a.d.). The respective C, H, N, O and S contents (from the ultimate analyses) of all the raw coal samples were in the range of 76-79wt.%, 3.9-4.1wt.%, 1.4-1.9wt.%, 13.6-17.5wt.% and 0.7-1.1wt.%, all on a dry, ash free basis. Atomic H/C and O/C ratios were approximately 0.61 and 0.15 respectively throughout. XRF analysis of the representative coal sample indicated that SiO₂ and Al₂O₃ were the largest constituents of the ash, while the mineral matter according to the XRD analysis consisted predominantly of kaolinite, dolomite, calcite and quartz. The exact origin of the Kwadela coal sample is unknown, however results obtained from the chemical-, mineralogical- (XRF) and petrographic analyses were similar to that of a typical Highveld seam 4 coal.

8.2.2 *The effect of final pyrolysis/devolatilisation temperature and coal particle size on the quantity and quality of the resulting products yielded.*

An in depth devolatilisation study was performed with the intent to provide insight with regards to the quantity and quality of the respective products (char, water, tar and gas) resulting from low-smoke fuel production, where coal is used as the raw fuel. Experiments were conducted using the NWU Fischer Assay setup. From devolatilisation of three particle size fractions (20, 30 and 40 mm) it could be concluded that the solid char constituted the largest portion of the products obtained, which is the low-smoke product fuel. Devolatilisation of the raw Kwadela coal was commenced at temperatures 450°C, 550°C, 650°C and 750°C, which is the temperature region known as low-temperature carbonisation. Overall, it was found that the products were predominantly dependant on the final pyrolysis temperature as it was observed that char yields decreased with increasing temperature, hence an increase in the degree of devolatilisation. No significant inconsistencies with regards to particle size variation was found, however small discrepancies were noted. The average char yields obtained from pyrolysis at 450°C, 550°C, 650°C and 750°C were 97wt.%, 93wt.%, 90wt.% and 87wt.% (d.m.m.f.) respectively, which stresses the decrease in char weight after pyrolysis. Inconsistent particle fragmentation was observed for the 40mm particles at the two higher devolatilisation temperatures of 650°C and 750°C. In contrast to the decreasing char yield, water and gas yields (d.m.m.f.) increased steadily with final pyrolysis temperature. Tar production (d.m.m.f.) increased until a maximum yield was obtained at temperatures ranging between 550°C and 650°C, after which it decreased slightly as the devolatilisation temperature increased further up to 750°C.

Proximate analyses of the solid low-smoke fuels produced at the four devolatilisation temperatures, indicated that volatile matter decreased, while fixed carbon content increased as final pyrolysis temperature increased. The increasing fuel ratio is a useful parameter to consider during devolatilisation as it is indicative of a fuel's ability to ignite, where a high fuel ratio may lead to a fuel having difficulty igniting. Fuel rank was found to increase with increasing temperature and gross calorific value (m.m.m.f.). From the ultimate analysis it was concluded that the carbon (d.m.m.f.) content increased with devolatilisation temperature, whereas, both the hydrogen (d.m.m.f.) and oxygen (d.m.m.f.) present in the char product decreased. The amount of N₂ (d.m.m.f.) in the solid char remained relatively constant throughout devolatilisation. No definitive remarks could be made regarding the sulfur content, as no obvious trends were observed. Atomic H/C and O/C ratios decreased as pyrolysis temperature decreased, which is indicative of increasing aromaticity.

Analyses of the respective tar samples (Simdis-, GC-MS/FID- and SEC-UV analysis) all found that neither final pyrolysis temperature nor particle size variation had major effects on the results thereof. A weight average boiling point of approximately 300°C was found (according to the

Simdis analyses) for all the tars analysed irrespective of pyrolysis temperature and particle size, with the largest fraction contributing to the boiling point of the tar being light vacuum gas oil, a relatively high boiling point fraction. With regards to molecular families (from the GC-MS/FID) it was concluded that mixed aliphatic and aromatic compounds mostly represented the largest group, followed by alkyl-phenols and aliphatic compounds. From the SEC analyses it was found that the heavy components represented the slightly larger proportion than the lighter components, which is in agreement with the findings from the Simdis: i.e. higher boiling point fractions and heavier components are present in large quantities in the tar.

From a molar compositional (mol.%) analyses of the gases evolved during coal pyrolysis it could be concluded that the main constituents included H_2 , CO, CO_2 and CH_4 , with CO_2 being the largest throughout. Significant effects regarding pyrolysis temperature were observed, while particle size seemed to be trivial. Hydrogen (mol.%) fractions increased considerably with increasing pyrolysis temperature, whereas CO_2 (mol.%) quantities were found to diminish. The increase in H_2 (mol.%) in the gas agrees well with the findings from the proximate analyses of the respective chars which indicated that the H_2 present in the chars decreased with increasing pyrolysis temperature. The lower quantities of H_2 present in the high temperature chars may result in it being difficult to ignite in comparison to coal.

Once the in depth investigation regarding the effects of final pyrolysis temperature and particle size was completed, low-smoke fuels could be produced in large quantities which would be evaluated in combustion performance experiments discussed in the following section.

8.2.3 *The Effect of final pyrolysis temperature on the fuel characteristics and emissions released from combustion of the low-smoke fuels versus that of the raw coal and anthracite.*

A series of low-smoke fuels were produced from the raw Kwadela coal at temperatures consisting of 450°C, 550°C, 650°C and 750°C. The respective quantities of low-smoke fuels obtained from pyrolysis at 450°C, 550°C, 650°C and 750°C were approximately 89wt.%, 83wt.%, 80wt.% and 76wt.% (as determined). The decrease in char yield is in agreement with the findings summarised in Section 7.2.2 with regards to the extensive devolatilisation study.

Fuels characterised other than the raw Kwadela coal, included a locally obtained anthracite and the low-smoke fuels produced during this investigation, however these fuels were only characterised according to proximate-, ultimate- and gross calorific value analyses. Classification of the anthracite and low-smoke fuels were also performed according to rank (ASTM-D388) and it was similarly found that fuel rank increased as the final pyrolysis temperature increased. Accordingly the fuel rank given in increasing order: Coal (medium rank

C coal)<Char-450 (high volatile B bituminous coal)<Char-550 (high volatile A bituminous coal)<Anthracite (semianthracite)<Char-650, Char-750 (meta-anthracite).

The proximate analysis of the different fuels revealed that volatile matter decreased with an increase in pyrolysis temperature, while fixed carbon increased, which is evident from the increasing fuel ratio as pyrolysis temperature increases. The anthracite investigated contained approximately 11wt.% (a.d.) ash and volatile matter respectively and a high fixed carbon content of 75.8wt.% (a.d.). Similar trends for the carbon, hydrogen and oxygen from the ultimate analyses were observed for the low-smoke fuel than that discussed in Section 7.2.2: i.e. carbon increased, while hydrogen and oxygen decreased with increasing final devolatilisation temperature. The N₂ and S remained relatively constant at approximately 1.9wt.% and 1wt.% (d.a.f.) respectively, however a discrepancy was observed for the sulfur (3wt.% (d.a.f.)) of the low-smoke fuel produced at 550°C. Atomic H/C and O/C ratios displayed similar trends than those described in Section 7.2.2.

A series of combustion performance experiments were conducted with the intent to determine the various emissions produced that contribute to air pollution as a result of household burning activities. In addition to the emissions measured, a set of physical parameters were developed which could be practically demonstrated to residents in Kwadela Township. A comparative study was therefore conducted to stress the differences in combustion behaviour of raw coal, anthracite and the low-smoke fuels produced. The emissions measured included NO_x, CO, CO₂, SO₂, total suspended particulate matter (TSP) and volatile organic compounds (VOC's). A reduction of approximately 76-82% was observed for the TSP emissions (measured according to US EPA Method 5) of all the low-smoke fuels including anthracite in comparison to coal. The differences in TSP emissions produced by the low-smoke fuels were insignificant. A significant reduction in VOC emissions was also found for all the chars as well as the anthracite, all within the range of an 80-90% reduction, while the trend displayed a sharp reduction between Char-450 and Char-550, after which the reduction stabilised as pyrolysis temperature increased. TSP and VOC emissions produced during combustion of the anthracite fuel resulted in similar quantities detected for the low-smoke fuels. The NO_x and SO₂ gas emissions were found to decrease as final pyrolysis temperature increased, however the char produced at 450°C produced approximately 20% more SO₂ than coal. A similar amount of NO_x was detected for Char-550, whereas further reductions were observed for the rest of the low-smoke fuels. The low-smoke fuel produced at and 750°C showed significant reductions in NO_x and SO₂ emissions released, being approximately 65% and 40% lower than that of raw coal. Char-650 produced around 25% less NO_x and 40% less SO₂ respectively. CO and CO₂ emissions from combustion displayed identical trends: i.e. an increase up to a maximum at 650°C followed by a decrease, however the quantities were still higher than that produced during combustion of the raw coal.

The only gas emission detected to be lower than that of coal was the CO₂ produced by Char-750. Combustion of the anthracite fuel resulted in lower quantities of CO and SO₂, whereas the NO_x and CO₂ emissions were similar to that of coal.

The combustion performance of the low-smoke fuels were evaluated according to two perspectives, i.e. the practical and emissions perspective. It should be remembered that the practical parameters are key to the practical feasibility of the low-smoke fuels acceptance, which may be the determining factor if these fuels will be used by residents in low-income households. In terms of ignitability (which is the first key influential practical parameter) it was found that the anthracite and low-smoke fuels ignited slightly more difficult than the coal, although, no conclusive trends could be observed for the respective low-smoke fuels produced. The time to boil 1L of water is an important parameter investigated during the combustion performance tests and it was found that the water boiled in the shortest period of time (~17 minutes) for the raw coal and anthracite. It took approximately 30 minutes for the water to boil for both the low-smoke fuels produced at 450°C and 550°C, followed by 37 minutes for the char produced at 650°C. The low-smoke fuel produced at 750°C took approximately 1 hour, indicating that this fuel would definitely not provide sufficient energy for cooking purposes in low-income households. With regards to the total time space heat is provided it was found that all the fuels provided heat for a longer period relative to coal, and the differences observed between the low-smoke fuels were fairly insignificant. The combustion efficiency found for the low-smoke fuels produced at 450°C and 550°C were 79% and 77% respectively, which is higher than for the raw coal (69%), while lower efficiencies were noted for Char-650 and Char-750, which was 67% and 63% respectively. The highest combustion efficiency was found for the anthracite fuel at a value of 80%.

A selection process was developed with the intent to compare the emissions as well as practical properties of the different fuels evaluated in the combustion performance tests. It is important to note that the practical parameters, especially the time to boil 1L of water and the ignition time are perhaps the two most important parameters regarding the low-smoke fuel investigation in terms of acceptance and implementation, possibly outweighing the emissions criteria. It is thus imperative that the ideal low-smoke fuel has the ability to fulfil the household energy needs of residents in Kwadela, while the quantity of emissions produced are simultaneously reduced. From an emissions perspective, the best viable option to replace coal was the low-smoke fuel produced at 750°C, as the highest reductions in TSP, VOC's, NO_x, SO₂, CO and CO₂ were observed, however, this fuel lacked the heat energy to boil 1L of water within an acceptable time frame. Consequently, the anthracite and char produced at 550°C performed well according to the two predominant practical parameters, while a significant reduction was observed for the TSP as well as VOC's. NO_x emissions of the anthracite was similar to that of coal. As an

alternative, the char produced at 450°C could also serve as a viable fuel to replace coal with the differences to Char-550 being: increased SO₂ emissions, lower NO_x emissions and a longer ignition time (10 minutes longer than char-550).

In conclusion, the anthracite and char produced at 550 °C is suggested as the most viable low-smoke fuel to replace coal as it performs well with regards to both the practical parameters as well as the emissions in relation to the other fuels evaluated. The major benefit during combustion thereof in household appliances include significant reductions in TSP and VOC emissions, while it is still practical.

Residents of low-income households buy coal at relatively low prices and a fuel that is intended to replace coal, should therefore have a cost within a similar range than that of coal. According to the basic techno-economic feasibility study performed, such a process would have a return on investment of 24%, which is just within (below) the minimum for moderate risk projects. At this stage, however, low-smoke fuel production from coal intended to replace coal as a household fuel are possibly regarded as a high risk venture that requires a ROI of 50%. On the other hand, it should be noted that such a project would not necessarily be driven from an economic perspective, but rather strategically to reduce air-pollution, and improve the quality of life of low-income communities. The relatively low ROI is therefore acceptable in this specific instance. Other profitability measures such as the net present worth and internal rate of return pointed towards a relatively positive investment, thus indicating that a low-smoke fuel production facility may be profitable, although it might be by a small margin. It was concluded that a low-smoke fuel production process would deliver an environmentally friendlier fuel to residents with low-incomes, while jobs are created due to LSF plant operation in low-income areas, thus resulting in community upliftment and a reduction in air pollution. The cost to deliver anthracite is approximately R1.50/kg, which is 50% higher than the selling price of the proposed low-smoke fuel (R1.00/kg), however no jobs would be created in low-income areas and would make a smaller contribution to the increase in quality of life of the residents in such areas.

8.3 Contribution to the knowledge field of low-smoke fuels to replace coal as household fuel

- Extensive characterisation understanding with regards to the chemical, mineralogical and petrographic aspects of the raw coal obtained in a South African township, providing insight on the quality of the coal being used to fulfil the energy needs of low-income households in South Africa has been obtained. Characterisation included that of large coal particles of different size fractions, thus gaining knowledge in relation to particle size variation within the same coal sample.

- An in depth pyrolysis investigation revealed the behaviour of three respective lump coal particle size fractions at various degrees of devolatilisation. Quantification of the products (char, water, tar and gas) as well as the quality thereof provided useful information regarding the production of low-smoke fuels from raw coal from which conclusions could be formulated regarding coal (of different sizes) pyrolysis at different temperatures. Characterisation of pyrolysis products in terms of chemical properties, stressed the effects of devolatilisation on the low-smoke fuel (char). Compositional analyses of the gas and advanced analyses of the tar (Simdis, GC-MS/FID, SEC) products proved useful when taking into consideration the possible economic potential of the gas and tar products.
- The production of low-smoke fuels (to different extents) from coal and evaluation of the combustion behaviour thereof, in a typical cast iron stove such as those used by residents in Kwadela Township, provided insight on the emissions produced as well as the technical viability of low-smoke fuels in comparison to coal. Such extensive evaluation of low-smoke fuels is the first of its sort as far as relevant literature was reviewed.
- The in depth combustion performance evaluation provides a solid basis for future work regarding low-smoke fuels produced from coal.
- Basic knowledge regarding a process suitable to produce low-smoke fuels from coal and the economic potential thereof were provided in which the possibility of community upliftment is stressed.

8.4 Recommendations for future studies

Based on the findings of this investigation it was established that certain aspects need to be studied further in order to better understand the production as well as combustion of low-smoke fuels produced from coal. Accordingly the following recommendations are suggested:

- Practical field testing of the low-smoke fuels in Kwadela is probably one of the most important suggestions resulting from this investigation, as findings from such a field test would prove if residents accept low-smoke fuels above coal. The performance with regards to the emissions produced as well as the practical parameters have to be evaluated within the township in comparison to coal.
- A collaborative industrial partner in the Secunda area should be identified with the view to jointly develop the low-smoke fuel production process further until successful implementation.
- The techno-economic feasibility study should be firmed up with a proper detailed design of such a facility in order to provide higher accuracy financial results.

- Investigate the pyrolysis behaviour of lump coal on a larger scale as to utilise samples more representative of the respective particle sizes. Therefore the pyrolysis products obtained would be more representative.
- Determination of the weight of gas evolved during pyrolysis, inside a vacuum enclosure wherein the gas bag containing the captured gas can be weighed.
- The influence of a combustion catalyst added to Char-750 and the cost implications thereof should be investigated in further studies. One of the catalysts that could be investigated is the CC-88 coal combustion catalyst, which is a dry powder catalyst that increases combustion efficiency and lowers the ignition temperature of the fuel it is added to.
- The price at which the coal derived tar could be sold to petrochemical companies such as Sasol should be investigated.
- Investigate lump coals of different rank and characteristics during in depth devolatilisation and evaluate the low-smoke fuels produced thereof. This would indicate if low-smoke fuels (with different inherent properties) that were produced at the same conditions as those evaluated in this study have similar/different combustion behaviour.
- Quantify the emissions produced during devolatilisation of coal in order to construct a complete cycle containing the total emissions produced during devolatilisation as well as combustion.
- It is proposed to employ flexible piping between the coal stove and chimney (supported by building structure) as the stove was placed on a balance and mass readings may be influenced in the event of the material expanding/contracting as heat is applied/removed. Flexible piping may allow for the effects of expansion and contraction, therefore not affecting mass readings of the balance.
- It is advised to utilise ignition fuel during combustion performance tests that is better controllable and equipment that includes a gas regulator. This will enable the operator to know the exact flow rate of the ignition fuel at any given time during the ignition period.
- The combustion of lump coal particles of different sizes, respectively, may prove useful as the heat transfer properties between large coal particles of different size fractions fluctuate.
- Utilise briquettes such as that used in fires for braai to determine the repeatability of the combustion experimental setup since these briquettes may have a more homogeneous nature. Results from combustion thereof may provide a more accurate indication of the repeatability of the experimental setup.
- Different household combustion appliances may be evaluated in order to determine the variations in combustion performance from both an emissions and practical perspective.

- The resultant health effects of emissions resulting from low-smoke fuel combustion in comparison to that of coal should be investigated in order to determine the viability of such a process from a medical perspective.
- Lastly, additional emissions resulting from the combustion of coal and low-smoke fuels should be measured, such as tropospheric ozone (O_3) and greenhouse gases other than CO_2 that includes CH_4 and N_2O to form a more holistic representation of the total emissions involved in coal combustion.

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APPENDIX A: COAL CHARACTERISATION

A.1 Mineral matter

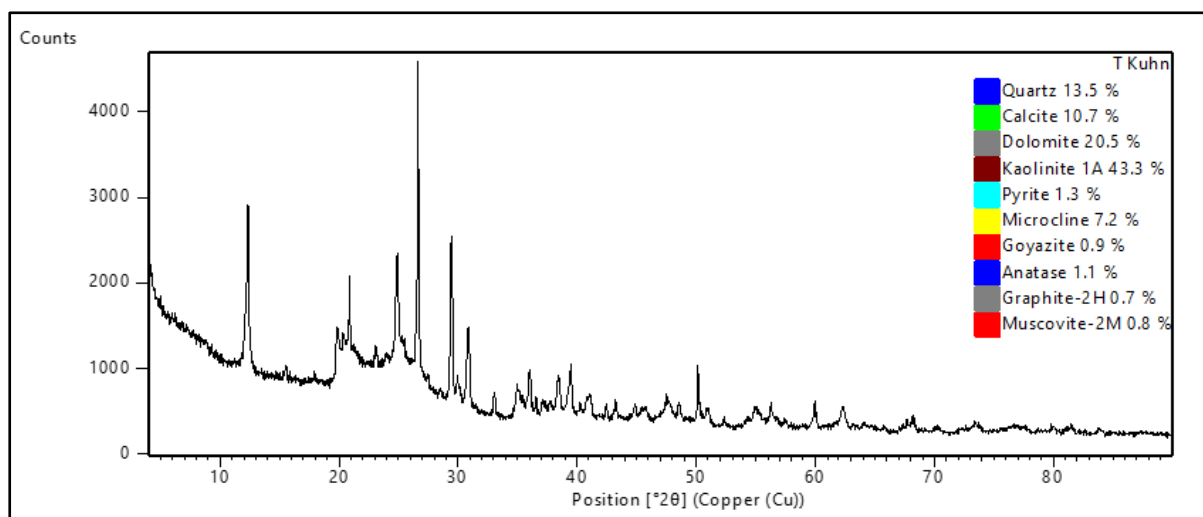


Figure A.1.1: XRD analysis results of the Kwadela representative coal sample.

APPENDIX B: GAS CALLIBRATION

B.1 Calibration gases used for combustion equipment

Table B.1.1: Details of calibration gases used to calibrate portable gas analysers.

Calibration gas standard #1		Calibration gas standard #2	
Certificate nr	2237283	Certificate nr	2139658
Component	Composition	Component	Composition
CO	500 ppm	NO	70-75 ppm
CO ₂	15%	N ₂	Balance
N ₂	Balance		
Calibration gas standard #3		Calibration gas standard #4	
Certificate nr	2139658	Certificate nr	2288187
Component	Composition	Component	Composition
NO	400 ppm	SO ₂	70 ppm
N ₂	Balance	N ₂	Balance

B.2 Gas burner used to ignite fuels during combustion



Figure B.2.1: Gas burner used to distribute flames.

APPENDIX C: PYROLYSIS PRODUCT YIELDS, QUALITY AND EXPERIMENTAL ERROR ON REPEATABILITY

C.1 Thermogravimetric analysis vs Fischer Assay

Table C.1.1: Thermogravimetric analysis vs. Fischer Assay char yields.

Particle size (mm)	20 mm				30 mm				40 mm			
Temperature (°C)	450	550	650	750	450	550	650	750	450	550	650	750
Char wt.%												
TGA	91.9	87.3	82.2	75.7	93.3	88.7	84.3	76.1	91.8	85.1	80.6	75.0
Fischer assay	90.2	84.1	80.1	77.3	90.9	86.5	81.3	77.4	91.7	86.5	82.8	79.7
wt.% Diff.	1.7	3.2	2.1	1.5	2.4	2.2	3.0	1.4	0.1	1.4	2.2	4.7

C.2 Pyrolysis product yields and experimental error on repeatability

Table C.2.1: Pyrolysis product yields on as determined basis.

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (a.d.)												
Char	90.2	84.1	80.1	77.3	90.9	86.5	81.3	77.4	91.7	86.5	82.8	79.7
Water	5.2	7.2	8.2	8.8	4.3	6.4	7.6	10.7	4.1	6.0	7.1	8.2
Tar	1.7	2.6	3.4	3.0	1.4	2.6	3.5	2.2	1.7	3.0	2.3	2.2
Gas	0.5	2.6	4.3	6.6	0.3	2.6	4.0	6.6	0.3	2.6	4.0	7.0
Total	97.6	96.5	96.0	95.7	96.8	98.1	96.4	97.0	97.9	98.0	96.2	97.1

Table C.2.2: Experimental error on repeatability on as determined basis.

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (a.d.)												
Char	1.5	3.5	1.0	0.8	4.4	1.9	4.4	1.1	1.9	3.0	1.5	2.4
Water	0.5	0.8	2.1	1.8	1.7	0.1	1.0	1.0	0.1	1.0	0.4	2.0
Tar	0.7	0.7	0.6	0.7	0.3	0.8	1.2	0.5	0.2	1.3	0.6	0.9
Gas	0.1	2.9	1.2	0.8	0.0	0.1	0.3	0.8	0.1	0.6	0.7	0.9

Table C.2.3: Pyrolysis product yields on as determined normalised basis.

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (a.d. normalised)												
Char	92.4	87.2	83.5	80.7	93.9	88.2	84.4	79.8	93.6	88.3	86.1	82.1
Water	5.4	7.4	8.5	9.1	4.4	6.5	7.8	11.1	4.2	6.1	7.4	8.4
Tar	1.7	2.7	3.5	3.2	1.4	2.7	3.6	2.3	1.8	3.0	2.4	2.3
Gas	0.5	2.7	4.5	6.9	0.3	2.6	4.2	6.8	0.4	2.6	4.2	7.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table C.2.4: Experimental error on repeatability on as determined normalised basis.

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (a.d. normalised)												
Char	0.3	3.8	3.4	2.1	1.6	0.8	2.8	1.1	0.5	2.3	1.8	3.3
Water	0.5	2.9	1.9	1.7	1.5	0.0	1.2	0.8	0.2	1.0	0.4	2.0
Tar	0.7	0.7	0.6	0.8	0.2	0.9	1.3	0.5	0.2	1.3	0.6	0.9
Gas	0.1	0.7	1.1	0.7	0.0	0.0	0.4	0.8	0.2	0.6	0.7	0.8

Table C.2.5: Pyrolysis product yields on dry-basis (d.b.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (d.b.)												
Char	97.6	94.2	91.3	88.9	98.2	94.3	91.6	89.8	97.8	94.0	93.0	89.6
Tar	1.8	2.9	3.8	3.5	1.5	2.8	3.9	2.5	1.9	3.2	2.6	2.5
Gas	0.6	2.9	4.9	7.6	0.3	2.8	4.5	7.7	0.4	2.8	4.5	7.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table C.2.6: Experimental error on repeatability on dry basis (d.b.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (d.b.)												
Char	0.8	1.2	1.9	1.4	0.2	0.9	1.9	0.5	0.4	1.7	1.5	1.9
Tar	0.8	0.8	0.7	0.9	0.2	0.9	1.4	0.5	0.2	1.4	0.7	1.0
Gas	0.1	0.9	1.3	0.9	0.0	0.0	0.5	0.9	0.2	0.7	0.8	1.0

Table C.2.7: Pyrolysis product yields on mineral matter free basis (m.m.f.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (m.m.f.)												
Char	92.1	85.5	81.1	77.7	94.1	86.6	81.9	77.7	93.7	86.8	84.1	79.1
Water	4.9	7.5	8.8	9.5	3.7	6.4	8.0	9.5	3.5	5.8	7.5	8.7
Tar	2.3	3.5	4.5	4.0	1.9	3.5	4.7	4.0	2.4	4.0	3.1	2.9
Gas	0.7	3.5	5.7	8.8	0.4	3.5	5.4	8.8	0.5	3.4	5.4	9.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table C.2.8: Experimental error on repeatability on mineral matter free basis (m.m.f.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (m.m.f.)												
Char	0.4	4.7	4.2	2.5	2.3	1.1	3.5	1.4	0.7	3	2.2	4.0
Water	0.7	3.7	2.4	2.1	2.1	0.0	1.4	1.1	0.2	1	0.5	2.4
Tar	1.0	0.9	0.7	1.0	0.3	1.1	1.6	0.6	0.3	2	0.8	1.1
Gas	0.1	0.9	1.4	0.8	0.0	0.0	0.4	1.0	0.2	0.7	0.9	1.0

Table C.2.9: Pyrolysis product yields on dry, mineral matter free basis (d.m.m.f.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (d.m.m.f.)												
Char	96.9	92.5	88.9	85.9	97.7	92.5	89.0	86.7	97.1	92.1	90.9	86.7
Tar	2.4	3.8	4.9	4.4	2.0	3.7	5.1	3.3	2.5	4.2	3.3	3.2
Gas	0.7	3.7	6.2	9.7	0.4	3.7	5.9	10.0	0.5	3.6	5.8	10.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table C.2.10: Experimental error on repeatability on dry, mineral matter free basis (d.m.m.f.).

	20 mm				30 mm				40 mm			
	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C	450°C	550°C	650°C	750°C
wt% (d.m.m.f.)												
Char	1.1	1.6	2.3	1.7	0.3	1.2	2.4	0.6	0.5	2.2	1.9	2.3
Tar	1.0	1.0	0.8	1.1	0.3	1.2	1.9	0.7	0.3	1.8	0.9	1.3
Gas	0.1	1.1	1.7	1.1	0.0	0.0	0.6	1.2	0.2	0.8	1.0	1.2

C.3 Mineral matter content calculation

Coal is composed of both organic and inorganic material where the inorganic material is often referred to as mineral matter. In order to report the products obtained from pyrolysis experiments on a mineral-matter-free basis it was necessary to determine the mineral matter content of the coal. Subsequently the mineral matter present in the coal was calculated

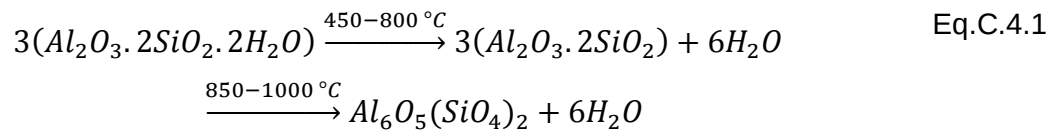
through use of the Parr formula (ASTM D-388), which applies the ash (iron-oxide-free) and sulphur contents as displayed in Equation C.1-1:

$$mm = 1.08A + 0.55S \quad \text{Eq.C.3.1}$$

where mm, A and S are the weight percentage mineral matter, ash and total sulfur respectively. Although the Parr formula is widely recognised as a means to determine the mineral matter content of coal, it is still a theoretical estimation, hence the possibility exists that true mineral matter present in individual coal particles may differ.

C.4 Correction for pyrolytic water

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is commonly found in coal according to numerous authors (Franklin, 1980; Vassileva & Vassilev, 2006; Yu *et al.*, 2007) At increased temperatures kaolinite undergoes transformation during which metakaolinite and water are formed and can be described by Equation C.2-1 (Alpern *et al.*, 1983; Ilić *et al.*, 2010; Prinsloo, 2008; Van Dyk, 2006; Vassilev *et al.*, 2009):



The decomposition of kaolinite (a clay mineral) is summarised as follows (Ilić *et al.*, 2010; Alpern *et al.*, 1983; Vassilev *et al.*, 2009):

- Loss of absorbed water (50-200 °C)
- Pre-dehydration process (200-450 °C)
- Loss of endothermic water (450-600 °C)
- Transformation to metakaolinite which may transform into various other products such as mullite, amorphous silica, spinel, cristobalite, corundum and aluminosilicate.
- Dehydroxylation occurs from 450°C to 900 °C
- Lattice destruction (850-1000°C)

Accordingly, the assumption was made that the quantity of water yielded from kaolinite transformation was constant at all the temperatures (450°C, 550°C, 650°C and 750 °C) at which the 20mm, 30mm and 40 mm coal particles were investigated. This assumption is within the correct range according to the provided literature. The molar ratios of equation C.2-1 were employed along with the coal sample mass, total mineral matter content and kaolinite quantity (obtained from XRD analysis of coal) to estimate the water yielded from

kaolinite present in the coal. Consequently the pyrolysis products could be calculated on a mineral-matter-free (m.m.f.) and dry-mineral-matter-free (d.m.m.f.) basis.

The dehydroxylation process where kaolinite forms metakaolinite and water is dependent on several factors that include the heating rate, pressure, water vapour pressure, particle size and shape as well as surface morphology. Therefore, the possibility exists that the true quantities of mineral water may differ to those estimated via Equation C.2-1. Coal particles are inherently heterogeneous, which may be further increased by an increase in particle (grain) size, and in turn also contribute to abnormalities in product yields (Manovic *et al.*, 2009).

C.5. Advanced tar analyses

Table C5.1: GC-MS/FID classification of tars into molecular families.

Molecular family	20 mm				30 mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
Unit	wt%											
Aliphatic compounds	13.0	8.9	12.6	10.1	18.9	18.3	13.9	10.1	17.3	8.5	8.7	11.1
Alkyl-Benzenes	6.7	7.4	9.0	9.7	9.9	14.1	8.8	7.5	6.4	7.9	8.1	8.0
Alkyl-Phenols	23.7	22.8	33.2	32.0	26.4	23.0	31.3	25.9	55.7	30.7	26.4	23.6
Aromatic ethers and esters	1.0	1.2	1.5	1.5	1.0	1.3	0.8	1.2	0.4	1.2	1.4	1.9
Alkyl-Indenes	2.4	1.6	2.8	2.2	3.1	2.3	2.3	2.5	2.2	2.7	2.3	1.7
Alkyl-Naphthalenes	5.3	5.0	7.6	6.2	6.8	6.5	8.2	5.8	5.0	5.9	6.1	6.7
Poly-aromatic hydrocarbons	0.8	0.8	1.1	1.5	0.9	1.0	1.3	0.8	0.3	0.9	1.0	1.1
Nitrogen heteroatoms	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mixed aliphatic and aromatic compounds	46.2	51.5	31.5	36.0	31.7	33.2	33.2	45.4	11.7	41.6	45.4	45.5
Alicyclic compounds	0.7	0.7	0.7	0.6	1.1	0.2	0.1	0.6	0.9	0.5	0.5	0.3
Other	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

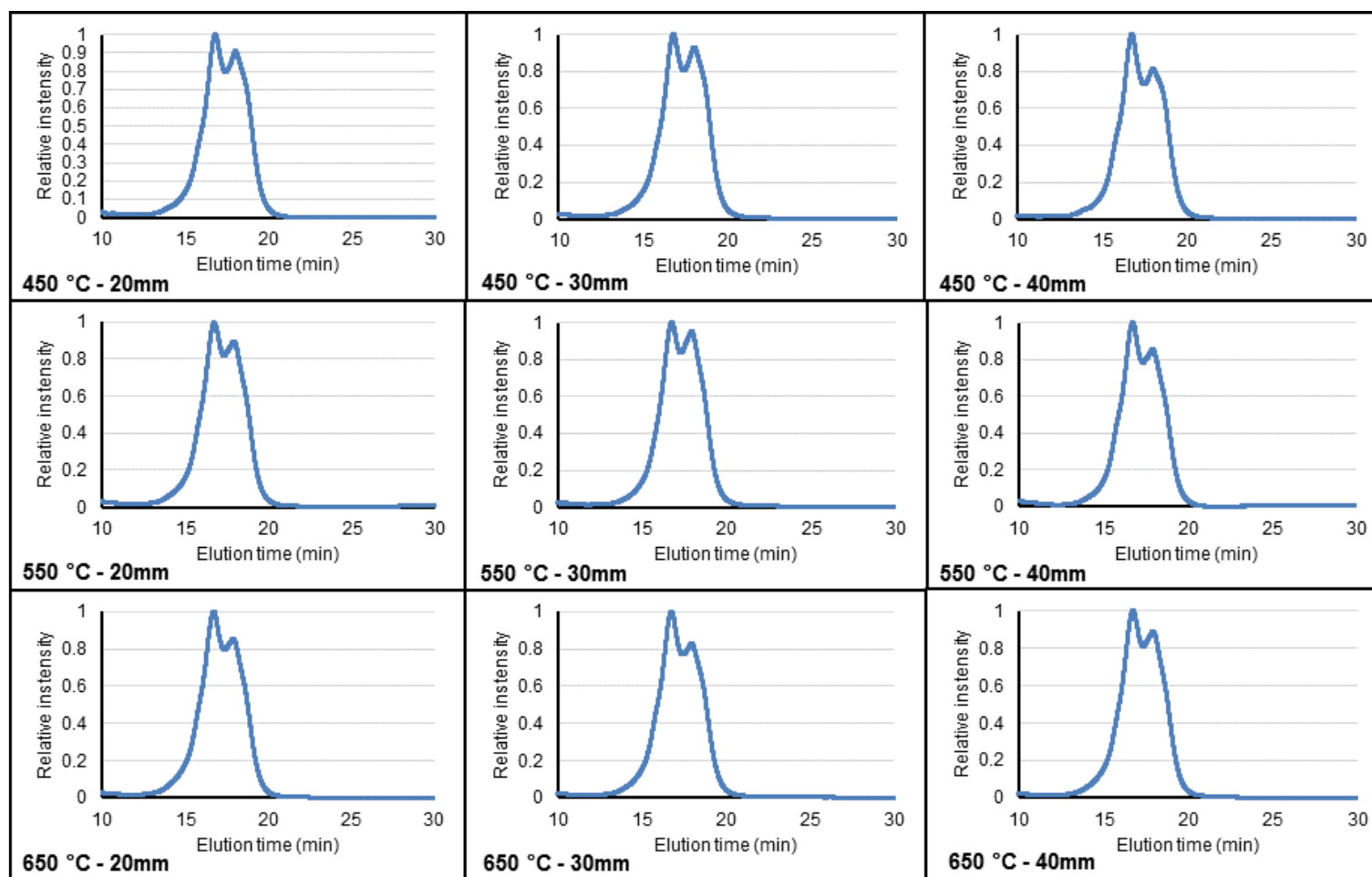


Figure C.5.1a: Elution times of respective Kwadela coal derived tar samples.

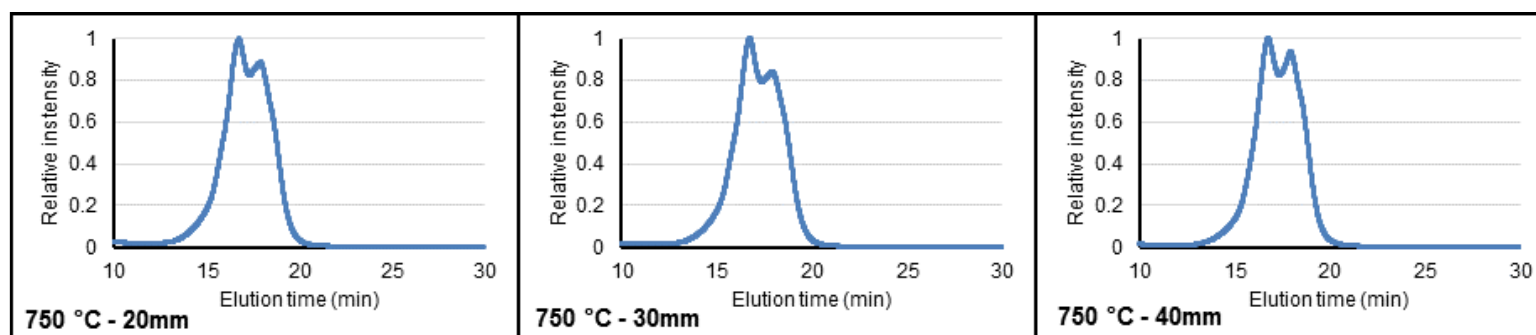


Figure C.5.1b: Elution times of respective Kwadela coal derived tar samples.

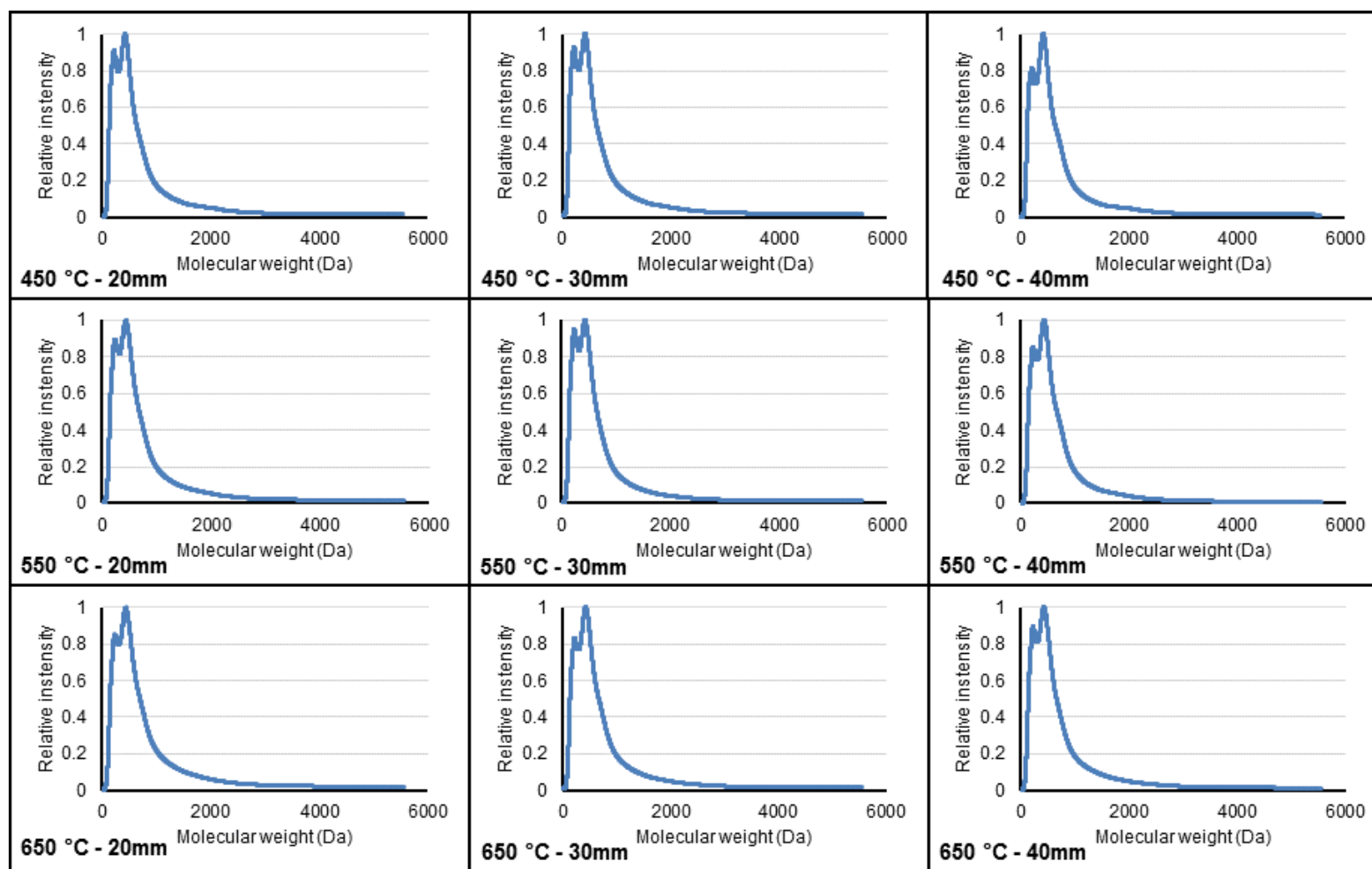


Figure C.5.2a: Molecular weight distribution curves of respective tars derived.

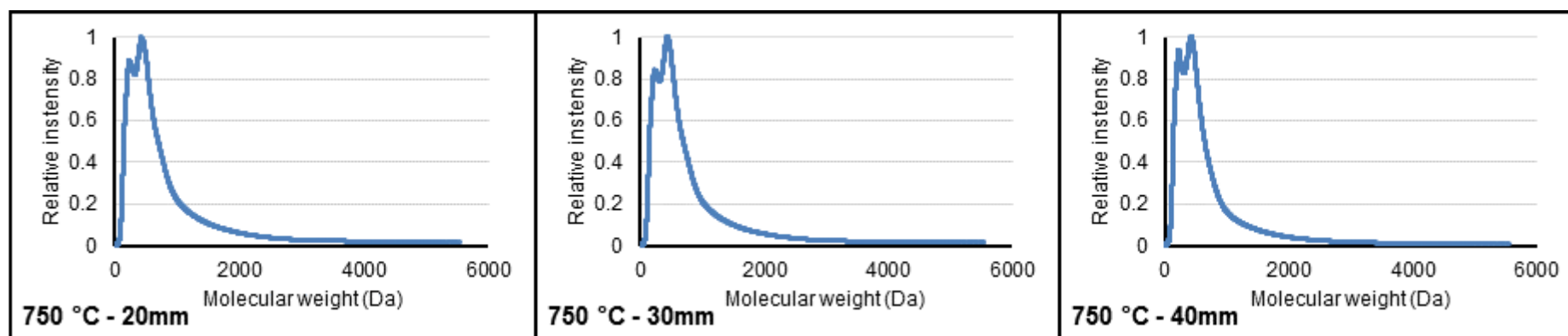


Figure C.5.2b: Molecular weight distribution curves of respective tars derived.

C.6 Gas chromatography analysis

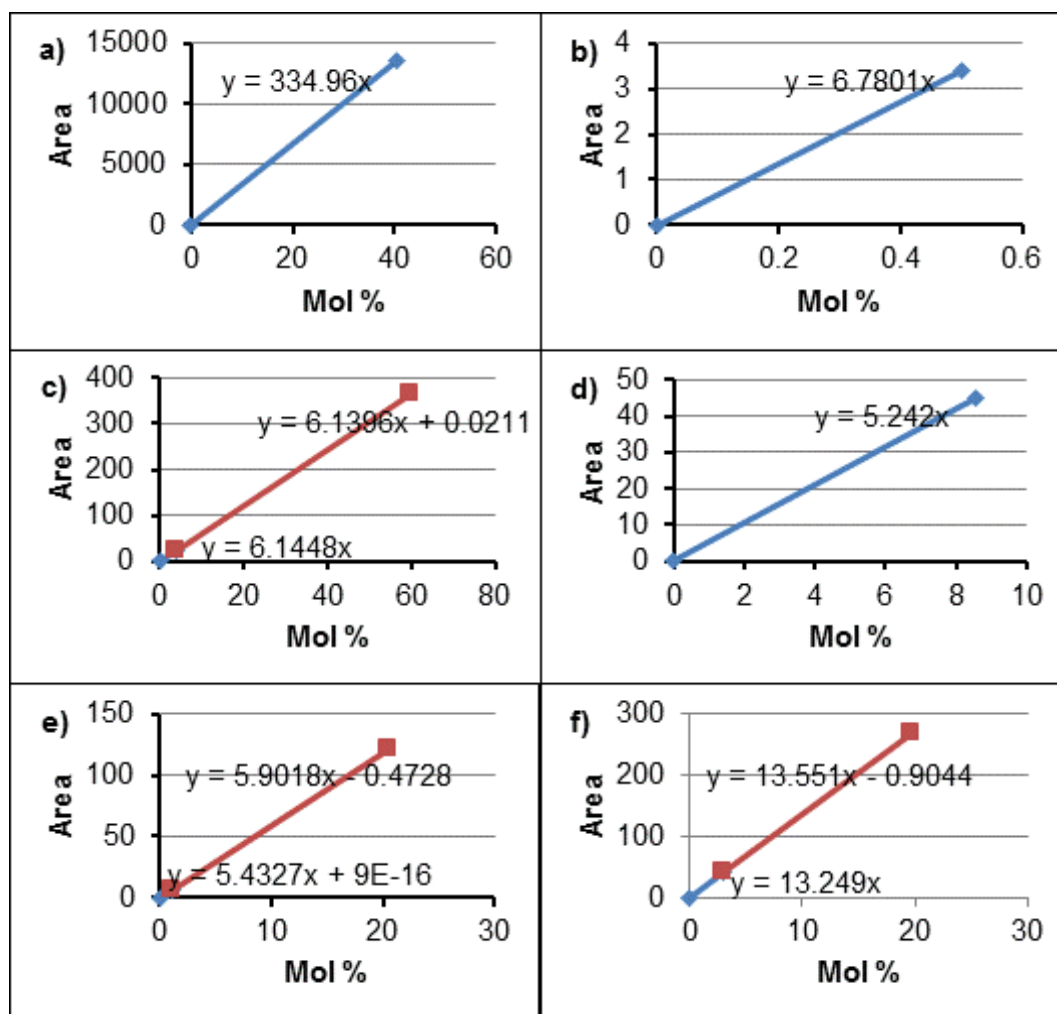


Figure C.6.1: Calibration curves for GC analyses of produced gases with a). H_2 , b) Ar, c) N_2 , d) CH_4 , e) CO and f) CO_2 .

Table C.6.2: Composition of gases evolved (wt.%)

Weight composition of gas formed (wt. %)												
Component	20 mm				30mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
H2	0.63	2.00	3.85	5.44	0.73	2.17	3.79	5.50	0.70	2.23	4.00	5.56
CH4	18.10	19.62	24.98	22.16	15.84	22.29	26.36	19.12	17.18	31.60	25.86	24.16
CO	15.05	16.54	19.90	26.99	14.06	14.96	19.89	28.83	14.64	14.71	19.13	24.22
CO2	58.59	53.66	42.85	38.98	63.70	50.67	40.70	42.58	58.28	37.01	43.13	38.12
C2H4	0.99	0.85	0.81	0.54	0.57	0.84	0.81	0.38	0.80	1.61	0.83	0.83
C2H6	5.83	4.99	4.79	3.11	4.44	5.65	4.80	2.12	5.07	9.14	4.60	3.68
C3H6	0.00	0.94	1.04	0.82	0.00	1.11	1.16	0.56	0.00	1.44	1.10	1.05
C3H8	0.80	1.28	1.44	1.10	0.66	1.59	1.47	0.75	0.38	1.97	1.35	1.28
C4s	0.00	0.12	0.34	0.87	0.00	0.72	1.02	0.16	2.96	0.29	0.00	1.10
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table C.6.3: Composition of gases evolved (mol.%).

Molar composition of gas formed (mol. %)												
Component	20 mm				30mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
H ₂	8.82	23.19	35.15	43.70	10.41	24.23	34.64	45.07	9.83	22.82	36.10	44.33
CH ₄	31.58	28.50	28.93	22.98	28.28	31.27	30.25	19.71	30.35	39.98	29.30	24.21
CO	15.08	13.89	13.07	15.59	14.41	12.00	13.11	17.02	14.84	10.87	12.39	13.90
CO ₂	37.60	28.56	18.16	14.65	41.66	25.89	17.10	16.25	37.82	17.38	17.86	13.93
C ₂ H ₄	0.99	0.72	0.54	0.33	0.58	0.68	0.53	0.22	0.81	1.16	0.54	0.48
C ₂ H ₆	5.42	3.90	2.98	1.76	4.23	4.23	2.93	1.18	4.76	6.13	2.78	1.97
C ₃ H ₆	0.00	0.52	0.46	0.33	0.00	0.60	0.50	0.22	0.00	0.68	0.47	0.40
C ₃ H ₈	0.51	0.68	0.60	0.42	0.43	0.82	0.61	0.28	0.24	0.90	0.55	0.47
C ₄ s	0.00	0.05	0.11	0.25	0.00	0.29	0.32	0.05	1.35	0.09	0.00	0.32
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table C.6.4: composition of gases evolved (mol).

Mol of gas formed (mol) (x10 ²)												
Component	20 mm				30mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
H ₂	0.16	2.57	8.18	18.33	0.09	2.80	7.57	18.14	0.12	2.85	7.94	19.30
CH ₄	0.58	3.17	6.68	9.39	0.25	3.61	6.62	7.92	0.37	5.07	6.44	10.53
CO	0.28	1.53	3.05	6.55	0.13	1.39	2.86	6.84	0.18	1.35	2.73	6.05
CO ₂	0.69	3.16	4.18	6.02	0.37	2.99	3.72	6.43	0.46	2.16	3.92	6.06
C ₂ H ₄	0.02	0.08	0.12	0.13	0.01	0.08	0.12	0.09	0.01	0.15	0.12	0.21
C ₂ H ₆	0.10	0.43	0.68	0.70	0.04	0.49	0.64	0.47	0.06	0.78	0.61	0.86
C ₃ H ₆	0.00	0.06	0.11	0.13	0.00	0.07	0.11	0.09	0.00	0.09	0.10	0.17
C ₃ H ₈	0.01	0.08	0.14	0.17	0.00	0.09	0.13	0.11	0.00	0.12	0.12	0.20
C ₄ s	0.00	0.01	0.03	0.10	0.00	0.03	0.07	0.02	0.02	0.01	0.00	0.14
Total	1.84	11.09	23.17	41.52	0.89	11.55	21.85	40.10	1.22	12.59	21.98	43.52

Table C.6.5: Composition of gases evolved (g).

Weight of gas formed (g)												
Component	20 mm				30mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
H ₂	0.00	0.05	0.16	0.37	0.00	0.06	0.15	0.37	0.00	0.06	0.16	0.39
CH ₄	0.09	0.51	1.07	1.51	0.04	0.58	1.06	1.27	0.06	0.81	1.03	1.69
CO	0.08	0.43	0.85	1.83	0.04	0.39	0.80	1.92	0.05	0.38	0.76	1.69
CO ₂	0.30	1.39	1.84	2.65	0.16	1.32	1.64	2.83	0.20	0.95	1.72	2.67
C ₂ H ₄	0.01	0.02	0.03	0.04	0.00	0.02	0.03	0.03	0.00	0.04	0.03	0.06
C ₂ H ₆	0.03	0.13	0.21	0.21	0.01	0.15	0.19	0.14	0.02	0.24	0.18	0.26
C ₃ H ₆	0.00	0.02	0.04	0.06	0.00	0.03	0.05	0.04	0.00	0.04	0.04	0.07
C ₃ H ₈	0.00	0.03	0.06	0.07	0.00	0.04	0.06	0.05	0.00	0.05	0.05	0.09
C ₄ s	0.00	0.00	0.01	0.06	0.00	0.02	0.04	0.01	0.01	0.01	0.00	0.08
Total	0.52	2.60	4.29	6.79	0.25	2.60	4.03	6.64	0.35	2.57	4.00	6.99

Table C.6.6: Weight (g) of gas per gram coal (d.m.m.f.).

Component	$g_i/g_{\text{coal d.m.m.f.}} (\times 10^3)$											
	20 mm				30mm				40 mm			
	450	550	650	750	450	550	650	750	450	550	650	750
H ₂	0.05	0.72	2.30	5.16	0.03	0.80	2.18	5.21	0.03	0.81	2.25	5.48
CH ₄	1.30	7.11	14.95	21.01	0.57	8.26	15.14	18.11	0.84	11.46	14.56	23.80
CO	1.08	5.99	11.91	25.59	0.51	5.54	11.42	27.31	0.72	5.34	10.77	23.86
CO ₂	4.22	19.43	25.65	36.96	2.31	18.77	23.38	40.35	2.85	13.42	24.28	37.56
C ₂ H ₄	0.07	0.31	0.48	0.51	0.02	0.31	0.47	0.36	0.04	0.58	0.47	0.82
C ₂ H ₆	0.42	1.81	2.87	2.95	0.16	2.09	2.76	2.01	0.25	3.31	2.59	3.62
C ₃ H ₆	0.00	0.34	0.62	0.77	0.00	0.41	0.66	0.53	0.00	0.52	0.62	1.03
C ₃ H ₈	0.06	0.46	0.86	1.04	0.02	0.59	0.85	0.71	0.02	0.72	0.76	1.26
C ₄ s	0.00	0.04	0.21	0.82	0.00	0.27	0.59	0.15	0.14	0.11	0.00	1.09
Total	7.20	36.21	59.85	94.81	3.63	37.05	57.43	94.74	4.89	36.26	56.29	98.51

Table C.6.7: Experimental error on gas yields of gram gas per gram coal (d.m.m.f.).

Component	20 mm				30mm				40 mm			
	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C	450 °C	550 °C	650 °C	750 °C
H ₂	0.02	0.25	0.95	2.85	0.01	0.17	0.23	1.57	0.01	0.09	0.49	0.75
CH ₄	0.64	2.69	4.35	6.06	0.24	0.08	4.70	5.16	0.40	5.15	3.65	2.26
CO	0.33	1.32	5.04	14.35	0.07	1.19	1.06	7.18	0.29	0.62	3.51	1.59
CO ₂	0.27	5.35	5.58	12.79	0.30	1.71	5.71	8.94	0.57	3.32	0.79	16.75
C ₂ H ₄	0.04	0.13	0.15	0.10	0.01	0.13	0.38	0.12	0.02	0.38	0.07	0.52
C ₂ H ₆	0.20	0.70	0.86	0.47	0.06	0.59	1.90	0.74	0.15	2.08	0.55	1.83
C ₃ H ₆	0.00	0.20	0.31	0.23	0.00	0.27	0.52	0.18	0.00	0.46	0.43	0.64
C ₃ H ₈	0.01	0.24	0.40	0.26	0.01	0.24	0.65	0.30	0.01	0.54	0.50	0.66
C ₄ s	0.00	0.14	0.67	1.14	0.00	1.00	2.21	0.50	0.55	0.35	0.00	0.30

APPENDIX D: LOW-SMOKE FUEL EVALUATION END TECHNO-ECONOMICS

D.1 Characterisation of low-smoke fuels produced

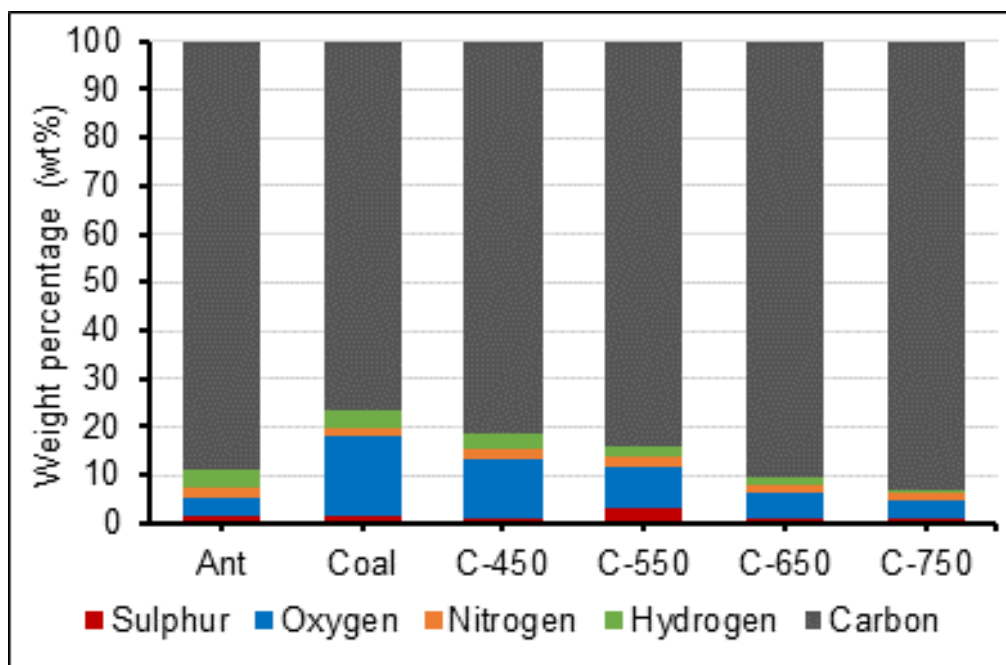


Figure D.1.1: Ultimate analyses of fuels tested in combustion experiments.

D.2 Results from low-smoke fuel production

Table D.2.1: Results from low-smoke fuel production

Fuel	Weight loss (wt.%)	Exp. Error (wt.%)
Char-450	10.7	1.03
Char-550	16.6	1.88
Char-650	20.3	0.90
Char-750	23.9	1.25

As expected the extent of devolatilisation increased with increasing final pyrolysis temperature, as indicated in Table D.1.1. The experimental errors on repeatability are also included and are relatively small, however 20 repeats were conducted for each fuel.

D.3 Emissions resulting from LPG combustion

Table D.3.1: Gas emissions measured from combustion of LPG

Fuel	NO _x	SO ₂	CO	CO ₂
Emission weight (mg)				
Coal	46	15	402	107 549
Anthracite	57	19	497	132 844
Char-450	68	23	594	158 832
Char-550	47	16	413	110 451
Char-650	56	19	486	129 942
Char-750	50	17	437	116 948

D.4 Emissions resulting from combustion experiments

Table D.4.1: Gas emissions from different fuels on a mg/kg_{fuel} basis.

Fuel	NO _x	SO ₂	CO	CO ₂	TSP	VOC's (x10 ²)
Emission weight (mg/kg _{fuel}) LPG free						
Coal	205	1 739	13 261	108 927	6.2	49.0
Anthracite	346	1 352	14 639	184 923	2.6	13.3
Char-450	170	2 380	17 048	132 534	1.8	12.4
Char-550	237	1 844	19 607	157 492	1.6	6.6
Char-650	165	1 180	18 815	145 595	1.7	5.0
Char-750	77	1 207	16 154	97 876	1.4	4.9

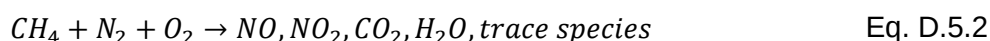
It should be noted that the amount of TSP and VOC emissions produced during LPG combustion was taken as negligible due to the fact that results indicated insignificantly low quantities.

D.5 Combustion reaction of NO_x

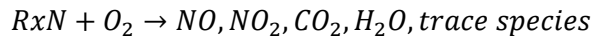
Thermal NO_x is formed at high temperatures when N₂ reacts with O₂ according to the Zeldovich mechanism (Baukal, 2005; US EPA, 1994):



The formation of prompt NO_x occurs via the considerably fast reaction between N₂, O₂ and hydrocarbon radicals respectively (Baukal, 2005):



Fuel NO_x is formed by the direct oxidation of organic N₂ compounds within the fuel via (Baukal, 2005):



Eq. D5.3

D.6 Ignition times and LPG fuel used

Normal Afrox Handigas (LPG) obtained locally in Potchefstroom was used as the ignition fuel. The LPG used in this investigation consisted primarily of a mixture of propane and butane (approximate ration 60:40 by mass), however it is not necessarily constant and some propylene, butylene and traces of ethane, ethylene, pentane and butadiene may also be included. The average gross calorific value of LPG is 49.6 MJ/kg. (Afrox). From Table D.6 the average gas flow measured prior to experiments, mass of LPG and mount of energy used as well as the ignition times for the respective fuels can be observed. The quantities of energy used in this study vary greatly from that found by Le Roux *et al.*, (2004) it must be remembered that two different types of appliances were investigated in the respective studies. The ignitions times however, were relatively similar in the two studies. A bubble flow meter was used to determine the flow of LPG prior to each combustion test. The flows are reported in Table D.6.

Table D.6.1: LPG gas used for ignition

Fuel	Average gas flow (L _N /min)	Mass used (kg)	Energy (MJ)	Ignition time (min)
Coal	8.53	0.39	19.18	24.83
Anthracite	7.35	0.39	19.18	30.67
Char-450	7.72	0.45	22.49	36.67
Char-550	7.29	0.32	15.87	25.50
Char-650	8.57	0.44	21.82	30.00
Char-750	6.86	0.33	16.20	27.00

D.7 Carbon dioxide (CO₂) to carbon monoxide ratio (CO) and combustion efficiency

Table D.7.1: CO₂ to CO ratio of the different fuels.

Fuel	CO ₂ /CO (mg/mg)	Combustion efficiency (%)	% LOI
Coal	9.77	69	38
Ant	14.35	80	57
450	9.57	79	31
550	9.12	77	28
650	9.07	67	33
750	7.46	62	34

$$\text{Combustion efficiency (\%)} = \left[1 - \frac{(\text{Carbon in residual ash}) \times 32.8}{\text{Batch start mass} \times G_{CV}} \right] \times 100$$

D.8 Fuel weight loss during combustion

An attempt was made to record the continuous weight of fuel lost during combustion with the intent to support the results of the combustion efficiency, however anomalies were observed as large increases in were observed for all the fuels as soon as the stove and chimney started to heat up. IT should be remembered that the stove was placed on top of a balance that recorder the weight throughout the duration of the combustion experiments.

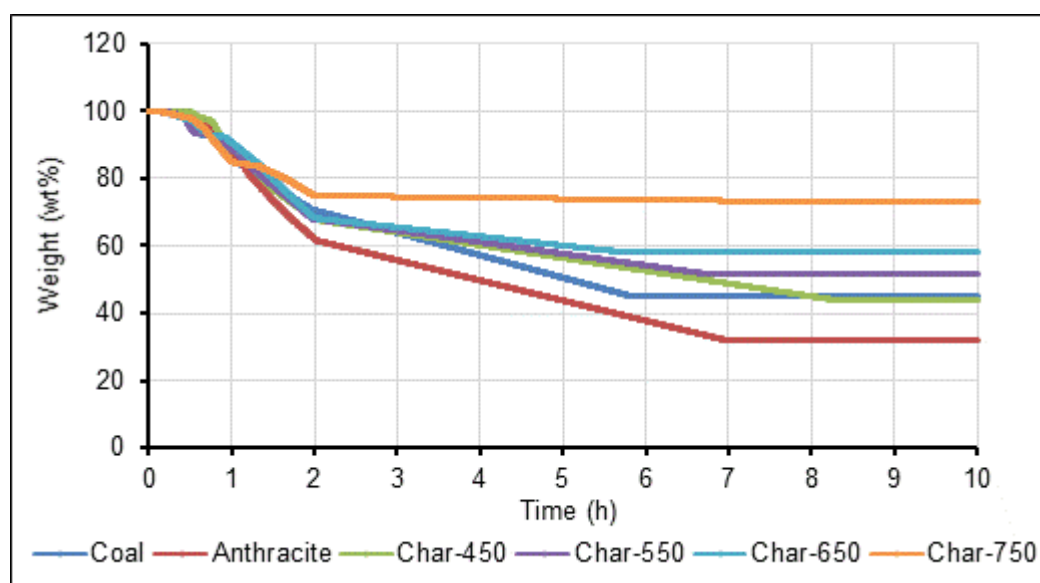


Figure D.8.1: Fuel weight loss over time during combustion.

The chimney, which was supported by the structure of the building, connected to multiple sampling probes and also to the stove may have caused the inconsistencies as materials expand and contract during heating and cooling respectively. The expansion and contraction may have caused increased forces being applied to the balance. Therefore it is recommended that a section of expandable piping be used to connect the chimney and stove in future studies to allow for expansion and contraction of the materials without having adverse effects on the weight. Nevertheless the overall trends were interpreted and are displayed in Figure D.6.1, where it can be observed that the fuel weight decreased significantly after approximately 30-40 minutes (just after ignition and LPG shut off). This decrease continued up to approximately 5-7 hours after which the weights remained relatively constant. The percentage of fuel weight lost during combustion correlates fairly well with the respective combustion efficiencies and the order thereof, in decreasing quantities obtained after combustion, is Char-750>Char-650>Char-550>Coal,Char-450>Anthracite. The order of increasing combustion efficiencies as discussed in Section 6.4.4 is Char-750<Char-650<Coal<Char-550<Char-450<Anthracite.

APPENDIX E: TECHNO-ECONOMIC EVALUATION

E.1 Cost estimation of low-smoke fuel production plant.

An estimation of the primary equipment and components necessary to construct a plant that will produce low-smoke fuels from coal is provided in Table E.1.1.

Table E.1.1: Purchased equipment cost estimation.

Purchased plant equipment		
Equipment	Qty.	Value (R)
Structural steel work		
Retort structure		209475
Conveyor		64937
Main access towers		16758
Pipe rack		54464
Flare stack		6284
Gas booster		10474
Other (cyclone separator and evaproative cooling)		20948
Components		
Retort	2	264600
Condenser (ESP)	2	250000
Cooler	2	55125
Liquor storage tank	1	8269
Liquor destructor	1	8269
Tar/oil tank	1	8269
Flare stack	2	16538
Coal hopper bunker	2	75000
Vibraing screen	1	62500
Magnetic separator	1	37500
Gas burner	2	200000
Oil/Water Separator	1	50000
Separator feed pump	1	60000
Total		1479408

The purchased equipment constituting the primary components of the plant add up to a total of R1.47 million, which is the basis from which the rest of the capital costs were estimated. The initial capital expenditure was calculated with the inclusion of a coal fired steam boiler and superheater to produce the necessary steam for the process. The capital expenditure was however, too high and the production costs would also increase as an additional 7.5 ton of coal per day would be required for steam production. Thus, it was assumed that the possibility exists that steam may be bought from Sasol, Secunda Plant

E.2 Profitability calculations

The equations used to calculate the different profitability measures are provided in this section of the appendix.

Return on investment (ROI):

$$ROI = \frac{N_{p,ave}}{FCI} \quad \text{Eq. E.2.1}$$

with $N_{p,ave}$ being the average net cash flow per year and FCI the fixed capital investment.

Payback period (PBP):

$$PBP = \frac{FCI}{A_j} \quad \text{Eq. E.2.2}$$

with A_j the annual cash flow.

Net return (R_n):

$$R_n = \sum_{j=1}^N N_{p,j} - m_{ar}(N \sum_{j=-b}^N TCI) \quad \text{Eq. E.2.3}$$

with $N_{p,j}$ being the net profit in year j and N the period of evaluation or plant lifetime.

Net present worth (NPW):

The NPW value was taken as the final cumulative discounted cash flow value displayed in Table E.3.7.

E.3 Cumulative cash flow analysis

The following information and formulas were employed in order to perform a cash flow analysis for the project.

Table E.3.1: Cash flow calculations A.

Capital investment	Value	
Fixed	R 6 252 564	
Working	R 1 109 556	
Costs		
Total production costs	R 5 323 189	per year
Revenue from sales	R 1 017.9	per ton coal treated
Tax rate	28%	
Discount rate	15%	m_{ar}
Inflation rate	5%	
Production rate	7500	kg/year
Plant lifetime	25	years (Starting in year 4 below)
Design and comissioning	3	years (Referred to as year 1 to 3 below)

Table E.3.2: Cash flow calculations B.

Year	Production %	Production rate	FCI	WC	Depreciation	Inflation factor	Total production costs
N	Production %	Production rate x Production %	FCI/2	WC	Depreciation over 4 years, starting with production	$(1+i)^{j-1}$	Fixed costs+general costs per annum x inflation factor

Table E.3.3: Cash flow calculations C.

Revenue	Gross profit before deprecation (GPBD)	Gross profit after depreciation (GPAD)	Tax	Net profit after tax
Revenue per kg x produced kg/year x inflation factor	Revenue - total production costs	Revenue - total production costs - depreciation	GPAD x tax rate	GPAD - tax

Table E.3.4: Cash flow calculations D.

Cashflow	Cumaltive cashflow	Discount factor	Discounted cashflow	Cumulative discounted cashflow
Net profit after tax + depreciation - capital payments	Cumaltive cashflow previous year + cashflow current year	$(1+dr)^{(i+1)}$	Cashflow x discount factor	Cumaltive discounted cashflow previous year + discounted cashflow current year

Table E.3.5: Cash flow calculations E.

Year	Production %	Production rate (kg/year)	FCI	WC	Depreciation	Inflation factor	Production cost
1	0		R 3 126 282			1.00	
2	0		R 3 126 282			1.05	
3	0			1109556		1.10	
4	50	3750			2473570	1.16	R 6 104 395
5	100	7500			1236785	1.22	R 6 409 615
6	100	7500			1236785	1.28	R 6 730 095
7	100	7500			1236785	1.34	R 7 066 600
8	100	7500				1.41	R 7 419 930
9	100	7500				1.48	R 7 790 927
10	100	7500				1.55	R 8 180 473
11	100	7500				1.63	R 8 589 497
12	100	7500				1.71	R 9 018 972
13	100	7500				1.80	R 9 469 920
14	100	7500				1.89	R 9 943 416
15	100	7500				1.98	R 10 440 587
16	100	7500				2.08	R 10 962 616
17	100	7500				2.18	R 11 510 747
18	100	7500				2.29	R 12 086 284
19	100	7500				2.41	R 12 690 599
20	100	7500				2.53	R 13 325 129
21	100	7500				2.65	R 13 991 385
22	100	7500				2.79	R 14 690 954
23	100	7500				2.93	R 15 425 502
24	100	7500				3.07	R 16 196 777
25	100	7500				3.23	R 17 006 616
26	100	7500				3.39	R 17 856 947
27	100	7500				3.56	R 18 749 794
28	100	7500				3.73	R 19 687 284

Table E.3.6: Cash flow calculations F.

Year	Revenue	Gross profit before depreciation	Gross profit after depreciation	Tax	Net profit after tax
1					
2					
3					
4	R 8 837 862	R 2 733 467	R 259 896	R 72 771	R 187 125
5	R 9 279 755	R 2 870 140	R 1 633 355	R 457 339	R 1 176 016
6	R 9 743 742	R 3 013 647	R 1 776 862	R 497 521	R 1 279 341
7	R 10 230 930	R 3 164 329	R 1 927 544	R 539 712	R 1 387 832
8	R 10 742 476	R 3 322 546	R 3 322 546	R 930 313	R 2 392 233
9	R 11 279 600	R 3 488 673	R 3 488 673	R 976 828	R 2 511 845
10	R 11 843 580	R 3 663 107	R 3 663 107	R 1 025 670	R 2 637 437
11	R 12 435 759	R 3 846 262	R 3 846 262	R 1 076 953	R 2 769 309
12	R 13 057 547	R 4 038 575	R 4 038 575	R 1 130 801	R 2 907 774
13	R 13 710 424	R 4 240 504	R 4 240 504	R 1 187 341	R 3 053 163
14	R 14 395 945	R 4 452 529	R 4 452 529	R 1 246 708	R 3 205 821
15	R 15 115 743	R 4 675 156	R 4 675 156	R 1 309 044	R 3 366 112
16	R 15 871 530	R 4 908 913	R 4 908 913	R 1 374 496	R 3 534 418
17	R 16 665 106	R 5 154 359	R 5 154 359	R 1 443 221	R 3 711 138
18	R 17 498 361	R 5 412 077	R 5 412 077	R 1 515 382	R 3 896 695
19	R 18 373 280	R 5 682 681	R 5 682 681	R 1 591 151	R 4 091 530
20	R 19 291 943	R 5 966 815	R 5 966 815	R 1 670 708	R 4 296 107
21	R 20 256 541	R 6 265 156	R 6 265 156	R 1 754 244	R 4 510 912
22	R 21 269 368	R 6 578 413	R 6 578 413	R 1 841 956	R 4 736 458
23	R 22 332 836	R 6 907 334	R 6 907 334	R 1 934 054	R 4 973 281
24	R 23 449 478	R 7 252 701	R 7 252 701	R 2 030 756	R 5 221 945
25	R 24 621 952	R 7 615 336	R 7 615 336	R 2 132 294	R 5 483 042
26	R 25 853 049	R 7 996 103	R 7 996 103	R 2 238 909	R 5 757 194
27	R 27 145 702	R 8 395 908	R 8 395 908	R 2 350 854	R 6 045 054
28	R 28 502 987	R 8 815 703	R 8 815 703	R 2 468 397	R 6 347 306

Table E.3.7: Cash flow calculations G.

Year	Cashflow	Cumulative cashflow	Discount factor	Discounted cashflow	Cumulative discounted cashflow
1	-R 3 126 282	-R 3 126 282	1.00	-R 3 126 282	-R 3 126 282
2	-R 3 126 282	-R 6 252 564	0.87	-R 2 718 506	-R 5 844 788
3	-R 1 109 556	-R 7 362 120	0.76	-R 838 984	-R 6 683 772
4	R 2 660 696	-R 4 701 425	0.66	R 1 749 451	-R 4 934 322
5	R 2 412 801	-R 2 288 624	0.57	R 1 379 527	-R 3 554 795
6	R 2 516 126	R 227 502	0.50	R 1 250 959	-R 2 303 836
7	R 2 624 617	R 2 852 119	0.43	R 1 134 694	-R 1 169 141
8	R 2 392 233	R 5 244 352	0.38	R 899 329	-R 269 812
9	R 2 511 845	R 7 756 196	0.33	R 821 126	R 551 314
10	R 2 637 437	R 10 393 633	0.28	R 749 724	R 1 301 038
11	R 2 769 309	R 13 162 942	0.25	R 684 531	R 1 985 569
12	R 2 907 774	R 16 070 716	0.21	R 625 006	R 2 610 575
13	R 3 053 163	R 19 123 879	0.19	R 570 658	R 3 181 233
14	R 3 205 821	R 22 329 700	0.16	R 521 036	R 3 702 269
15	R 3 366 112	R 25 695 812	0.14	R 475 728	R 4 177 997
16	R 3 534 418	R 29 230 229	0.12	R 434 360	R 4 612 357
17	R 3 711 138	R 32 941 368	0.11	R 396 590	R 5 008 947
18	R 3 896 695	R 36 838 063	0.09	R 362 104	R 5 371 051
19	R 4 091 530	R 40 929 593	0.08	R 330 617	R 5 701 668
20	R 4 296 107	R 45 225 700	0.07	R 301 867	R 6 003 535
21	R 4 510 912	R 49 736 612	0.06	R 275 618	R 6 279 153
22	R 4 736 458	R 54 473 070	0.05	R 251 651	R 6 530 804
23	R 4 973 281	R 59 446 350	0.05	R 229 768	R 6 760 573
24	R 5 221 945	R 64 668 295	0.04	R 209 789	R 6 970 361
25	R 5 483 042	R 70 151 337	0.03	R 191 546	R 7 161 907
26	R 5 757 194	R 75 908 530	0.03	R 174 890	R 7 336 797
27	R 6 045 054	R 81 953 584	0.03	R 159 682	R 7 496 479
28	R 6 347 306	R 88 300 890	0.02	R 145 797	R 7 642 276

E.4 Sensitivity analysis

Table E.4.1: Minimum acceptable rate of return

Minimum acceptable return after income taxes (m_{ar})				
		ROI	PBP	NPW
Base	15%	23%	4	7359667
-40%	9%	23.4%	4.3	18900588
-30%	11%	23.4%	4.3	14962990
-20%	12%	23.4%	4.3	11851836
-10%	14%	23.4%	4.3	9366414
0%	15%	23.4%	4.3	7359667
10%	17%	23.4%	4.3	5722844
20%	18%	23.4%	4.3	4374769
30%	20%	23.4%	4.3	3254295
40%	21%	23.4%	4.3	2314940

Table E.4.2: Total variable production cost

Total variable production cost				
		ROI	PBP	NPW
Base	4380647.595	23%	4	7359667
-40%	R 2 628 389	41%	2	17465191
-30%	R 3 066 453	37%	3	14938810
-20%	R 3 504 518	32%	3	12412429
-10%	R 3 942 583	28%	4	9886048
0%	R 4 380 648	23%	4	7359667
10%	R 4 818 712	19%	5	4833286
20%	R 5 256 777	15%	7	2306905
30%	R 5 694 842	10%	10	-219476
40%	R 6 132 907	6%	17	-2745857

Table E.4.3: Total fixed capital investment

Total fixed capital cost				
		ROI	PBP	NPW
Base	R 6 252 564.26	23%	4	7359667
-40%	R 3 751 539	40%	2.52	11113323
-30%	R 4 376 795	34%	2.9	10174909
-20%	R 5 002 051	30%	3.3	9236495
-10%	R 5 627 308	26%	3.8	8298081
0%	R 6 252 564	23%	4.3	7359667
10%	R 6 877 821	21%	5	6421253
20%	R 7 503 077	19%	5.3	5482839
30%	R 8 128 334	17%	5.9	4544426
40%	R 8 753 590	15%	6.5	3606012

Table E.4.4: Coal feedstock cost.

Coal feedstock cost				
		ROI	PBP	NPW
Base	R 226.00	23%	4	7359667
-40%	R 135.60	30%	3.3	11269788.45
-30%	R 158.20	29%	3.5	10292258
-20%	R 180.80	27%	3.7	9314728
-10%	R 203.40	25%	4.0	8337198
0%	R 226.00	23%	4.3	7359667
10%	R 248.60	22%	4.6	6382137
20%	R 271.20	20%	5.0	5404607
30%	R 293.80	18%	5.4	4427076
40%	R 316.40	17%	6.0	3449546

Table E.4.5: Revenue per ton.

Revenue per ton				
		ROI	PBP	NPW
Base	R 1 017.93	23%	4	7359667
-40%	R 610.76			
-30%	R 712.55	0.01	95.7	-5590068
-20%	R 814.34	0.09	11.7	-1273490
-10%	R 916.14	0.16	6.3	3043089
0%	R 1 017.93	23%	4.3	7359667
10%	R 1 119.72	31%	3.2	11676246
20%	R 1 221.52	38%	2.6	15992824
30%	R 1 323.31	46%	2.2	20309403
40%	R 1 425.10	53%	1.9	24625982

E.5 Recycle gas calorific value

Calculation regarding the calorific value of the gas produced during devolatilisation of the coal is provided in Table E.5.1. The uncondensable fraction of the pyrolysis gas is recycled back to the reactor section and combusted to provide additional heat.

Table E.5.1: Coal pyrolysis gas.

Component	wt.%	Fractional calorific value (MJ/kg)
H ₂	2.14	3.04
CH ₄	24.60	13.66
CO	15.46	1.56
CO ₂	47.29	0.00
C ₂ H ₄	1.11	0.03
C ₂ H ₆	6.61	0.20
C ₃ H ₆	1.17	0.03
C ₃ H ₈	1.62	0.82
Total	100.00	19.33