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SYSTEMATIC INVESTIGATION OF SMOKE EMISSIONS FROM PACKED-BED RESIDENTIAL COAL COMBUSTION DEVICES

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Abstract

A review of health effects of emissions from solid fuel combustion shows clear links between morbidity and mortality, and residential combustion smoke exposure. On the interior plateau of the South African Highveld, use of coal fuel in informal domestic braziers – *imbaulas* – constitutes a major source of local ambient and household air pollution. This thesis aimed to develop an improved understanding of the complex processes of packed-bed combustion in small domestic devices studying smoke emissions from informal domestic stoves.

A robust dilution sampling system for testing emissions from residential coal-burning appliances was developed and used in the emission studies. Systematic experiments were carried out to evaluate thermal performance and emissions of coal braziers, varying fire ignition method, ventilation rate, fuel moisture and fuel quality. Three field-collected and three laboratory constructed braziers were tested, with a range of ventilation hole-densities. The variables measured are particle mass (PM2.5 and PM10), gases (CO, CO\textsubscript{2}, NOx), and particle composition and morphology. Emission factors, referenced to zero excess oxygen are reported.

Two fire-ignition methods are evaluated namely: the conventional bottom-lit updraft (BLUD) method, and the top-lit updraft (TLUD)–the so-called *Basa njengo Magogo* method. PM2.5 and PM10 emissions reduced by 80% on average when using the TLUD in contrast to the business-as-usual BLUD method. High smoke emissions from the BLUD method during pyrolysis are found to be associated with an oxygen deficit, allowing products of incomplete combustion to be emitted. Influences of ventilation rates on the stove emissions are reported – products of incomplete combustion (PM2.5 and CO) are higher for low ventilation rates. For a given device, PM2.5 and PM10 emission factors reduce by ~50% from low to high ventilation rates (an advantage offset by firepower too high for convenient cooking).

Emissions from A-grade (low ash-14%) and D-grade (high ash-24%) coal are compared. There are no significant differences in particle emissions between the two fuel qualities when using the BLUD method. For the TLUD method, PM emissions increase (~2-fold) with a switch from D-grade to A-grade coal. Comparisons of CO, CO\textsubscript{2} and NOx are reported.

The influences of coal moisture content (fresh coal 8.6% and air-dried 2.4%) on emissions and efficiencies of the braziers are reported. Emissions of PM10, CO increase with increasing coal moisture. Higher moisture content reduces the combustion efficiency and firepower (heat delivery), while increasing the cooking efficiency.
Polycyclic aromatic hydrocarbons (PAHs) are sampled using multi-channel rubber traps, applied as pre-concentrators of PAH emissions from real-world combustion of coal fuel. PAHs detected by chromatographic analysis are primarily naphthalene, fluorene and phenanthrene. Changes in combustion conditions have a marked effect in the ratios of various PAH emissions—relative concentrations of phenanthrene and fluorene, normalized to naphthalene, are higher in BLUD than in the TLUD ignition method.

The morphology and chemical composition of the particles are investigated by SEM/EDS analysis. We classify the pyrolysis phase of a coal brazier fire into two stages: stage I and stage II. Filter samples collected during pyrolysis stage I reveal continuous layers of merged tar-like deposits with no discrete particles visible. During pyrolysis stage II, filters collect particles that retain their morphology on impact, presenting on the electron micrographs as discrete particles with a range of morphologies. Increasing combustion temperature yields decreasing emissions of coarse particles (>10 µm). Giant carbonaceous conglomerates are observed in abundance from BLUD fires but are sparse from TLUD fires. Morphological differences are observed between particles sampled directly above the fire (<1 m) and aged by ~2 s by passing through a 5 m chimney.

This thesis presents the first comprehensive, systematic study of condensed matter (smoke) emissions and emission factors from informal packed-bed coal stoves in use in South Africa. The thesis has generated new insights into the factors influencing combustion behaviour and emissions. An original contribution is dividing the pyrolysis phase into two stages, and presenting evidence on how the different combustion conditions during these two stages affect the morphology of condensed matter emissions, and explain previous failures of attempts to sample such emissions. A comprehensive set of emission factors in units [g s⁻¹] is presented per hour and three-hour full burn cycle. These contributions lay the groundwork for improvements in the design of existing coal braziers and development of novel low-emission combustion technologies, and understanding potential health impacts of condensed matter emissions. The insights gained will assist in selecting appropriate strategies and technologies to mitigate health, indoor and local air pollution associated with domestic coal combustion. The reported emission factors from coal braziers provides the first comprehensive, systematic set of emission factors for this source category, and fills a major gap in the previous efforts to conduct dispersion modelling of South African Highveld air quality.
Affidavit

To whom it may concern

This serves to confirm that I, Tafadzwa Makonese, Passport Number DN888449, Student number 200946372, enrolled for the qualification PhD (Energy Studies) in the Faculty of Science, herewith declare that my academic work is in line with the Plagiarism Policy of the University of Johannesburg, with which I am familiar.

I further declare that the work presented in the thesis: SYSTEMATIC INVESTIGATION OF SMOKE EMISSIONS FROM PACKED-BED RESIDENTIAL COAL COMBUSTION DEVICES is authentic and original unless clearly indicated otherwise, and in such instances full reference to the source is acknowledged, and I do not pretend to receive any credit for such acknowledged quotations, and that there is no copyright infringement in my work. I declare that no unethical research practices were used or material gained through dishonesty. I understand that plagiarism is a serious offence and that, should I contravene the Plagiarism Policy notwithstanding signing this affidavit, I may be found guilty of a serious criminal offence (perjury) that would amongst other consequences compel the UJ to inform all other tertiary institutions of the offence and to issue a corresponding certificate of reprehensible academic conduct to whomever request such a certificate from the institution.

Signed at Johannesburg on this _______ day of _______________ 2015

________________________________________
Tafadzwa Makonese

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Affidavit certified by a Commissioner of Oaths

This affidavit conforms with the requirements of the JUSTICES OF THE PEACE AND COMMISSIONERS OF OATHS ACT 16 OF 1963 and the applicable Regulations published in the GG GNR 1258 of 21 July 1972; GN 903 of 10 July 1998; GN 109 of 2 February 2001 as mended.
Declaration

The work contained in this thesis is my own, unless otherwise acknowledged. This thesis has not been presented for examination at any other university. Parts of this thesis have been presented at various national and international conferences, or published in journals during the course of the research, as follows:


Dedication

I would like to dedicate this Doctoral thesis to my father Tapfumaneyi Phellimon Makonese and to my mother, Anna Makonese (nee Chidare).

There is no doubt that without their continued support, counsel, and supplications I would not have made it this far.
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I am indebted to several individuals, groups and organisations for making this study a success. First, I would like to express my sincere gratitude to my supervisor and mentor, Professor Harold John Annegarn. I am grateful to him for organising and providing the necessary equipment for the smooth running of the study. Importantly, I am indebted to him for exposing me to the academic science and stove community, and for providing me with the much-needed financial support. Thank you believing in me, for your patience, counsel, and support throughout the duration of the study. Here is hoping that you are proud of your faithful investments in me.

I would like to thank Dr. Patricia Forbes for her co-supervision since the inception of this project. She took time from her busy schedules to attend to my paper drafts, and for introducing me to monitoring of polycyclic aromatic hydrocarbons from domestic fuels and stoves. I further thank Crispin Pemberton-Pigott for contributing his valuable time in analysing my experimental data and results. He continually reviewed the spreadsheet to meet demands for quality. His expertise in the stove designing/testing field was a pillar in the progress of this thesis. I am indebted to my colleagues and team members at the SeTAR Centre for encouraging me to soldier on – David Kimani Kimemia, Daniel Masekameni and Thokozile Sithole.

Special thank you goes to the Laboratory for Separation Science, Department of Chemistry, University of Pretoria, for use of the GCxGC-TOFMS; Lorraine Mudau (University of Pretoria) for the work she put in analysing PAHs data from our experimental coal fires, without which this study would not have been a success; Thapelo Chalatsi (University of Pretoria) for assisting with sampling; David Masemula (University of Pretoria) for preparing the silicone rubber traps and Dr Yvette Naudé (University of Pretoria) for assisting with the GCxGC-MS analyses and Antoinette Buys (University of Pretoria) for assisting with the SEM analyses.

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Glossary of Terms

This section defines terms as they are used in this thesis. In other contexts, the same terms may be used to define different parameters, some of which are discussed in the body of the text.

Ash: Refers to the solid residue of combustion. The chemical composition of an ash depends on the substance burned. Coal ash contains metal silicates (e.g. aluminosilicates) and oxides formed from metals originally compounded in the coal.

Bottom-lit updraft (BLUD): In the BLUD fire ignition method, the fuel is ignited from the bottom and the method relies on the upward movement of draft to keep the flame alive. The hot zone starts at the bottom and the hot pyrolysis front migrates upward until reaching the top of the fuel pile. The order of laying the fire proceeding is as follows: a few lumps of coal on the grate, paper, wood, ignition, after which the bulk of the coal is added at an appropriate time after the wood fire is established [Makonese, 2011].

Bottom-lit downdraft (BLDD): The BLDD ignition method entails igniting the fuel from the bottom and the method relies on the downward movement of drafts to keep the flame alive. The flame is projected downward below the fuel bed by a draft induced by the chimney, while there is an upward migration of the pyrolytic zone through the bed of coal [Makonese, 2011].

Basa njengo Magogo: Also referred to as the top-lit updraft (TLUD) method, the Basa njengo Magogo ignition method is an alternative way of igniting a fire in a brazier/imbaula stove. The order of laying the fire is bulk of the coal on the grate, paper, and then wood, with a few lumps of coal added at an appropriate time after the fire has been lit. This is the reverse order of components from the conventional BLUD method. The TLUD ignition method entails that the fuel is ignited from the top and the upward movement of drafts through the stove keeps the flame alive. The hot zone starts at the top and the hot pyrolysis front migrates downward until reaching the bottom of the fuel pile [Makonese, 2011].

Burn Cycle: The combustion of fuel from ignition to extinction, at power levels and durations at these levels required to perform a specified performance test or cooking cycle. The initial fuel load is normally adjusted to be at least adequate for the completion of the cycle. The product manufacturer may recommend a standard ignition or extinction method or methods.

Burn rate (r): Rate of fuel mass loss during combustion [g min\(^{-1}\)].

Coking: Refers to the formation of a solid residue of impure carbon from bituminous coal after removal of volatile matter by pyrolysis or destructive distillation of the fuel.

Calorific Value (CV): Specific heat energy available from fuel containing moisture, expressed in unit [MJ/kg].

Combustion efficiency: An indicator of the completeness of the conversion of fuel carbon into carbon dioxide, expressed as the CO/CO\(_2\) ratio. [%]

Condensed matter: Any solid or liquid matter. In the context of combustion emissions, this term is used to denote solid particles (e.g. mineral matter–ash, elemental carbon - soot) or condensed hydrocarbons, which may be in the form of solid or semiliquid complex organic mixtures.

Conduction: “...heat transfer across a surface, or transfer of heat through a material by passing from one molecule to another.” Conduction is one of the three primary forms of energy transfer. www.greenwoodtechnologies.com/glossary.htm
Convection: “The transfer of heat that occurs due to the circulation of air” or liquid. Convection is one of the three primary forms of energy transfer. www.greenwoodtechnologies.com/glossary.htm

Cooking Efficiency: Synonym for Thermal Efficiency and is expressed in units [%]

Cooking cycle: The cycle that uses the heat available from a burn cycle for the preparation of food or the heating of water. An entire cooking cycle is normally contained within the burn cycle, though in special cases retained heat stoves might continue cooking after the fire has been extinguished.

Draft: Refers to a current or movement of air through a stove

Dilution Ratio (DR): Defined as the ratio of the CO, CO$_2$ or PM concentration in the dilution tunnel and CO, CO$_2$ or PM in the stack flue gases.

Emissions: Gaseous and particulate matter by-products of the combustion process that are discharged into the atmosphere.

Emission Factor (EF): The mass of a gaseous pollutant (e.g. CO, CO$_2$ or NOx) or particulate matter (e.g. PM2.5 and PM10) emitted during a burn cycle. Emission factors are determined by dividing the mass by the net heat gained, yielding emission factors in unit mass of emissions per net Mega Joule. In the context of this thesis and the conventions used at the SeTAR Centre, emission factors are calculated for zero per cent excess air. [mg MJ$^{-1}$ or g MJ$^{-1}$].

Excess air: The amount of air used in excess of the amount required for complete (stoichiometric) combustion of the fuel. [%]

Fuel consumed: The fuel consumption of a coal-burning stove is defined as the mass of new fuel drawn from a supply that is sourced outside the cooking system needed to conduct any one of a series of identical replications of a burn cycle, save the first. [kg]

Fuel remaining: Fuel, which is unburned, partially or almost completely burned, remaining after a burn cycle is complete, and which can be used in the same stove during the next replication of the cycle, is considered unburned fuel.

Fire-power (P): Rate of energy release by the fuel during combustion [kW].

Flue gas: The hot combustion gases that flow from the combustion chamber and out the chimney (if a chimney is present).

Grate: A framework of iron bars or a perforated galvanised iron sheet (in the case of coal braziers) to hold fuel in a stove.

Heterogeneous stove Testing Protocol (HTP): The HTP is a protocol to assess the performance of a stove across a range of conditions, using stove conditions, fuels and pot sizes for which the stove was designed. It requires that thermal and emissions performance tests be carried out using two pot sizes over the full range of a stove’s adjustable power settings [Makonese, 2011].

Ignition: The action of setting the kindling or fuel on fire. Synonyms include fire-lighting and fire-start up.

Lower heating value (LHV): Refers to the “theoretical maximum amount of energy that can be extracted from the combustion of the moisture-free fuel if it is completely combusted and the combustion products are cooled to room temperature but the water produced by the reaction of the fuel bound hydrogen remains in the gas phase” [Bailis et al., 2007:21].

Heat transfer efficiency: A measure of how efficient is the exchange of thermal energy between the burning fuel and the pot. The fundamental modes of heat transfer are radiation, conduction and convection. [%].

High power: The highest power setting at which the stove can operate. [kW].

PM: Particulate matter, referring to particles in a condensed phase.
**PMx**: Particulate matter with an aerodynamic diameter less than x μm. [Tissari, 2008].

**Pot-swapping method**: Water is heated in a series of pots that are replaced if the water reaches a predetermined temperature selected to avoid evaporation, normally 70°C. The mass of pots and water, and the change in temperature are used to calculate the total heat gained during a burn cycle or cooking cycle.

**Pyrolysis**: The destructive distillation of a hydrocarbon fuel in the absence of oxygen yielding a mixture of gaseous components and a solid char residue [Makonese, 2011].

**Radiation**: The transfer of heat by emission and absorption of electromagnetic radiation, in this context in the thermal infrared and visible wavebands. Radiation is one of the three primary forms of heat transfer [Makonese, 2011].

**Smoke**: A dense, visible aerosol, comprising a mixture of solid or liquid particles in a gas stream derived from the combustion of a fuel. Smoke is often an indicator of incomplete combustion [Makonese, 2011].

**Soot**: Complex mixture consisting mainly of amorphous elemental carbon (EC) and organic material. Typically the blacker the smoke is the higher is the elemental carbon content [Tissari, 2008].

**Thermal Efficiency** ($\eta$): Synonym for **Cooking Efficiency**. The ratio of energy received by water (in the pot) to the energy released by the fuel combustion. The energy absorbed by the pot itself is not regarded as part of the function. [%]. [Makonese, 2011].

**Ventilation rate**: The volume of air passing into the stove through primary and secondary air holes per given time. It is a function of the size and distribution of the primary and secondary holes. The more holes there are in the stove, the greater the ventilation rate.

**Water Boiling Test (WBT)**: Any test of a stove or water heater that uses a pot or pots of water heated from an initial to a final temperature (sometimes but not necessarily the boiling point).
Abbreviations

BC: Black Carbon
BLUD: Bottom-Lit Updraft
BLDD: Bottom-Lit Downdraft
BrC: Brown Carbon
BSE: Backscattered Electron
BTEX: Benzene, Toluene, Ethyl-benzene and Xylene
BOSS: Brigham Young University organic sampling system
CCN: Cloud Condensation Nuclei
CO: Carbon Oxide
CO$_2$: Carbon Dioxide
CVS: Continuous Volume Sampling
DAF: Dry-Ash-Free Basis
D$_f$: Fractal Dimension
D$_m$: Mobility Diameter
DMA: Differential Mobility Analyser
DME: Department of Mineral and Energy
D$_p$: Particle diameter
DR: Dilution Ratio
EC: Elemental Carbon
EDS: Energy-Dispersive Spectroscopy
EF: Emission Factor
GCxGC-TOFMS: Two Dimensional Gas Chromatography Time of Flight Mass Spectrometry
GC-FID: Gas Chromatography Flame Ionisation Detector
GC-MS: Gas Chromatography-Mass Spectrometry
H$_2$S: Hydrogen sulphide
HAP: Household Air Pollution
HEPA: High Efficiency Particulate Air
HHV: Higher Heating Value
HRSEM: High Resolution Scanning Electron Microscopy
HTP: Heterogeneous stove Testing Protocol
IARC: International Agency for Research on Cancer
IHCES: Integrated Household Clean Energy Strategy
IOGAPS: Integrated Organic Gas and Particulate Sampler
IOVPS: Integrated Organic Vapour-Particle Sampler
IR: Infrared
LHV: Lower Heating Value
NDIR: Non-Dispersive Infrared
NO: Nitrogen Oxide
NO₂: Nitrogen Dioxide
NOx: Nitrogen Oxides (NO+NO₂)
OC: Organic carbon
PAS: Photoelectric Aerosol Sensor
PDMS: Polydimethylsiloxane
PPAH: Particle-bound Polycyclic Aromatic Hydrocarbons
PAH: Polycyclic Aromatic Hydrocarbons
PIC: Product of Incomplete Combustion
PM: Particulate Matter
PM₁/₂.₅/₁₀: PM with aerodynamic particle diameters <1/2.₅/1₀ μm
POM: Particle organic matter
ppb: Parts per billion
ppm: Parts per million
PSD: Particle Size Distribution
PSL: Polystyrene Latex
PUF: Polyurethane Foam
RAMS: Real-time total Ambient Mass Sampler
SANS: South African National Standards
SEI: Secondary Electron Imaging
SEM: Scanning Electron Microscopy
SPME: Solid-Phase Micro-extraction
SMPS: Scanning Mobility Particle Sizer
SO₂: Sulphur Dioxide
SVOC: Semi Volatile Organic Compound
SVM: Semi-Volatile Material
TEOM: Tapered Element Oscillating Microbalance
TLUD: Top-Lit Updraft
TOC: Total Organic Compounds
VOC: Volatile Organic Compounds
XRD: X-Ray Diffraction
CHAPTER ONE

This chapter introduces an overview of residential coal use in South Africa and other developing countries, and presents air pollution issues, health and environmental challenges. The research problem statement is stated, the domain of the study specified, and the specific research objectives are presented. A justification of the study is presented and the scope of the study is highlighted. An overview of the thesis layout is given at the end of the chapter.

1. Introduction and Background

1.1 A Perspective on Residential Coal Combustion

Approximately three billion people worldwide are exposed daily to household air pollution (HAP) from use of solid fuels such as biomass or coal. Combustion of these fuels releases products of incomplete combustion such as carbon monoxide, particulate matter (PM) and volatile organic compounds [Gordon et al., 2014]. The WHO Global Health Observatory has reported that HAP caused 4.3 million premature deaths worldwide in 2012, and ambient air pollution caused a further 3.7 million deaths [WHO, 2014]. HAP is associated with many health effects such as acute and chronic respiratory disorders, pulmonary and systemic diseases [Gordon et al., 2014].

Coal will continue to be a major source of energy in both the developed and developing countries into the future [Finkelman et al., 2002]. In many developing countries such as South Africa, China and India, coal will continue to be used as a primary source of energy for generation of electricity, industrialisation and enhancement of standard of living for the increasing populations [Finkelman et al., 2002]. In South Africa, coal is still a survival commodity for the vast majority of low-income households on the interior plateau of South Africa, commonly known as the Highveld. In the domestic sector, the fuel is used for cooking, water heating and space heating services.

The combustion of coal in a fixed (non-fluidized) bed of fuel pieces, with combustion air supplied from beneath the bed by natural draft ventilation, is widely used in many household energy systems (cooking and heating stoves). In the interior provinces of South Africa interior, the majority of low-income households combust coal in braziers, in the form of metal drums with roughly punched ventilation holes around the sides, colloquially known as imbaulas [Makonese, 2011; Kimemia et al., 2011; Le Roux, 2009; Standish et al., 2007]. During the austral winter (May–August), these devices are used extensively for cooking and space heating, resulting in indoor and ambient air pollution [Makonese, 2011; Kimemia et al., 2011; Annegarn & Sithole, 1999]. Source-apportionment studies have identified residential coal burning as the greatest single source of airborne aerosols among other

1 Although the colloquial use of the term imbula is commonly understood in South Africa, for clarity of meaning for an international readership the term brazier will be used throughout this thesis.
pollutants in South Africa’s coal-burning townships [Mdluli, 2007; Scorgie et al., 2001; Annegarn et al., 1998]. The levels of combustion particles are particularly high on cold days with little wind, especially when low-lying inversion layers suppress mixing dilution of the boundary layer atmosphere [Namork et al., 2004].

Residential coal combustion has been identified to be a major source of fine particle mass emissions, particulate polycyclic aromatic hydrocarbons (PAHs) and gaseous pollutants such as volatile organic compounds (VOCs) throughout the developing world [Finkelman et al., 2002]. A recent study has shown that in South Africa, residential coal combustion accounted for over 65% of stationary emissions in the low-income urban stratum, especially in winter [Scorgie, 2012]. Fine and ultrafine particulate matter emissions from coal combustion are receiving significant attention, from both regulatory authorities and environmental scientists, because of their effects on health [Bai et al., 2011; Teramae & Takarada, 2009; Nelson, 2007; Yi et al., 2008; Bockhorn, 2000]. Coal generated fine particulate matter is usually rich in organic compounds (polycyclic aromatic hydrocarbons - PAHs) and heavy metals. Heavy metal trace elements that occur in coal (e.g. mercury, arsenic and selenium) are subject to scrutiny because of public health implications [Vejahati et al., 2010:904]. Hence, fine particulate formation mechanisms and partitioning, and influencing factors need to be studied to develop novel technologies that are less polluting [Bai et al., 2011]. The literature holds a number of extensive studies on the consequences of coal mining, coal processing, coal combustion and related problems such as greenhouse gases, acid rain, acid mine drainage on the environment [Finkelman et al., 2002].

1.2 Residential Coal Combustion and Air Quality Issues in South Africa

The energy economy of most developing countries has long been dominated by coal, which accounts for over 75% of total primary energy consumption. In South Africa, although the majority of coal is used primarily for electricity generation, high levels of household coal use have been reported in regions close to coalmines and areas experiencing cold winters–essentially the South African Highveld region [Balmer, 2007]. An estimated eighteen million people live in three million informal dwellings [Wentzel, 2006] and rely on cheap solid fuels such as wood and coal to meet their basic energy needs. In Mpumalanga, a large share of households (7.9%) continues to rely on coal as the predominant energy source for cooking. On the Highveld (i.e. most of Mpumalanga, Limpopo, Gauteng, North West and Free State) and in parts of KwaZulu-Natal, coal is widely used among the poor for purposes of cooking and space heating [Lloyd, 2014]. According to Statistics South Africa, [2012], the shares of coal consumption used in the domestic sector in Gauteng and Free State provinces are 0.7% and 1.7%, respectively, while the national average share of household coal consumption is 1%.

The fuels are burned in self-fabricated and inefficient cooking devices (i.e. imbaulas/braziers) resulting in elevated levels of indoor and local ambient air pollution. Typically, the brazier is lit outdoors, and allowed to burn until the visible smoke has subsided. When the brazier stops smoking,
it can then be used either outdoors or indoors, for cooking or heating [Lloyd, 2014]. In formal settings (e.g. low-to-medium income households), despite having access to electricity, many households continue to use illuminating paraffin and coal to meet their cooking and heating needs. Electricity is used for lighting, entertainment purposes and occasional cooking [Wentzel, 2006]. It is suggested by Qase et al. [2000] that households consume about one million tons of coal annually, small in comparison to the tonnage used in the electricity generation and metallurgical industries.

The majority of householders understand the dangers posed by braziers to their immediate health and environment. As soon as they are able, they invest in a cast iron stove [Lloyd, 2014]. The cast iron stoves on the market in South Africa were originally designed for burning wood. However, they are able to burn coal cleanly after the ignition phase. During the initial combustion, the stove emits copious quantities of smoke, and it is only once flames are observed over the whole bed of coal that smoke emissions die down [Lloyd, 2014]. The built-in cast iron stoves have chimneys venting to the exterior, so the smoke from such stoves does not affect severely the indoor air quality. Although the emitted smoke poses substantial health risks (i.e. coal smoke is rich in polycyclic aromatic hydrocarbons), Lloyd [2014] argues that the greatest loss is an economic one. He further contends that smoke amounted to about 15% by mass of the coal, and carried over 20% of the heat content of the raw coal.

A remarkable finding by Lloyd [2014] is that the cast iron stove was one of the earliest purchases by many migrants from the rural communities to the city. The author found that a second-hand stove sold for at least R 2 000; a new entry-level stove cost R 4 000. To enhance the sales of these stoves, many coal merchants ran micro financing schemes to assist householders to purchase the appliances. Further investigation gave some indication of why such expensive units were desired among the migrants. These stoves were reported to be multi-purpose, providing cooking, space and water heating, and even garbage disposal [Lloyd, 2014].

1.2.1 Air quality issues

According to Engelbrecht et al. [2002] D-grade coal (i.e. poor quality) is widely used due to its abundance, relative availability, and associated low cost. The smoke from the combustion of this poor coal type in the townships was found to contribute to as much as 30% of the particulate pollution in the industrialized areas of South Africa country [Engelbrecht et al., 1998]. According to Lloyd [2014], the inefficient combustion of one million tonnes of coal in the household sector in South Africa [Qase et al., 2000] is responsible for 40% of the total particulate load in South African skies. Scorgie et al. [2003] found that in Gauteng, household coal burning was the largest contributor to air pollution at 65%, while electricity generation contributed 5%, with industrial and commercial activities contributed 30%. In a similar study, Mathee [2004] found source contributions to quantifiable particulate emissions in the city of Johannesburg attributable to domestic coal burning to be 48%, 22% to scheduled processes, 20% vehicle-tailpipe emissions and 10% to tailings impoundments [Wentzel, 2006]. Residential combustion of D-grade coal has been found to be the greatest source of particulate matter in a township in the Free State, contributing 62% of PM2.5 and
43% of PM10 [Engelbrecht et al., 2002]. However, Lloyd [2014] is of the opinion that the coal that is burned in these Highveld poor communities is of surprisingly high quality. He contends that the users will not accept less than B-grade, and prefer A-grade coal.

Scorgie [2012] contends that in South Africa, the SANS PM10 daily limit of 75 µg m$^{-3}$ was exceeded at almost all monitoring stations, with the annual limit of 40 µg m$^{-3}$ exceeded at over 40% of the stations. These air quality guidelines and limits have been adopted by the DEA as national limits with compliance date set to 1st January 2015. High levels of fine particulate matter are experienced in coal and wood burning areas with peak daily averages of PM10 up to 500 µg m$^{-3}$. Daily peak PM10 averages can be classified into three categories depending on the concentration levels: moderate (50–75 µg m$^{-3}$), high (75–100 µg m$^{-3}$), and very high (> 100 µg m$^{-3}$). High to very high levels occur frequently with the daily PM10 limit of 75 µg m$^{-3}$ exceeded on 40% to 60% of days within coal-burning areas [Scorgie, 2012].

In South Africa, there are currently insufficient data available from monitoring stations to make systematic assessments of health risk potentials within the environments selected [Scorgie, 2012]. Air quality limits for PM2.5 were only established in 2012. However, reference is made to PM2.5 levels recorded during campaigns within residential coal-burning areas. For example, in 1997 ambient PM2.5 monitoring was undertaken in a coal-burning area in Soweto. Seasonal average PM2.5 levels varied from 20 µg m$^{-3}$ during summer to 150 µg m$^{-3}$ during the winter season [Scorgie, 2012]. Daily average winter PM2.5 levels ranged from 50 to 300 µg m$^{-3}$. Household coal burning contributed significantly to winter particulate matter loadings resulting in the increased percentage of fine particles [Annegarn et al., 1999].

SO$_2$ levels within the household set-up are seldom exceeded on an annual basis. In South Africa, the annual air quality limit for SO$_2$ has been set at 50 µg m$^{-3}$. High levels of SO$_2$ have been reported for Orange Farm monitoring stations and this has been attributed to residential combustion of coal for cooking and heating purposes. However, air quality limit exceedances are infrequent, with annual average SO$_2$ levels only ~30% of the annual air quality limits. This is due to the relatively low sulphur content of the coals in use (typically 0.6% S) [Scorgie, 2012].

High volatile organic compounds (VOC) have been reported in the residential coal-burning areas of South Africa. Ongoing monitoring of VOCs is mainly restricted to benzene, toluene, ethyl-benzene and xylene (BTEX). According to Scorgie [2012], annual benzene levels are generally in the range 3 to 9 µg m$^{-3}$. Exceedances of the SANS annual limit of 5 µg m$^{-3}$ were recorded close to highways, filling stations and within residential coal-burning areas [Annegarn et al., 2007]. Peak period-average benzene levels within the residential coal-burning areas of ~30 µg m$^{-3}$ have been recorded during monitoring campaigns [Scorgie et al., 2003].

The post-apartheid government in South Africa developed energy policies designed to improve access to adequate and cheap energy services for urban and rural households [Madubansi & Shackleton, 2006; Davis, 1998]. The policies were aimed at providing cleaner and safer forms of energy for low-income households [Spalding-Fetcher & Matibe, 2003]. The Department of Mineral and Energy
Affairs embarked on an accelerated electrification programme in most rural areas and low-income suburbs of South Africa [DME, 1998]. Because much of the population of rural South Africa is located in areas far from the current and anticipated electricity grid connections, off grid renewable energy resources, particularly photovoltaic, played a role in the electrification exercise. The department believed that rapid electrification of these areas would solve air quality issues from domestic smoke combustion. Despite 97% electrification of townships, coal smoke problems persist because the fuel is readily available (on the Highveld) and relatively affordable compared to other forms of energy.

Realising that rapid electrification does not result in an automatic and complete switch to cleaner fuels [Madubansi & Shackleton, 2006; Davis, 1998], the South African government has encouraged the dissemination and uptake of a domestic coal ignition method known as the *Basa njengo Magogo* (TLUD) as a no-cost way of reducing smoke emissions [Makonese, 2011; Standish *et al.*, 2007; DME, 2004]. The TLUD approach is a simple intervention in the way domestic fires are lit, involving a top-down approach to fuel loading and ignition in braziers and stoves [Wagner *et al.*, 2005; CSIR, 2005], and has become a national priority energy intervention programme. This method is estimated to result in an 80% reduction in ambient particulate air pollution and a 20% reduction in coal use at no additional cost to the households [Le Roux *et al.*, 2009; van Niekerk *et al.*, 1997]. However, on examination, these reports showed limitations that could have profound implications on the reported emission factors. The authors did not carry out systematic evaluations of the braziers in terms of fuel quality, ventilation rates, and fuel moisture content. The influence of these parameters on emission factors warrants further investigations, and this is the starting point for this thesis.

1.3 Residential Coal Combustion in the Developing World

1.3.1 Residential coal combustion in China and other developing countries

Air pollution in China is dominated in the cold winter season by coal smoke [Bi *et al.*, 2008]—traffic emissions are the other dominant source. It is estimated that a quarter of the global anthropogenic carbonaceous emissions are attributed to China, of which about 70% is due to coal combustion [Cooke *et al.*, 1999]. In China, coal accounts for approximately 70 – 75% of the primary energy consumption [Millman *et al.*, 2008] and more than 80% is burned directly for purposes of cooking and heating [Bi *et al.*, 2008]. Although in-home coal use is banned in all Chinese cities, about 10% of urban households still use coal as their primary source of fuel to meet demands of heating and cooking [IARC, 2010a]. The majority of rural households rely heavily on the use of coal fuel to meet their basic energy needs. The use of coal in both rural and urban settings is a function of availability/access to the fuel and household income. About 40% of all households in rural China rely on coal for heating or cooking [National Bureau of Statistics, 2005].

The use of coal for heating does not equate with the use of the same fuel for cooking. According to IARC [2010a], some households that use coal for heating may use wood for cooking. The National Bureau of Statistics [2006] showed that the distribution of coal use for cooking varied according to...
the geographic region, with coal being used for cooking in 19% of homes in Eastern China, 38% in Central China, 27% in Western China, and 7% in North-eastern China. In a study in the Shaanxi province, Hubei and Zhejiang, about 65% of the total households surveyed reported that they heated with coal in winter, compared to 0.2% in Zhejiang and 28.5% in Hubei [Sinton et al., 2004]. In the same survey, 70% of the households in Shaanxi used coal for heating, compared to 1.5% in Zhejiang and 6% in Hubei [Sinton et al., 2004]. As a result, the Chinese government has advocated for the adoption of improved cooking stoves and the use of less polluting honeycomb coal briquettes for the residential sector.

There is little literature and evidence about coal use and resultant health and environmental impacts outside China. However, some documented evidence can be found in the literature that dates back to the 1980s. For example, the link between burning coal and adverse health was made clear in Dublin, Ireland in the 1990s [Lockwood et al., 2009]. In the 1980s, when the price of oil increased dramatically, many households in Dublin switched from oil to bituminous coal for purposes of home heating and hot water provision. This resulted in elevated household air pollution (HAP) and local ambient air pollution - associated with an increase in in-hospital deaths due to respiratory diseases. In 1990, the Irish government banned the marketing, sale, and distribution of bituminous coal, citing environmental and health concerns. Due to the 1991 ban, black smoke concentrations declined by 70% (~35.6 μg m⁻³), deaths related to respiratory failure fell by 15.5%, and cardiovascular deaths fell by 10.3% [Lockwood et al., 2009]. Although combustion of coal was not the only cause of these illnesses, it contributed immensely to the production of a complex mixture of airborne pollutants with mutable adverse effects on human health.

A few measurements of particulate size fractions were carried out in peri-urban households in Gujarat (Western India) where coal is the predominant fuel for cooking and heating [Aggarwal et al., 1982; Raiyani et al., 1993]. According to Raiyani et al. [1993], the proportion of suspended particulate matter less than 9 μm released during cooking were 92% and the proportion less than 2 μm was 70%. Particulate PAH size distributions measured in these same indoor environments showed that in households that used coal, 76% of the PAH mass was contained in particulates < 2 μm [Raiyani et al., 1993]. A study carried out in Santiago, Chile in the winter season on urban households found that levels of PM10 were 250 μg m⁻³ and SO₂ were 295 ppb in the kitchen area [Cáceres et al., 2001].

In Mongolia, particularly in Ulaanbaatar, the main sources of air pollution during winter are related to domestic coal/peat burning for heating and cooking activities. The pollution levels are exacerbated by local meteorological conditions. Due to increased energy demands from a growing economy and rapidly urbanising population, ambient air pollution in Ulaanbaatar has been reported to be among the highest concentrations in the world [Gunchin et al., 2012]. Results of ambient monitoring in Ulaanbaatar showed that PM2.5 mass concentrations were seven to nine times higher than national air quality standards and nine to eleven times higher than the WHO guideline. Source contributions for PM2.5 from coal/peat combustion were found to be 35% at a residential site and 90% at a non-residential site [Gunchin et al., 2012].
1.4 Problem Statement and Knowledge Gaps

The literature holds a number of studies and models for processes during moving chain grate, fluidised bed and pulverised fuel injection combustion for coal-fired boilers. However, few relevant investigations on lump-coal in fixed-bed combustion systems have been detected [Wang & Luo, 2009]. Specifically, little has been documented on small household coal-burning devices (packed-bed combustion) in use in the developing world. Only limited measurements have been conducted, none of which can be used for the development of quantitative emission factors [Makonese, 2011]. Such data are needed in order to make valid comparison between the characteristics (e.g. size distribution, chemical composition, morphology) of household coal-burning combustion emissions determined in the laboratory vs. those obtained from the field. This information is needed for air quality source apportionment studies, such as those carried out by Scorgie et al. [2001] and Annegarn et al. [1998]. Particle measurements may be conducted as part of procedures for compliance with emission or air quality standards. In cases where there are no national air quality or emission standards available, the results of the measurements are compared with either national or international guidelines, such as the WHO Guideline for Air Quality [WHO, 1999].

Primary particulate matter (PM) is formed directly from combustion sources, while secondary particles are formed in the atmosphere from condensation or reactions of gaseous precursors [Seinfeld & Pandis, 1998]. In South African townships, domestic coal combustion devices are a source for both primary and gaseous precursors that react in the atmosphere to create secondary PM. The space in between the transition zone of VOCs and semi VOCs involves rapid processes, making it complex to classify accurately particles into primary and secondary aerosols. Upon leaving the combustion chamber, the particle sized spectrum and composition changes rapidly on time scales ranging from milliseconds to several hours, depending on factors such as rate of dilution and atmospheric conditions (temperature, humidity, background particle levels) [Abdul-Khalek et al., 2000]. The time scale and sequence of the physical processes of cooling and dilution will influence the size, morphology and characteristics of the aerosol emerging from the combustion system.

Residential coal fires contribute significantly to local ambient condensed matter emissions, yet their aerosol formation mechanisms and resulting particle properties are poorly understood and parameterized in climate and air quality dispersion models. In the context of climate change, soot (black carbon) emitted from residential coal fires contribute to one of the largest uncertainties in current estimates of radiative forcing [Bond et al., 2013]. This inherently large uncertainty emanates from poor understanding of the microphysical properties of residential coal fire-emitted soot and their parameterizations in models [Chakrabarty et al., 2014]. In recent years, efforts have been placed on characterising soot properties emitted from small-scale biomass combustion systems to simulate real-world natural wildfires in their soot formation mechanism and emitted particle properties [China et al., 2014]. However, there is paucity of information and knowledge pertaining to soot in small-scale residential coal-burning devices. This study seeks to address this knowledge gap and present possible modes of formation of soot particles in packed-bed small residential coal combustion devices.
Characteristics of coal combustion have been studied for many years since the invention of the fixed-bed stoker system in 1822; the firing of pulverized coal in a brick-kiln in 1831; and the invention of fluidised beds in the 1930s. However, the complexity of factors in particle formation such as moisture content of the fuel, fire ignition methods, fuel types and grade, and ventilation rates are still unclear issues in our understanding of coal fuel combustion in fixed bed combustion systems such as domestic coal-burning braziers. To the best of the author’s knowledge, there has been no attempt to analyse systematically variations in morphological characteristics as a function of operational practices of residential packed bed coal-burning devices, specifically in terms of fuel characteristics, ignition methods and ventilation rates.

Current analytical techniques for atmospheric PAH determinations are generally complex and time consuming involving the use of solvent extraction of samples. This has the potential to limit widespread sampling and analysis of PAH samples for spatial and temporal trend determinations [Forbes, 2010]. A novel technique was therefore developed and investigated at the University of Pretoria, which allows for the rapid screening of PAHs prior to comprehensive quantitative analysis. This technique has been used in this study to investigate PAH emissions from coal fires.

Single-particle electron microscopy analysis has been shown to be useful in providing crucial information toward accurate and size unconstrained characterization of aerosol microphysical properties [China et al., 2014; Chakrabarty et al., 2014]. Furthermore, information on the aerosol formation mechanism can be deduced from single-particle electron micrographs [China et al., 2014; Chakrabarty et al., 2014; Chakrabarty et al., 2009, Pósfai et al., 1999, Abel et al., 2003]. There have been only a limited number of studies conducted to investigate aerosols emitted from small-scale residential coal combustion devices using the electron microscope [Gwaze, 2007; Wentzel, 2000]. The majority of these studies sampled particles in the ambient and the household environment but not directly from the fire [Liu et al., 2014; IARC 2010a; Shi et al., 2003; Wentzel et al., 1999]. Earlier studies have identified the occurrence of unusually large soot aggregates from coal combustion fires [Wentzel et al., 1999], but the investigators failed to distinguish the microphysical properties of these particles from conventional sub-micron soot aggregates. Consequently, “these unique observations have gone unnoticed, and there has been no follow-up investigations conducted to determine the formation mechanism and frequency of occurrence of these unusually large soot aggregates and their microphysical properties” [Chakrabarty et al., 2014:2].

1.4.1 Aim

This study aims to develop an improved understanding of the complex processes of packed-bed combustion in small (few kilowatts) domestic devices, by carrying out a systematic investigation of the behaviour of packed-bed coal combustion in informal domestic stoves, specifically with respect to the quantity and quality of condensed matter (smoke) emissions.
1.4.2 Hypothesis

It is hypothesized that the formation of condensed matter emissions from domestic packed-bed coal combustion are a consequence of poor combustion conditions relating to method of ignition, ventilation rates and fuel properties (moisture and quality).

1.4.3 Objectives

To achieve the above aim, the following objectives were set:

a. To review scientific literature concerning adverse health effects from ambient air pollution in relation to domestic coal combustion.

b. To design a dilution sampling system for emission measurements in residential coal-fired appliances.

c. To systematically determine the characteristics and quantities of selected *gaseous emissions* (CO₂, CO, NOx, NO and PAHs) from informal domestic coal-burning braziers as a functions of (i) fire-ignition method; (ii) ventilation rate; (iii) coal grade; and (iv) coal moisture; and to report related emission factors as [g MJ⁻¹] and [mg MJ⁻¹] and emission rates as [g s⁻¹].

d. To systematically determine the characteristics and quantities of *particulate matter emissions* from informal domestic coal combustion braziers as a function of (i) fire-ignition method; (ii) ventilation rate; (iii) coal grade; and (iv) coal moisture; and to report related emission factors as [g MJ⁻¹] and emission rates as [g s⁻¹].

e. To carry out an investigation of the morphology of condensed matter particles formed during different phases of combustion, and compare the morphologies between bottom-lit updraft (BLUD) and top-lit updraft (TLUD) fires.

f. To synthesize results, and perform a logical analysis in terms of the hypothesis.

1.5 Relevance of Study

This work is relevant in that it builds on the work of Wentzel *et al.* [1999] regarding the properties of particles emitted from domestic coal combustion, and is a valuable contribution to the body of knowledge and a necessary tool and guide for health and environmental policy makers. Unlike the work of Wentzel *et al.* [1999] which focused mainly on secondary combustion particles, this work extends the study to primary combustion particles which are directly emitted to the atmosphere from the combustion devices. Information from this study is useful to predicting emission formation in the design of energy production units to meet emission regulations and to assess the environmental effects of different alternatives [Sippula, 2010]. Information on the physical and chemical characteristics of particles is useful for the health sector and needed for tracing the deposition patterns of particles in the lungs (e.g. size and morphology), and partly for identifying the sources (e.g. isotopic ratio, morphology, chemical signatures). This study seeks to provide the first comprehensive systematic study of emission factors/rates from residential coal combustion devices with different ventilation...
rates, for use in air quality dispersion and climate models, thus contributing towards the already existing research on domestic burning (especially domestic coal combustion) emissions inventory for South Africa.

1.6 Scope of the Study

The arguments and examples contained herein are limited to coal braziers. Although, particulate emissions from wood and other fuels such as kerosene are important for human health and climate reasons, they are not included in this study.

Development of instrumental and measurement techniques is limited to the design of a portable dilutor for use in the evaluation of emissions from residential coal combustion, in the South African context. The critique on existing dilution systems highlighted in this study is to present a point of departure, demonstrating how the need for new, portable and robust testing dilutors arose. The dilutor, which we have termed the ‘SeTAR dilutor’, is used in this study as part of the laboratory equipment assembled to perform a systematic evaluation of field and lab-designed coal braziers with different ventilation configuration, ignition methods and coal qualities.

The experiments presented herein were all carried out in the laboratory although reference has been made to field emissions monitoring of polycyclic aromatic hydrocarbons. An attempt was made to measure H\textsubscript{2}S and SO\textsubscript{2} emissions from the coal fires, but there were unresolved instrument calibration and response functions that rendered the results unusable. Inter-comparison of laboratory results with field tests is an important component of current international improved stove programmes, but is not within the scope of this thesis.

The variables in our systematic investigation included four parameters–fire ignition method, coal type, fuel moisture content, and ventilation rates. Other important parameters such as (a) fuel size distribution and fuel load size, (b) stove diameter, and (c) grate height were kept constant. For practical purposes, primary air was assumed as the air entering from below the fire grate, and secondary air as the air entering above the grate, into the packed bed or the space above. In the range of laboratory built stoves, primary and secondary holes were uniformly distributed and of uniform diameter. In exploring changes in the diameters of ventilation holes, the ratio of primary to secondary and distribution of ventilation holes warrants further investigation. However, this did not form part of this work.

Monitoring of PAH emissions was carried out during the pyrolization phase only, which is for the first 10 to 15 minutes after ignition–no attempt was made to characterize PAH emissions across an entire burn cycle. Extensive laboratory tests for PAH emissions were not carried out due to lack of equipment for continuous monitoring of complex hydrocarbons. Comparing the laboratory evaluations of PAH emissions with field-based tests is an important future task, but will not be considered in this thesis.
We did not monitor the optical properties, chemical properties and particle size distribution of the primary nano-particles from residential coal combustion, as appropriate apparatus were not yet available in the laboratory. Evidence has pointed out that large variation in emissions of light absorption particles results from different coal composition and burning conditions [Bond et al., 2002]. There is therefore a need, in future, to look at optical properties of particles from coal-brazier fires. This would assist in more detailed emission inventories, which take into consideration coal combustion and combustion practices, in order to curb uncertainties in radiative forcing predictions by transport models.

1.7 Research Outline

Chapter 1: Introduces domestic lump-coal use as a domestic fuel in South Africa and other developing countries worldwide. A problem statement is formulated, the domain of the study specified, aim and objectives set out. A justification of the study is presented and the general approach to the study is outlined.

Chapter 2: Reviews previous work on residential coal combustion processes, emission factors, and smoke reductions from alternate ignition methods. The influences of coal smoke on human health are summarised, to contextualise the importance of coal smoke as a public health issue. A brief review of various dilution systems is given and their limitations highlighted.

Chapter 3: Presents the experimental materials and procedures used in this study. This involves technical details of the analytical instruments, measurements, quality control measures and the laboratory set-up for emissions monitoring. The development of the SeTAR dilutor as an original contribution is discussed. The chapter ends with a quality control/quality assurance evaluation of the experimental procedures.

Chapter 4: Results of systematic investigation of emissions

Gas and particle emissions from braziers: Comprehensive results are presented for combustion of A-grade and D-grade coal fuels (two moisture contents for D-grade) for two different ignition methods top-lit updraft (TLUD) and bottom-lit updraft (BLUD), three air supply rates (low medium and high natural draft ventilation rates). Results are presented for PAHs and of filter samples collected for SEM composition and morphology analysis using different ignition methods and ventilation rates.

Chapter 5: Synthesis and Conclusions

Through presentation and discussion of representative results, we illustrate how selected parameters affect gaseous and particulate emissions from residential coal combustion. As part of the synthesis of the results, a logical analysis is carried out to demonstrate the validity or otherwise of each component of the hypothesis, drawing on the diverse set of experimental results presented. The originality and significance of the findings are discussed, together with recommendations for further investigations to address outstanding issues identified in the course of the investigations.
CHAPTER TWO

A literature survey of residential coal use in South Africa and other developing countries, and related health implications is given. The current literature review serves as a background in facilitating efforts to develop an appropriate aerosol source emissions measurement methodology (i.e. hardware and procedures) that can be applied for expanding key areas of particulate emissions database.

2. Context of Coal Combustion Emissions and Particle Analysis

The distribution of hazardous elements in fine particles, and the morphology of the particles are needed to assess their potential mobility in the environment. The specific path trace elements take to transform from the vapour phase to the condensed phase is important in assessing the toxicity of the waste product. A fundamental understanding of the mechanisms leading to the formation of the fine particle size distribution (PSD) region and of how this formation influences trace element partitioning is an important step to minimizing the environmental and health impact of fine particulate emission.

In the past, much attention has been focused on gaseous pollutants such as CO, CO$_2$, NOx and SO$_2$ due to their impacts on climate change, acid rain, and indoor air pollution [Zhang et al., 2008]. In recent years strong scientific evidence has emerged which suggests that particulate air pollution contributes to excess mortality and morbidity [Gordon et al., 2014; Titcombe & Simcik, 2011; Teramae & Takarada, 2009; WHO, 2006; Pope et al., 2002]. The emission of fine particles is closely associated with the emission of toxic trace elements from coal combustion because fine particles are often enriched with these toxic elements [Teramae & Takarada, 2009]. Exposure to fine particles has been associated with lung inflammation and cardiovascular effects, and acute respiratory conditions [Gordon et al., 2014; Titcombe & Simcik, 2011; Teramae & Takarada, 2009; Yi et al., 2008; Taylor, 2009; Pope et al., 2002]. Morphological properties of atmospheric particles have been shown to play an important role in their transport behaviour, deposition patterns in the human respiratory system [Oberdörster, 2001] and interactions in the human lung [Stearns et al., 2001]. However, how particles interact with the human body remains a matter of debate. It is unclear whether the number of inhaled particles, the morphology, the surface chemistry, and other physico-chemical parameters are responsible for the toxicity of the airborne materials [Kaegi & Holzer, 2003:4354].

2.1 Health Impacts of Residential Coal Smoke

Household air pollution (HAP) from solid fuels was classified the 8$^{th}$ top health risk worldwide, fourth top health risk in developing countries with high child mortality, third top health risk in India [Barnes, 2006], after malnutrition and water bone diseases [WHO, 2002]. It is estimated that indoor air pollution from burning biomass, coal, and crop residues in open fires and poorly fabricated stoves, cause between 2.7 and 2.8 million deaths annually [Bruce et al., 2000]. According to Lim et al.
[2012], a recent global systematic analysis of all major health risks has concluded that cooking with solid fuels kills four million people annually. Acute respiratory infections are considered the number one killer of children under the age of five [Titcombe & Simcik, 2011; Naeher et al., 2007; Smith et al., 2000]. In South Africa, acute lower respiratory infections accounts for approximately 14% of deaths amongst children less than five and is ranked, together with diarrheal disease, as one of the top killers of young children [Barnes et al., 2004; von Schirnding et al., 1991].

There is a substantial body of toxicological and epidemiological data describing the short- and long-term adverse effects of atmospheric PM on human health [Uski, 2014]. According to Braun-Fahrländer [2001], the epidemiological link between air pollution and death was established many years ago by a series of smog episodes, which affected countries and states such as (i) Belgium, Meuse Valley in 1930; (ii) Pennsylvania, Donora in 1948; and (iii) the United Kingdom, London in 1952. In all of these episodes, stagnant weather conditions made concentrations of smoke, sulphur oxides, and other noxious gases and substances rise to levels that were higher than current conditions in the developed world [Braun-Fahrländer, 2001]. For the London episode, deaths because of high levels of ambient pollution were estimated to be over 4 000. Since the mid-1970, much focus has been placed on research on the health effects of air pollution. Health impacts of particulate matter emitted from coal combustion have received substantial attention since the 1980s. Over the past three decades, air pollution measurements in many European countries and the US have vastly improved [Braun-Fahrländer, 2001].

According to [Braun-Fahrländer, 2001], the majority of air pollution epidemiological studies fall into two broad classification: short-term and long-term exposure studies. Short-term exposure studies are generally time-series studies that are dependent on temporal changes as a source of exposure variability. As such, short-term exposure studies evaluate immediate short-term changes in health end-points associated with short-term changes in pollution. Since experimental methodologies fail to address complexities of real-world exposures to particulate matter, the majority of recent reports on associations between PM exposure and health have been based on observational epidemiology studies, thereby limiting the utility of this investigatory tool [Braun-Fahrländer, 2001]. On the other hand, long-term exposure studies employ information on spatial differences in pollution as a source of exposure variability. Long-term exposure studies compare various health outcomes across communities or neighbourhoods with different levels of pollution. The assessments are cross-sectional in design, employing the use of longer-term pollution data (i.e. usually a year or more). These studies are often interpreted as evaluating the long-term or cumulative effects or exposure [Braun-Fahrländer, 2001].

2.1.1 Studies showing link between diseases and exposure to coal smoke

In epidemiological studies, ultrafine and fine particles have been associated with an increased prevalence of stroke and cardiac outcomes [Uski, 2014; Franchini & Mannucci, 2011; Madl & Pinkerton, 2009; Mills et al., 2009]. Detrimental effects of these particles on human health have been attributed to reactive organic species and metals [Uski, 2014; Mills et al., 2009]. According to Uski
there is limited scientific data about the toxicological properties and related chemical constituents of fine and ultrafine particles, which are released from primary combustion sources (For example, small-scale coal combustion).

In 1996, The US Environmental Protection Agency (EPA) published their results on an extensive study on health implication of coal smoke and concluded that apart from mercury, there was no compelling evidence suggesting health impacts as a result of trace elements emitted from coal-burning electricity generating utilities [Finkelman, 2007; EPA, 1996]. However, there is documented evidence, which suggests that there is a link between diseases such as impaired hearing [Bencko & Symon, 1977] due to exposure to high arsenic emissions and fluorosis from exposure to fluorine from coal combustion. Several case–control studies from China and India, for example, have demonstrated an increased risk for lung cancer and other diseases including gastro-intestinal and nervous system disorders, fluorosis, and selenosis, associated with exposure to emissions from residential coal combustion.

According to IARC [2010a], lung cancer has been associated with continued use of coal fuel over a long period of time [Dai et al., 1996]. This includes continued use of Kang (heated by coal) [Dai et al., 1996]; cooking and heating with coal [Hosgood et al., 2008], amount of coal used [Kleinerman et al., 2002], and quality of ventilation in households that use coal for cooking indoors [Le et al., 2001]. A cohort study carried out in Xuanwei, China, evaluated the association between the risk of lung cancer and domestic coal use [Lan et al., 2002]. The study reported that among lifetime users of low-grade coal, households that changed from traditional to improved stoves with chimneys, experienced a decreased risk of developing lung cancer compared to households that continued to burn coal in traditional fire pits. Again, a reduction in lung cancer mortality was observed among lifetime users of low-grade coal who changed to portable improved and efficient stoves [Hosgood et al., 2008]. According to IARC [2010a], both analyses were adjusted for average tons of fuel used annually, years of tobacco smoking, years of cooking, history of spousal lung cancer, family history of lung cancer, and other potential confounders.

In a multicentre study conducted in seven European countries including the Czech Republic, Hungary, Poland, Romania, Russia, Slovakia and the United Kingdom, Lissowska et al. [2005] evaluated the association of risk of lung cancer and heating/cooking with solid fuels. The study included 2 861 cases and 3 118 matched population-based controls [IARC, 2010a] and for coal use specific analysis, there was not found evidence to suggest that long-term use of coal related to the risk of lung cancer, after adjusting for tobacco smoking and other factors [Lissowska et al., 2005]. In another study in India, Sapkota et al. [2008] conducted a multi-centre hospital-based case-control study to investigate lifetime fuel usage as risk factors for three different cancer types. They found out that the risk for hypo-pharyngeal, laryngeal and lung cancer increased with years of coal usage.

A study conducted in Dublin, [Kabir et al., 2007] evaluated the impact of outdoor concentrations of black carbon smoke from coal burning on lung cancer mortality using data from 1981 to 2000. However, in 1990 the use of coal for domestic purposes was banned in Dublin. After the ban (i.e.
1991–2000), a strong decline in black carbon (from 46.4 μg m\(^{-3}\) before the ban to 18.2 μg m\(^{-3}\) after the ban) was noted. After adjusting for age, sex and smoking, it was found that annual mean black carbon emissions were not related to annual death rates from lung cancer. However, the IARC work group contended that the post-ban period was relatively short to see any changes in lung cancer mortality [IARC, 2010a].

2.1.2 Health effects of individual metals

Metals in coal smoke are normally attached to particles either in elemental or in compound form. Some metals such as mercury can persist in the gas phase as a vapour. Domestic coal combustion emits metals including lead, arsenic, chromium, and mercury, in quantities potentially harmful to human health. There are other metals, which are potentially poisonous. Exposure to smoke from domestic coal fires may result in exceedance of safe limits by many households.

In separate studies undertaken in Shenyang City in northern China and in Xuanwei County, China, some carcinogenic mineral elements were released during the combustion of lignites. According to Ren et al. [2004, 1999] as cited in IARC [2010a], lignites from a local Shenyang coal field had high concentrations of nickel (75 ppm) and chromium (79 ppm) when compared with the levels reported elsewhere in the world (i.e. 0.5–50 ppm for nickel and 0.5–60 ppm for chromium) [Swaine, 1990]. In the Guizhou Province of China, particles emitted from residential coal burning have been reported to contain high levels of chemicals including fluorine, arsenic and mercury [Gu et al., 1990; Shraim et al., 2003; Yan et al., 2004].

**Arsenic**

Arsenic is produced from domestic combustion of bituminous coals and anthracites. In humans, the acute inhalation of inorganic arsenic may cause gastro-intestinal and nervous system disorders. Many cases of chronic arsenic poisoning have been reported in the Guizhou Province, China [Zheng et al., 1996]. Symptoms of arsenic poisoning include hyper-pigmentation, hyper-keratosis, Bowen’s disease, and squamous cell carcinoma [Finkelman, 2007]. The effects of burning mineralized coal (with high arsenic content) in a residential environment are exacerbated by roasting maize mealies and meat directly over the coal fires. Zheng et al. [1996] have shown that drying chili pepper directly on coal fires is an important factor in arsenic poisoning in the Guizhou Province. Finkelman [2007] argued that apart from inhaling indoor air polluted by arsenic from coal combustion, it is possible for significant amounts of this toxicant to come from other tainted food items, and from the ingestion of kitchen dust containing high levels of the pollutant.

**Fluorine**

Fluorine is volatilized during combustion of the coal and when it is ingested over prolonged periods, it causes a disease known as fluorosis. Fluorosis, due to residential coal combustion has been reported in more than 13 provinces and municipalities in China [Ando et al., 1998]. According to Finkelman [2007], more than 10 million people around the Guizhou Province in China suffer from different forms of fluorosis. Typical signs and symptoms of this disease include “corrosion of tooth enamel
(dental fluorosis), osteosclerosis, limited movement of the joints and outward manifestations such as knock-knees, bowlegs, and spinal curvature” [Finkelman, 2007:103]. Similar to arsenic poisoning, fluorosis is derived from foodstuffs prepared directly over coal fires. In South West China, the problem of fluorine poisoning is exacerbated by the use of clay as a binder in briquetting. The clay used is enriched in fluorine derived from the leaching of the limestone substrate [Finkelman, 2007]. Ando et al. [1998] estimated that over 97% of reported cases of fluorine exposure came from the consumption of fluorine-tainted food and less than 3% from direct inhalation of coal smoke emitted from domestic coal combustion.

**Selenium**

Selenosis is a disease caused by selenium poisoning. In the South West regions of China, the disease is attributable to emissions from ‘stone coal’, and from the continued use of coal ash as a soil supplement resulting in food crops taking up large amounts of selenium. The primary targets of acute selenium toxicity in food animal species are the cardiovascular, gastrointestinal, and haematopoietic systems [Raisbeck, 2000]. In humans, symptoms of this disease include fatigue, gastrointestinal disturbances, garlic odour of the breath, hair and nail loss [Finkelman, 2007]; and in animals symptoms include hair and hoof loss [Raisbeck, 2000].

### 2.1.3 CO poisoning: A case of South Africa

Carbon monoxide is a colourless and odourless, toxic gas emitted from the incomplete combustion of fuels. Because CO is initially non-irritating and tasteless, it is difficult to detect it without monitoring instruments. Exposures at greater than 100 ppm have the potential to cause harmful health effects. Symptoms of CO poisoning include light-headedness, confusion, vertigo, headaches, and flu-like general symptoms. CO causes health effects in humans by competing for haemoglobin to form carboxy-haemoglobin in the blood. Generally, haemoglobin has a higher affinity for CO than it has for oxygen. This prevents haemoglobin from releasing oxygen in tissues leading to a condition known as hypoxia.

Domestic CO poisoning can be detected early by using household carbon monoxide detectors or monitors. Carbon monoxide poisoning is responsible for many deaths especially in developing countries where there is continued use of fossil and biomass fuels for purposes of heating and cooking. In South Africa, there have been reports (from the 1990s) in local newspapers about accidental deaths of families due to CO poisoning from coal braziers. Lloyd [2014] noted that in the Highveld region of South Africa, and especially in winter, studies of death notices in Soweto, Johannesburg from local newspapers in the 1990s showed that, during the winter months, there were typically three families a week in which every member died ‘accidentally’ during the night.

### 2.1.4 Environmental risks of air pollution

Environmental risks related to airborne particles include those caused while they are airborne, and after deposition. A major environmental risk relates to the nature and magnitude of climatic forcing
by particles while they are airborne on local, regional and global scales. Bond and Bergstrom [2006] contend that optical properties of irregular particles may significantly differ from a compact sphere. Aerosols particles have direct, semi-direct and indirect radiative forcing on the Earth’s radiation balance [Gwaze, 2007; Charlson et al., 1992]. Direct forcing relates to the extinction of incoming solar and outgoing infra-red radiation by particles under clear skies [Gwaze, 2007]. In semi-direct forcing, the absorbing nature of aerosols in and around a cloud may cause increased temperatures and reduce humidity profiles, leading to low-cloud cover and cloud formation [Gwaze, 2007; Johnson et al., 2004]. Indirectly, aerosol particles perturb the radiation budget through interaction of clouds with radiation [Gwaze, 2007]. High particle concentrations have been linked to the increase in the number of cloud droplets that may be formed, but reduce the mean size of droplets needed to initiate precipitation [Hobbs, 1993]. According to Gwaze [2007], studies have shown that anthropogenic particles produce brighter clouds by this effect, coupled with suppressed precipitation [Rosenfeld, 2000].

Particles cause environmental impacts when they deposit on surfaces of plants, buildings, hydrological systems and geological structures. In this case, the total mass deposited could be of importance if it affects a plant’s ability to photosynthesis. The particle’s chemistry is of importance if it influences the integrity of the surface. In particular, the acidity of the particles can cause severe damage to plant structures, affect building surfaces including walls and exterior decorating designs, and speeds up weathering processes of rock structures.

Poor visibility due to fine PM is a familiar phenomenon in major urban cities world-wide and during seasonal biomass burning episodes in the tropics [Gwaze, 2007]. Residential coal combustion contributes to the formation of smog through the release of oxides of nitrogen, which in turn reacts with volatile organic compounds in the presence of sunlight to produce ground-level ozone, the primary ingredient in smog [Lockwood et al., 2009]. Fine PM is the single greatest contributor to visibility impairment in pristine areas [Lipsky et al., 2002]. Fine particulate matter plays an important role in climate forcing because of their ability to scatter and absorb light and because they act as cloud condensation nuclei (CCN) [Seinfeld & Pandis, 1998; IPCC, 1996]. For example, elemental carbon containing fine particles are known to absorb sunlight, thus contributing to global warming [Sippula, 2010]. In contrast, sulphate particles especially from coal combustion scatter sunlight, and therefore have a cooling effect [Shindell & Faluvegi, 2009; IPCC, 2007]. Thus, the net effect on surface temperature depends upon these complex interactions of energy absorption and transfer [Mitra et al., 2002].

2.2 Coal Combustion in Fixed-Bed Systems

Raw coal may be used in many forms, which include lumps and briquettes (mainly in fixed-bed combustion processes) and fine powders (i.e. in fluidized combustion processes). Before the advent of fluidised systems, fixed-bed was the only know way of burning coal. In this system, coal is supported on a grate, which may be fixed or movable. The primary air needed for combustion is supplied to the
system from the bottom of the coal bed, by chimney draught, natural draught, or by a fan. In some exceptions, primary air may be supplied to the system from above the coal bed and drawn downwards through forced or natural draughts. The fuel may be added into the combustion chamber in three ways: over-feed, under-feed, and cross-feed.

In small-scale domestic coal combustion devices, an over-feed fixed-bed fixed grate is the simplest way of burning coal. Fresh coal is spread manually on the grate and ignited. Successive batch loads of coal are added onto the surface of the already burning bed of coal. From the grate to the surface of the coal bed, the bed is divided into different combustion zones: (i) oxidation zone (ii) reducing zone and (iii) flame zone. The combustion air is supplied below the grate, flowing upwards through the bed of coal. The air is first heated by the burning coal embers spread on the fuel grate before it reacts with the high temperature coal char. The combustion reaction produces CO\textsubscript{2} and heat, resulting in a rapid increase in the bed temperatures. The oxygen is eventually used up because of the progressing oxidation reactions. The high temperature bed layer where the oxidation takes place is referred to as the oxidizing zone. In cases where the thickness of the coal-bed is greater than the oxidizing zone, a reducing zone will appear on top of the oxidizing layer resulting in CO\textsubscript{2} reacting with C at high temperatures to form CO.

Measurements of particle size distribution (PSD) from the braziers are significant in explaining the mechanisms of fine particle formation [Teramae & Takarada, 2009] in these devices. These particles appear to be of great concern from a health stand point, because of their high number density, ability to penetrate deep in the lungs, and enrichment in toxic constituents such as heavy metals, arsenic, mercury, polycyclic aromatic hydrocarbons (PAHs), silica, fluorides, and black carbon (BC) [Zhang et al., 2008].

2.2.1 The conventional/ traditional fire ignition method

The classical method of igniting a coal fire, also referred to as the conventional method has been used in most Townships in South Africa. The bottom-lit updraft (BLUD) is the conventional/traditional way of igniting a coal fire, with the order of laying the fire proceeding as follows: paper, wood, ignition, after which coal is added at an appropriate time after the wood fire is established. In the conventional method, semi volatile emissions from the heated coal rise through the cold zone and condense into droplets before escaping into the atmosphere. Consequently, the smoke that is emitted from this type of fire is not burnt. Hence, the method gives out a lot of smoke during the ignition stages through to pyrolysis (Figure 1).
2.2.2 The top-lit updraft (TLUD) fire ignition method in South Africa

In principle, the TLUD stoves use either forced ventilation or natural draft. Forced ventilation is achieved in a number of ways. Natural convection provides poor mixing of air with fuel gases and can result in incomplete combustion, soot and emissions in open stoves. For the downdraft gasifiers, there is a need for a chimney to aid the draft and improve the combustion of the fuel [Reed et al., 2000]. However, in small-scale enclosed stoves the addition of a chimney could introduce complications, as it requires wasting heat to operate. A common approach is to use a battery powered electric fan. The battery may need to be replaced from time to time for the stoves to perform optimally or the batteries are recharged by the stove during operation. Typically, the stoves are designed so that when the stove is lit, primary air is blown through the fuel bed. The hot air, blown above the fuel bed, drives off the volatile components from the burning fuel. The emitted volatile components are thoroughly mixed with air before combustion. This combustion process is more controlled, allowing for greater mixing of gases, and resulting in the volatile matter burning cleanly and efficiently.

During TLUD fires, the combustion process can be split into different stages. Firstly, the fuel is dried as fuel moisture is driven off. Some of the heat from the combustion process is used to drive off excess moisture. When the burning fuels are dry, pyrolysis the takes place, where the volatile matter is driven off from the solid fuels due to high combustion temperatures. Secondary air is introduced above the burning fuel bed to ensure complete combustion of the emitted volatile matter.

In South Africa, the TLUD method for igniting a coal fire was first introduced by the Nova Institute and Sasol Infrachem (Sasolburg), to the eMbalenhle community near Secunda [van Niekerk & Swanepoel, 1999]. The method is a simple intervention in the way domestic fires are lit, involving a top-down approach to fuel loading and ignition in imbulaus and stoves [Wagner et al., 2005], and has
become a national priority energy intervention programme [Makonese, 2011]. The method was named after granny Mashinini who perfected the top-down fire ignition method during the campaigns. According to Wentzel [2006], granny Mashinini represented one of ten households who were recipients of the old ‘Scotch-fire’ ignition method. Nine of the households reported that the method did not work resulting in a lot of smoke during the ignition phase; Granny Mashinini reported that she got the method to work by adding a handful of coal on top of the burning wood in the brazier [Wentzel, 2006].

The Department of Minerals and Energy (DME) formulated an Integrated Household Clean Energy Strategy (IHCES) with emphasis on the TLUD intervention in the short-to-medium term. This method is estimated to result in at least an 80% reduction in ambient particulate air pollution and a 20% reduction in coal use at no additional cost to the household [Le Roux et al., 2009]. Since the method can potentially reduce ambient air pollution caused by the use of household coal in a relatively short period, it represents the highest impact on health from a benefit-cost and employment point of view. The method holds a potential, not only to reduce air pollution but also to result in coal and monetary savings for low-income households. The method is a low cost option with a great potential for reducing coal smoke and reduce the health burden associated with coal combustion as it does not require changes in the fuel or corresponding devices used but a change in user behaviour.

2.2.3 The bottom-lit downdraft coal stoves

In conventional downdraft gasifiers, air is passed downwards from the top of the fuel bed through the fuel mass, then to the flaming pyrolysis zone where the volatiles and tars are burned while making charcoal and pyrolysis gas [Reed et al., 2000]. The combustion of the volatile matter is separate from the pyrolysis of the solid fuel a phenomenon believed to result in clean combustion. The produced charcoal further reduces CO\(_2\) and H\(_2\)O to CO and H\(_2\). In an inverted (top-lit) downdraft gasifier, air passes through the fuel and meets the flaming pyrolysis zone where the reaction generates charcoal and fuel gas.

During combustion, there is a pyrolysis zone in the fuel bed, which is a region where the fuel is heating up and giving off combustible gases. This pyrolysis zone starts at the top with the ignition of the fuel and migrates downwards (rate of movement dependent upon the fuel burn rate) through the fuel bed. Above the pyrolysis zone is char, which has previously been pyrolyzed [Andreatta, 2007]. Below the pyrolysis zone is unburned fuel, which is essentially at lower temperatures relative to the top layer of the fuel bed.

The Sustainable Energy Technologies and Research (SeTAR) Centre, situated at the University of Johannesburg, has been involved in the design and development of the bottom-lit downdraft (BLDD) coal stoves [Ibraimo et al., 2014]. The University of Johannesburg holds a patent to this design. The first SeTAR BLDD prototype was an attempt to build a space heater. Components of the first device (a basic space heater) included a fuel chamber, combustion chamber, a 230 mm cube body and a
75 mm diameter chimney. The grate was made from high temperature element wire which can operate at 1 300°C [Pemberton-Pigott et al., 2009].

The BLDD is able to maintain a flame projecting downward below the grate because the ash keeps falling away exposing the burning coke. Tests run at New Dawn Engineering in 2004 showed that the ash formed at the burning face of the grate of a BLDD coal stove fall naturally downward, as the coke is combusted. Principally, the BLDD uses gravity and the draft to get rid of the ash [Ibraimo et al., 2014; Makonese, 2011; Pemberton-Pigott et al., 2009]. Gases are drawn downward through the coke bed. The volatile and semi-volatile hydrocarbons that are produced from the solid coal during pyrolysis are efficiently combusted in the coke bed. Thus, the major source of particulate matter from domestic coal burning is eliminated [Makonese, 2011].

2.3 The Combustion Processes and Mechanisms of Coal Fuel

The combustion process of solid fuels involves both physical and chemical processes. Coal fuel contains inorganic matter that may pass through the combustion system unreacted and/ may oxidise or undergo phase changes to form liquid matter that becomes slag or fouling deposits [Miller & Tillman, 2008]. The oxygen required for the combustion process comes from air, which contains 3.76 moles of nitrogen per mole of oxygen, with varying amounts of moisture, depending on the humidity profiles of the air. All these contribute to the products of combustion, including the amount of heat that may be released from the fuel [Miller & Tillman, 2008].

The process of coal combustion involves various steps, which are viewed in terms of reactions of a single particle [Miller & Tillman, 2008]. The combustion process of coal is complex [Bruce, 2005] but it is generally presented in its simplest form in the literature. The generally accepted mechanism according to Miller & Tillman [2008] involves the following processes:

- Particle heating and drying
- Pyrolysis or devolatilization
- Volatile oxidation
- Char oxidation
- Formation of airborne emissions
- Reactions of inorganic matter
- Combustion and heat release.

The following sections give an overview of the above listed combustion mechanisms.

2.3.1 Constituents and classification of coal

Coal is a complex polymer consisting primarily of carbon, hydrogen, oxygen, nitrogen and sulphur [Sami et al., 2001]. However, coal is a highly variable fuel, which ranges from high heating-value anthracite through various forms of bituminous coal to intermediates such as lignite and peat. This fuel is generally classified as lignite, sub-bituminous, bituminous, and anthracite. Lignite is brown to black in colour with high volatile matter, ash, and moisture contents. Lignites have low heating values.
compared to other col types. Sub-bituminous coal is black and similar to bituminous coal in colour. Sub-bituminous coal has lower moisture content compared to lignite but is still of relatively low heating value. Bituminous coal has high to medium volatile matter content, high heating value, low moisture content, and is relatively easy to ignite. Anthracite coal is jet black in colour, hard and brittle. It has high carbon content, high heating and low moisture content but is difficult to ignite and burn-out [Shen, n.d.]. Each of these types of fuel contains different levels of moisture, non-combustible inorganic material (also referred to as ash), sulphur, and sometimes significant levels of other impurities, e.g. arsenic, fluorine, lead and mercury [IARC, 2010a].

According to Sami et al. [2001], the ranking of coal is a function of the relative proportions of volatile matter and fixed carbon present in the coal. Upon heating coal in an inert atmosphere, pyrolysis occurs, resulting in combustible gases evolving from the coal arising from thermal decomposition of the solid material. The remaining skeletal matter in the solid is called char, and is predominantly fixed carbon. Generally, coal rank increases with decreasing volatile matter. Typically, a high rank coal has 10% volatile matter and about 90% fixed carbon.

The higher heating values for a particular coal sample can be measured or estimated by using the ultimate analysis of the fuel. The heating value of coal fuel is used to denote heat release during coal combustion [Flagan & Seinfeld, 1988]. The two measures of heat release from combustion processes is generally specified in terms of higher heating values (HHV) and lower heating values (LHV). The HHV can be determined on an as-received basis or dry-ash-free basis (DAF) [Sami et al., 2001]–corresponding to the heat of reaction when the latent heat of condensation of water is recovered [Flagan & Seinfeld, 1988]:

\[ HHV = -\Delta h_{c(1-2)}(T_1) \]  
Equation 1

On the other hand, the lower heating value corresponds to the heat of reaction where fuel moisture is present as vapour:

\[ LHV = -\Delta h_{c1}(T_1) \]  
Equation 2.

Flue gas temperatures of most combustors are sufficiently high to release water as vapour. At flame temperatures water is released only as vapour; thus lower heating values are more relevant [Flagan & Seinfeld, 1988].

Processing of coal may be as simple as forming coal balls or cakes by hand followed by sun-drying, or it may be a sophisticated procedure, blending coal into a uniform mixture with binders to reduce sulphur and particulate emissions and formed into briquettes designed to burn efficiently and cleanly in special stoves.

2.3.2 Particle heating and drying

The solid coal fuel enters the combustion device containing moisture. The fuel is placed in the combustion device at a relatively low temperature, typically room temperature. When the fuel enters the combustor, it is then heated to the combustion device temperature. Any moisture in moisture in
the fuel particles is driven off, leaving behind a heated and dry fuel ready for further reactions. Because most of the low rank coal fuels are porous, they may contain moisture in the pore structure and the process of drying may explode the single fuel particle into multiple fuel particles [Miller & Tillman, 2008]. The process of heating and drying retains the particle temperature until all the moisture has been driven off.

The process of heating and drying is an endothermic reaction that is governed by heat transfer to the particle, heat transfer within the fuel particle, and by the heat capacity of the fuel [Miller & Tillman, 2008]. Because drying takes place at temperatures slightly above 100ºC, the steam evolving provides cooling of the particle and because of this, heat transfer within the particle is substantial [Miller & Tillman, 2008]. The formula governing heat transfer within the fuel particle is given as follows:

\[ q = kA \frac{(T_1 - T_2)}{x} \]  

Equation 3

where \( q \) is the flow of the heat, \( k \) is the thermal conductivity of the fuel, \( A \) is the surface area of the fuel particle, \( T_1 \) is the temperature of the particle at the surface, and \( T_2 \) is the temperature at the centre of the fuel particle. Assuming that the coal particle is spherical, \( x \) is the radius of the fuel particle [Tillman, 1991].

2.3.3 Pyrolysis and devolatilization of coal fuel particles

Devolatilization is the first process, after drying, during solid fuel combustion. Devolatilization (pyrolysis) is defined as the heating of the fuel to cause oxidation of the carbon, hydrogen and sulphur within the fuel matrix [Miller & Tillman, 2008]. The pyrolysis of solid fuels involves a series of endothermic reactions. In the first stage of pyrolysis, the bridges between aromatic clusters that make up the fuel are broken resulting in the formation of chars and tars. The second stage of pyrolysis involves the stripping of functional groups and atoms from the aromatic clusters, resulting in the formation of non-condensable volatile matter. According to Miller & Tillman [2008], this second stage can occur separately or simultaneously with the first stage.

The specific mechanisms of pyrolysis are dependent upon the composition and characteristic of the coal fuel structure. Of importance are considerations such as (i) the number of aromatic rings per fused aromatic structure, (ii) the specific composition of the bridges between aromatic clusters, (iii) the number and composition of functional groups attached to the aromatic structures, and (iv) the number and location of hetero-atoms e.g. nitrogen and sulphur. Furthermore, the percentage and nature of inorganic constituents of the fuel is important in pyrolytic and devolatilization mechanisms [Miller & Tillman, 2008]. Figure 2 shows a schematic of the processes involved in the pyrolysis of coal.
The yield of volatile matter from the pyrolysis and devolatilization of a fuel particle is a function of both the chemical composition and structure of the fuel, and of the temperature at which the reactions take place. The kinetics of devolatilization is a function of fuel composition especially the aromaticity and the average number of aromatic carbon atoms per cluster [Miller & Tillman, 2008]. As a result, fuel rank is also a function of aromaticity. The evolution of heteroatoms, such as nitrogen and sulphur in volatile form, is a function of the rank of the fuel. Nitrogen is considered to evolve, initially as HCN for some more reactive coals and lignites. On the other hand, sulphur atoms tend to become part of the char matrix. However, some sulphur may evolve in the volatile form as H$_2$S [Miller & Tillman, 2008].

Apart from volatile matter being produced in the pyrolysis process, nitrogen is evolved from the fuel in the form of NH$_3$, HCN and other nitrogen containing species, which are presented as “XN” in Figure 2a. Nitrogen evolution normally occurs later during pyrolysis. The nitrogen evolved from the fuel undergoes oxidation to NOx and is called fuel NOx, in contrast to thermal NOx, which is produced by oxidation of atmospheric nitrogen at temperature above ~1 200ºC [Sami et al., 2001].

2.3.4 Volatile oxidation reactions

Volatile oxidation involves a series of free-radical reactions that include chain initiation, chain propagation and chain termination [Miller & Tillman, 2008]. Chain initiation occurs with the volatile species and fragments evolving from the solid fuel matrix. The concentration of hydroxyl radical
plays a significant role in this reaction. Hydroxyl radicals are among the most reactive species in the combustion process, promoting both chain initiation and chain propagation reactions [Miller & Tillman, 2008]. Volatile oxidation reactions occur very rapidly. Examples of chain initiation reactions are given as follows:

\[ C_2H_6 + M \rightarrow \cdot CH_3 + M \quad \text{Equation 4} \]
\[ CH_4 \rightarrow \cdot CH_3 + \cdot H \quad \text{Equation 5} \]
\[ H_2O \rightarrow OH + \cdot H \quad \text{Equation 6} \]

where M represents heat removal matter such as inorganic constituents in the fuel.

Once chain initiation reactions have terminated, with the formation of numerous free radicals such as hydroxyl ions, chain propagation commences at a faster rate. Examples of chain propagation reactions are as follows:

\[ \cdot H + O_2 \rightarrow H - O - O \cdot \quad \text{Equation 7} \]
\[ H - O - O \rightarrow OH + O \quad \text{Equation 8} \]

According to Miller & Tillman [2008], the potential for such reactions is limitless. As a result, one can deduce hundreds of reactions comparable to those shown above. Chain termination completes the process and a few typical examples of chain termination are given as follows:

\[ CO + \cdot O + M \Rightarrow CO_2 + M \quad \text{Equation 9} \]
\[ \cdot OH + \cdot O + M \Rightarrow H_2O + M \quad \text{Equation 10} \]

Sami et al. [2001] argued that one-step kinetics mechanisms over-predict the rate of release of chemical energy. The rate of heat release changes depending on the reaction scheme, thereby affecting the volatile combustion time scale.

### 2.3.5 Char oxidation reactions

The skeletal char remaining after pyrolysis is essentially composed of fixed carbon. The carbon undergoes heterogeneous reactions with gaseous species [Sami et al., 2001]. However, char oxidation is a highly complex process. Char oxidation is likely to commence when volatile release is largely complete [Miller & Tillman, 2008]. Oxygen adsorption onto the char surface then plays a significant role in the oxidation process. For example, char oxidation is generally diffusion controlled, with char oxidation rates governed by partial pressure of oxygen in the furnace and at the surface of the char particle, and char particle temperature [Tillman, 1981]. Reactive solid fuels with lower aromaticities and with fewer aromatic carbons per cluster, generally exhibit lower activation energies for char oxidation [Miller & Tillman, 2008]. Smoot and Smith [1985] proposed that heterogeneous reactions of the char matrix are generally governed by the following processes:

- diffusion of gas phase oxidizing reactant species to the particle surface;
- adsorption of gas phase species;
- chemical reaction of the adsorbed species;
• desorption of the gaseous oxides;
• diffusion of gas phase products through the boundary layer to the free stream [Sami et al., 2001].

Oxygen transfer to carbon/char can occur via O$_2$, CO$_2$ and/or H$_2$O [Sami et al., 2001]. The heterogeneous combustion of carbon/char occurs primarily via one or more of the following reactions as proposed by Bradbury and Shafizadeh [2009]:

\[
C + O_2 \rightarrow C(O) \rightarrow C(O)_m \rightarrow CO + CO_2 \quad \text{Equation 11}
\]

\[
C + O_2 \rightarrow C(O)_s \rightarrow CO_2 \quad \text{Equation 12}
\]

where C(O)$_m$ is a mobile C(O) site and C(O)$_s$ is a stable C(O) site [Miller & Tillman, 2008].

According to Mulcahy and Young [1975], char oxidation can also proceed by reactions of the hydroxyl radical as follows:

\[
2 \cdot OH + C \rightarrow CO + H_2O \quad \text{Equation 13.}
\]

This reaction is particularly interesting because it illustrates the impact of the hydroxyl radical on the heterogeneous gas-solid char oxidation reactions.

According to Miller and Tillman [2008], gasification reactions contribute to char oxidation, especially at high temperatures. Tillman [1981] suggested the following gasification reactions:

\[
C + CO_2 \rightarrow 2CO \quad \text{Equation 14}
\]

\[
C + H_2O \rightarrow CO + H_2 \quad \text{Equation 15}
\]

\[
2C + H_2O \rightarrow C(O) + C(H_2) \quad \text{Equation 16.}
\]

Although these gasification reactions are present during combustion, they do not contribute significantly to the char oxidation reactions [Tillman, 1981].

Many reactions can be proposed to describe char oxidation reactions. The above listed reactions are examples of commonly proposed simplified char oxidation reactions. The dominant reaction in char oxidation reactions are those reactions where oxygen diffuses to the surface of the char particle, reacting with carbon on the surface and releasing CO [Miller & Tillman, 2008]. However, in boiler burners and other combustion devices, the fuel particles are closely spaced resulting in limited oxygen availability to each fuel particle. Combustion under such conditions is called cloud combustion [Sami et al., 2001]. During cloud combustion, the reduction reactions (i.e. Equations 15 and 16) may become dominant, especially at high temperatures [Sami et al., 2001]. Char oxidation for high ash fuels (e.g. lignites and low-grade bituminous coal) is influenced by the presence of inorganic compounds. These compounds have the potential to absorb the available heat to drive oxidation reactions [Miller & Tillman, 2008].
2.3.6 Formation of gaseous and particle emissions

Combustion reactions produce airborne emissions in the form of gases (i.e. CO, CO\(_2\), SO\(_2\), NOx) and condensed matter (droplets and solid particles), including condensed hydrocarbons and mineral matter. CO emissions occur in the absence of sufficient oxygen for complete combustion of the fuel carbon to CO\(_2\). It also occurs when the conversion of CO to CO\(_2\) is inhibited by insufficient temperatures to support complete combustion [Miller & Tillman, 2008].

SO\(_2\) is directly formed as a combustion product from the complete oxidation of the sulphur present in the fuel. Some may be captured by calcium contained in the inorganic matter of the fuel. This is typically between 10–13% depending on the fuel type [Miller & Tillman, 2008]. Some of the SO\(_2\) is further oxidized to SO\(_3\) in the aqueous phase, and then oxidised further to SO\(_4\), which remains in the condensed phase as a sulphuric acid droplet or a neutralised sulphate salt particle. These sulphate particles may affect visibility, contributing to regional haze. Production of H\(_2\)S occurs during combustion under limited oxygen conditions, where the abundance of hydrogen favours the formation of H\(_2\)S [Nuwarinda, 2007].

NOx is a class of compounds including NO, NO\(_2\), N\(_2\)O. Of these compounds, NO is the dominant product of combustion. NO can be further oxidised in the ambient air to NO\(_2\). NOx formation may occur either by oxidation of nitrogen from the fuel. Thermal NOx requires high temperatures to promote the Zeldovich mechanism. According to Miller and Tillman [2008], the Zeldovich mechanism is typically represented by the following reversible reactions:

\[ N_2 + O \leftrightarrow NO + N \]  
\[ N + O_2 \leftrightarrow NO + O \]  
\[ N + OH \leftrightarrow NO + H \]

Equations 17, 18, 19.

Of these reactions, Equation 19 is generally considered the rate-determining step due to very high activation energy [Miller & Tillman, 2008]. Equation 18 shows an equation that is principally governed by the availability of oxygen [Palmer, 1974]. According to Tillman [1981], thermal NOx can be formed by the reaction with hydrocarbon fragments produced during solid particle pyrolysis. The initial reactions are given as follows:

\[ CH + N_2 \leftrightarrow HCN + N \]  
\[ C + N_2 \leftrightarrow CN + N \]

Equations 20, 21.

Volatile nitrogen radicals and compounds are formed and these can be readily oxidized to extend the Zeldovich mechanism reactions or can be oxidized in the usual conventional volatile oxidation reactions.

2.3.7 Reactions of inorganic matter

Coal fuel contains varying amounts of inorganic mineral matter, including the major inorganic that comprise silicon, aluminium, titanium, iron, calcium, magnesium, potassium oxides. In fuel analyses,
these inorganic elements are expressed as oxides (see Section 3.2). The behaviour of inorganic materials during combustion is driven by temperature. Trace metals either can exist in the fuel matrix as discreet inorganic minerals within the porous structure of the fuel (e.g. arsenopyrites) or can exist bonded to the fuel structure as chelates [Miller & Tillman, 2008]. Trace metals in coal fuels may vary as a function of coal rank and of individual coal deposits. Trace metals can be classified either as chalcophiles (i.e. affinity for sulphur) or as lithophiles (i.e. affinity for oxygen). Chalcophiles tend to volatilize more readily and to produce products in the vapour phase. Lithophiles tend to melt or decompose at higher temperatures, and thus may concentrate more in bottom ash than in the fly ash [Miller & Tillman, 2008].

Upon entering the combustion zone, some trace metals may volatilize completely (e.g. mercury). Other semi-volatile metals, such as cadmium and lead, may volatilize and re-condense on fly ash particles. Other trace metals such as manganese are distributed equally between the bottom ash and fly ash [Miller & Tillman, 2008].

2.3.8 Combustion and heat release

The overall purpose of combustion of solid fuels (e.g. coal and biomass) is to provide useful heat to meet basic energy requirements. The efficiency of heat release is a function of flame temperature, and the effectiveness of the heat transfer method and equipment [Miller & Tillman, 2008]. According to [Miller & Tillman, 2008] adiabatic flame temperatures can be calculated by incorporating CO₂ dissociation and other similar reactions using the Gibbs Free Energy minimization techniques. Using the Gordon and McBride CET-89 computer code for flame temperature, the flame temperature (T_f) approximation equations for bituminous coal can be calculated as follows:

\[
T_f (^\circ F) = 3852 + 0.066(HHV) - 1087(SR) + 0.64(T_a)
\]

Equation 22

where HHV is the higher heating value of the coal in Btu/lb, SR is the stoichiometric ratio, and T_a is the temperature of the combustion air above 77 ºF [Tillman, 1981].

2.4 Requirements for Complete Combustion of Coal

The most important parameters for complete combustion conditions are (i) high combustion temperatures, (ii) sufficient supply of primary air, (iii) good fuel/air mixing [Van Loo & Koppejan, 2008; Tissari, 2008], and (iv) adequate time in the combustion zone for reactions to go to completion.

2.4.1 Combustion temperature

The combustion temperature affects primarily the burnout of combustion compounds [Tissari, 2008]. At higher temperatures, the oxidation reactions tend to be quicker and more complete, resulting in faster combustion than at lower temperatures. The combustion temperatures in a stove is a function of the thermal mass, thickness, insulation and surface temperatures of the material used in the fire hopper/combustion chamber. For complete combustion, there is need to minimize heat losses from the combustion chamber. In small residential stoves, a higher combustion chamber temperature can be
achieved by improving the insulation of the combustion chamber. The capability of heat storage (ceramic material) in the rocket elbow stoves and brickwork lining in huge institutional wood stoves and cast-iron coal stoves enable higher combustion temperatures.

In small residential solid fuel stoves, the heat can be transferred by conduction, convection or radiation [Tissari, 2008]. In rocket elbow stove, the hot closed firebox surface reflects heat back into the flame and creates the gas turbulence needed for complete combustion [Tissari, 2008]. In open fireplaces and coal-burning braziers, much heat is often lost to the surroundings due to the lack of radiative heating from the combustion chamber, thereby restricting the combustion temperature and combustion rate [Van Loo & Koppejan, 2008; Tissari, 2008]. The temperature of the combustion chamber can be considerably increased by preheating the air and introducing it back into the combustion chamber as secondary air [Tissari, 2008]. According to Van Loo & Koppejan [2008], the vaporisation of the fuel-moisture uses energy released from the combustion process; it lowers the temperature in the combustion chamber, which slows down the combustion process.

In most small residential solid fuel burning appliances, there is generally an overall excess of oxygen (typically referred to as excess air–EA) to ensure a sufficient fuel/air ratio for complete combustion. According to Tissari [2008], the combustion temperature decreases as a function of the excess air ratio due mainly to the heating of inert nitrogen in the air.

2.4.2 Combustion air supply and excess air

A sufficient air supply is critical for complete combustion [van Loo & Koppejan, 2008]. Although, a combustion process may generally have an excess of air, there could be a deficiency in air needed for complete combustion due to poor fuel–air mixing [Tissari, 2008]. A lack of oxygen results in smouldering combustion conditions. In residential coal combustion, the gasification rate is controlled by the primary air supplied to the stove, but the fuel size and batch sizes (total area of coal nuggets) affect the gasification rate of coal in batch combustion. Hence, a restriction of the air supply and large fuel batches in relation to ventilation rates/air intakes, cause an insufficiency of air supply.

The supply of air in residential coal combustion appliances can be achieved by natural draught or by forced ventilation. In natural draught appliances, the chimney damper is used to control the flow conditions in the combustion chamber. However, extremely low draughts lead to insufficient air resulting in the quenching of the fire. On the other hand, extremely high draughts lead to lower combustion temperatures due to high excess air [Tissari, 2008]. In braziers, the draught is not controlled during combustion. Braziers with many ventilation holes tend to have more draught compared to braziers with fewer ventilation holes. However, there needs to be a check and balance in terms of the number of holes that can be drilled on the stove and the amount of draught that can be generated from such a design consideration as more than necessary air holes may lead to low combustion temperatures.
The amount of air above the stoichiometric requirement for complete combustion is referred to as excess air. The excess oxygen is the amount of oxygen in the incoming air not used during the combustion process. The excess air in its simplest form can be calculated as:

\[
EA = \frac{O_2 + \frac{1}{2} CO}{(209 500 - [O_2 + \frac{1}{2} CO])} \times 100% \quad \text{Equation 23}
\]

\[
\text{Lambda}(\lambda) = \frac{EA}{100}% \quad \text{Equation 24.}
\]

The gas quantities are given in parts per million volume (ppmv).

According to Pemberton-Pigott et al. [2009], \( \lambda \) can be used to calculate an emission factor (EF) for gases and particulates in samples measured at the same time. The dilution of the sample by transient air makes no difference to the resulting EF provided (i) the dilution factor is relatively steady, and (ii) the instruments have approximately the same response time. The authors argue that if these preconditions are met, emission test results will be comparable [Pemberton-Pigott et al., 2009].

### 2.4.3 Fuel air mixing ratios

If combustion takes place in a combustion chamber with a perfectly mixed fuel and combustion air supply, then low levels of CO and other products of incomplete combustion would be expected [Fitzpatrick et al., 2009]. In batch-fed and fixed-bed fires, mixing of the devolatilized products with the combustion air can be very poor, resulting in the emissions of products of incomplete combustion. These products may thermally rearrange or pass through the combustion chamber relatively intact, depending on temperature and mass-transfer processes, leading to high CO, VOC and semi-volatile organic emissions. Semi-volatile organic compounds may undergo further reaction to form soot [Fitzpatrick et al., 2009].

### 2.4.4 Efficient coal combustion

For the efficient and more complete combustion of coal in fixed-bed systems, the following requirements have to be met: sufficient supply of air to ensure complete oxidation; sufficiently high temperature for chemical reaction kinetics; sufficiently long residence time at high temperature and sufficient fuel-air mixtures [Uski, 2014; Tissari et al., 2008; Sippula et al., 2007]. The combustion of coal in fluidized-bed systems, and in high efficient boilers, usually achieves the above-mentioned combustion conditions. However, in small-scale fixed-bed systems these conditions are more difficult to meet and optimise. The OC and EC content are relatively low in the PM emitted from efficient combustion conditions [Torvela et al., 2014; Löndahl et al., 2007].

In efficient combustion, the particles are formed from vaporised inorganic elements [Uski, 2014] from the burning coal fuel. The combustion temperature has a major influence on the vaporisation of inorganic compounds from the burning coal fuel. Consequently, high temperature combustion produces more ash particles than at a lower temperature [Uski, 2014; Knudsen et al., 2004; Davidsson et al., 2002].
2.5 Inefficient Combustion of Coal in Fixed-bed Systems

Burning coal with a high moisture and volatile matter content, overloading the stove or providing an insufficient air supply can cause incomplete combustion resulting in low combustion temperatures and increased PM emissions. Due to the low combustion temperatures, PM emitted from incomplete combustion is dominated by organic carbon (OC) [Hays et al., 2003]. When the combustion temperatures increase and sufficient oxygen is available, more elemental carbon (EC) is present in the emissions [Uski, 2014] resulting in greater numbers of soot aggregates [Tissari et al., 2008]. Emissions from the inefficient combustion conditions are dominated by gases including: CO, H₂, SO₂, NOx, and partially combusted hydrocarbons, and different solid particles [Uski, 2014]. Inefficient coal combustion produces a variety of organic compounds including highly oxygenated organic species and PAH compounds [Mu et al., 2014; Shen et al., 2013; Chen et al., 2010]. The emitted organic compounds are in either gaseous form or bound to particles [Uski, 2014; Klucinininkas et al., 2011]. PAHs are generally formed in the flame when hydrocarbons polymerize [Uski, 2014; Verhoeven et al., 2013]. Furthermore, aerosols produced from inefficient coal combustion include liquid or tar-like components [Uski, 2014]. These particles are typically formed from condensed organic vapours [Pyykönen et al., 2007].

Soot particles are formed first during the inefficient combustion of coal in a fixed-bed system. Soot particles may be formed in the flame from hydrocarbons [Uski, 2014]. The formation of soot is a complex process involving many elementary steps, but it is believed to occur via PAH clusters, particle inception, surface growth and coagulation [Wilson et al., 2013].

2.5.1 Soot formation

Soot consists of elemental carbon that is produced by a sequence of chemical reactions involving the progressive loss of hydrogen and oxygen from the original molecular structures. The soot formation mechanisms are complex and our understanding of these formation mechanisms is limited [Wiinikka, 2005]. Figure 3 shows a schematic of soot formation in pre-mixed gaseous combustion.
Soot forms under fuel-rich conditions in which hydrocarbon fragments have a greater probability of colliding with other hydrocarbon fragments and growing rather than be oxidised to CO and CO$_2$ [Wiinikka, 2005]. In pre-mixed flames soot forms when the C/O ratio exceeds 1.0. In non-premixed flames soot forms even in the presence of excess air, since oxygen-deficient conditions will always persist on the fuel side of the flame front, e.g. the flame in a kerosene lamp. The hydrocarbon fragments are breakdown into smaller pieces and react with one another to form aromatic rings. Alkyl groups are then added to the aromatic rings to form polycyclic aromatic hydrocarbons (PAHs). It is now believed and accepted that further growth of the PAHs leads to soot [Wagner, 1979; Bockhorn, 1994, Wiinikka, 2005]. Soot particles grow larger by surface reactions and coagulation. In the late phase of soot formation when, surface growth and coagulation are no longer feasible due to lack of surface growth, soot agglomeration takes place. Soot formation in non-premixed flames usually occurs early in the flame. This process is followed by oxidation reactions as the soot is convected through the tip of the flame [Wiinikka, 2005]. The soot oxidation rate is a function of the oxygen concentration and the combustion temperature. However, as soon as the temperature drops below a certain threshold value, the oxygen concentration plays an insignificant role. Consequently, the introduction of excess cool air reduces the temperature and thus increases the production and emission of soot particles. If the residence time for complete oxidation is short, high soot particle emissions may persist over the combustion cycle.

For solid fuel, such as coal burning particles, experiments have shown that soot nucleation occurs early in the flame zone around the burning particle [McLean et al., 1981; Seeker et al., 1981; Timothy
During the initial phases of combustion of the coal particle, volatiles are released to the gas phase. Secondary reactions of these volatiles, especially coal tar, are thought to be the major soot production mechanism in coal flames [Wiinikka, 2005; Fletcher et al., 1997, Ma et al., 1996].

Figure 4 shows a schematic representation of the formation of soot in the envelope flame surrounding a devolatilizing coal particle. According to Wiinikka [2005], soot particles are formed in the coal particle boundary layer flow around the particle and agglomerate in the particle wake. Ma et al. [1996] and Mitra et al. [1987] studied the influences of coal type on the formation of soot and found a clear correlation between the tar production capability of coal and the formation of soot. Generally, high volatile, low rank coals exhibit the highest formation and emissions of soot particles [Wiinikka, 2005].

Soot formation in small-scale combustion systems takes place in the cluster-dilute aggregation regime, in which average aggregate–aggregate separation in the aerosol system is much larger than aggregate size [Chakrabarty et al., 2009]. Aggregation in this regime proceeds via a three-dimensional, diffusion-limited growth mechanism [Chakrabarty et al., 2014], governed by the mean-field Smoluchowski equation [Sorensen et al., 2011; Chakrabarty et al., 2009]. Fractal dimension $D_f$ is used to describe the resultant morphology of aggregates emitted into the atmosphere from this regime. Typically soot emitted directly from the fire has a fractal dimension $D_f < 1.8$, maximum lengths up to 1 $\mu$m, mobility diameter $D_m < 1$ $\mu$m, and aerodynamic diameter $D_a < 300$ nm [China et al., 2014; Gwaze, 2007]. These soot aggregates consist of tens to a few hundred monomers, with each monomer typically 30–50 nm in diameter [China et al., 2014; Chakrabarty et al., 2014]. Through atmospheric processing, it is possible for these aggregates to collapse into sphere-like morphologies with $D_f < 2.6$ [Kahnert et al., 2012; Zhang et al., 2008]. For purposes of climate models and model parameterization, it is assumed that bare soot aggregates are spherical in shape [Bond et al., 2013; Cappa et al., 2012].

---

**Figure 4:** Schematic representation of the formation of soot in the envelope flame surrounding a devolatilizing coal particle in the presence of oxygen

[Adopted from: Fletcher et al., 1997]
2.5.2 Condensable organic particles

At low temperatures and insufficient air supply, the emissions of condensable organic compounds (COC) as pyrolysis products can be significant. Tar is a complex mixture of condensable hydrocarbons with a molecular weight larger than benzene (benzene has a molar mass of 78.11 g mol\(^{-1}\)) [Devi et al., 2003]. The tar forms primary organic aerosols, and contributes to brown carbon in the ambient air. COCs are formed directly from the pyrolysis of the fuel, proceeding along one of the following pathways:

At low temperature, volatile or condensed organic compounds are formed from fuel pyrolysis with characteristic compounds and properties depending on the residence time, heating rate, temperature and other operational parameters [Nussbaumer, 2010]. At moderate temperatures and low oxygen concentration, organic compounds can be converted to secondary and tertiary tars including polycyclic aromatic hydrocarbons (PAH), which can appear as condensables [Nussbaumer, 2010].

2.5.3 PAHs and PAH derivatives

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion of all carbon-based fuels and organic materials, including coal. At typical ambient temperature, lower molecular weight PAHs (with 2–4 aromatic rings) are present predominantly in the gas phase while higher molecular-weight PAHs are present in the particle phase [Forbes, 2010]. Because PAHs of higher cancer potency are predominantly present in the particle phase [IARC, 2010a], combustion particles have often been subject to compositional analysis for PAHs and PAH derivatives. Ample evidence, summarized in IARC [2010c], supports the role of PAHs in lung cancer due to exposure to indoor emissions from coal combustion.

A detailed analysis of PAHs in dichloromethane extracts of soot deposits from coal-burning stoves in several homes of Hunan Province, China, has identified 32 individual PAHs ranging in size from three to eight fused aromatic rings. The PAHs found in the soot deposits included 20 benzenoid PAHs, six fluoranthene benzologues, one cyclopenta-fused PAH, one indene benzologue, three oxygenated PAHs and one ring-sulphur-containing aromatic compound [Wornat et al., 2001]. Carcinogenic PAHs, methylated PAHs and nitrogen-containing heterocyclic aromatics were detected in the particles emitted from smoky coal combustion, as typically found in numerous households in Xuanwei County, Yunnan Province, China [Mumford et al., 1987; Chuang et al., 1992]. In the aromatic fraction, coal combustion particles appeared to contain high concentrations and many species of methylated PAHs [Chuang et al., 1992]. However, profiles of specific PAHs and their abundance vary largely, depending on the fuel grades and combustion conditions [Tian, 2005].

Polycyclic aromatic hydrocarbons (PAHs) compounds are absorbed through the respiratory tract; as adsorbed particulates, they can be swept back up the tract or they can be swallowed into the gastrointestinal tract and even reach the skin. Smaller molecules (2–3-ring) are absorbed more rapidly than larger ones [Forbes, 2010; IARC, 2010c]. The rate and extent at which the PAHs adsorbed on particles are absorbed by the respiratory tract is generally dependent on particle size, which
determines regional deposition in the respiratory tract and the rate of release of PAHs from the particle. Highly lipophilic PAHs released from particles and deposited in the conducting and bronchial airways are largely retained for several hours and absorbed slowly by a diffusion-limited process [IARC, 2010a]. In contrast, PAHs that are released from particles in alveolar airways are generally absorbed within minutes [Gerde & Scott, 2001; IARC, 2010c]. Once absorbed by the human body, PAHs are distributed widely to most organs and tissues but they tend to accumulate in fatty tissue [WHO, 1998; IARC, 2010c]. Once absorbed they are metabolized rapidly to more soluble metabolites, e.g. phenols, dihydrodiols, and phenol dihydrodiols, and in some cases to more reactive species like epoxides, dihydrodiol epoxides, quinones and tetrols [IARC, 2010a]. Some of these metabolites are electrophilic and tend to DNA and proteins resulting in genotoxic effects [Xue & Warshawsky, 2005].

2.5.4 Hydrocarbons and partially oxidized organic compounds

Hydrocarbons identified in coal emissions include alkanes with 1–10 carbons, alkenes with 2–10 carbons (including 1, 3-butadiene) and aromatic compounds (e.g. benzene, xylenes, toluene, styrene). Partially oxidized organic compounds identified in coal emissions include alkanols, aldehydes and ketones (carbonyls), carboxylic acids, alkyl esters and methoxylated phenolic compounds [Rogge et al., 1998].

2.5.5 Fly ash particles

Ash is derived from non-combustible material introduced in the stove along with the fuel or from mineral inclusions in the fuel and from heteroatoms, which are present in the fuel molecules [Flagan & Seinfeld, 1988]. For example, solid fuels such as coal or biomass contain inorganic species, such as potassium, that produce a combustion product called ash [Wiinikka, 2005]. The study of ash from combustion processes received relatively little attention as an air pollutant until Davison et al. [1974] showed that the relative concentrations of many toxic elements in ash increased with decreasing particle size [Flagan & Seinfeld, 1988]. Annegarn et al. (1983) determined a larger fine mode at 0.3 µm ad compared to findings by McElroy et al. (1982) and they attributed this to the ageing of the aerosols as their samples were collected outside the stack. The mean diameter of the mineral inclusions in coal fuels is typically about 1 µm and these inclusions eventually form ash as the carbon burns out. The largest ash particles (i.e. up to several mm in diameter) are often called bottom ash since they are left in the combustion chamber after combustion [Wiinikka, 2005]. The ash particles that are entrained in the combustion gases are called fly ash [Flagan & Seinfeld, 1988].

According to Flagan and Seinfeld [1988] earlier studies of the evolution of ash during pulverized coal combustion have revealed two major mechanisms by which ash particles are formed. First, the ash residue particles that remains when the carbon burns out account for most of the mineral matter in the raw coal. Flagan & Seinfeld [1988] are of the opinion that as the carbon is consumed mineral inclusions adhere to one another, forming larger ash agglomerates. Since the temperature of a burning pulverized coal particle is generally high enough that the ash melts, these agglomerates coalesce to
form large droplets of molten ash on the surface of the burning char (Figure 5). However, the fragmentation of the char limits the degree at which agglomeration of the ash may occur within a single fuel particle, as a result a number ash residue particles are produced from each parent coal particle [Flagan & Seinfeld, 1988].

The residual ash particles that are formed include some intriguing morphologies. As the ash melts at high temperatures, especially in pulverized coal combustion, it coalesces into spherical particles due to surface tension. Gas evolution within the molten ash leads to the formation of hollow particles, known as cenospheres [Flagan & Seinfeld, 1988].

![Figure 5: Schematic diagram of the processes involved in ash particle formation](Adopted from: Flagan & Seinfeld, 1988)

The second ash particle formation mechanism involves that small fraction of the ash, which vaporises due to the high combustion temperatures. According to Flagan and Seinfeld [1988], part of the volatilized ash homogeneously nucleates to form even smaller particles, which then grow by coagulation and condensation of additional vaporised ash. At high temperatures, the agglomerated particles may coalesce into dense spheres, but when the combustion gases cool below the melting point of the condensed material, the liquid solidifies and coalescence ceases [Flagan & Seinfeld, 1988]. Coagulation of the resulting solid particles produces chain agglomerates; the chain agglomerate structure is common in high temperature systems where aerosols are produced by vapour
nucleation. The same phenomenon is typical in the formation of carbonaceous soot particles produced by a variety of high temperature combustion processes.

Particle growth by coagulation leads to a predicted narrow mode in the particle size distribution in the size range 0.01 to 0.1 µm, much smaller than mineral inclusions found in coal particles. The remaining portion of the volatilized ash heterogeneously condenses on existing particles, including those formed by homogeneous nucleation and residual ash fragments [Flagan & Seinfeld, 1988].

2.5.6 Carbonaceous aerosols

For the past decades strong emphasis has been placed on black carbon (BC) as a major potent climate forcing agent, accounting for as much as 60% of the greenhouse absorption of excess carbon dioxide [Bond et al., 2013; Ramanathan & Carmichael, 2008; Jacobson, 2002]. Only quite recently has it been established that brown carbon (BrC) - a substantial part of the carbonaceous continuum between pure graphite and non-absorbing organic aerosol - contribute significantly to atmospheric light absorption globally [Tóth et al., 2014; Chung et al, 2012]. Most climate models have so far ignored the effect of BrC on climate forcing [China et al., 2014; Tóth et al., 2014]. BrC is estimated to contribute by as much as 20% to the total absorption at 530 nm [Liu et al., 2014; Chung et al., 2012].

Tar balls falls within this group of atmospheric particles referred to as BrC [Alexander et al., 2008], and were first described in biomass smoke plumes [Pósfai et al., 2003, 2004] with a contribution to particle number as high as 90%, especially in aged smoke from smouldering fire [Hand et al., 2005]. According to Tóth et al. [2014], tar balls can be easily recognized using transmission electron microscopy (TEM) by their relatively narrow size range, almost perfectly spherical shape and their chemical composition. In contrast to other spherical aerosol types such as sulphates, tar balls do not volatilize under the electron beam and are refractory in nature. These particles are distinctly different from BC particles in that they have much larger geometric sizes than nanospheres of BC [Tóth et al., 2014]. Again, these particles occur externally mixed (i.e. without being coagulated with one another or other particles) and unlike other BC particles, they do not have the internal microstructure of concentrically wrapped, curved graphene-like layers. According to electron energy-loss elemental mapping of individual particles, and determination of elemental composition of these particles using EDS, tar balls consist mostly of carbon and oxygen and sometimes with traces of sulphur, potassium, chlorine and silicon. Generally, these elements are homogeneously distributed over the entire volume of a relatively fresh tar-ball particle [Tóth et al., 2014].

It has been reported in the literature that the C/O atomic ratio in atmospheric tar balls varies widely. Several studies established high C/O ratios (between 7 and 10) [Adachi & Buseck, 2011; Niemi et al., 2006; Hand et al., 2005; Pósfai et al., 2003, 2004]; whereas others found significantly lower C/O ratios of between 1 and 2 [China et al., 2014; Tivanski et al., 2007]. According to Tóth et al. [2014] tar-ball particles might undergo ageing processes in the atmosphere resulting in a significantly enhanced oxygen ratio in the outermost layer of the particles at a thickness of 30–40 nm [China et al., 2014; Tivanski et al., 2007; Hand et al., 2005]. During long-range atmospheric transport of tar-ball
particles, they occasionally form aggregates with up to 10 particles, including but not limited to, coagulation with dust particles [Deboudt et al., 2010; Hand et al., 2005]. Pósfai et al. [2004] hypothesized that tar-ball particles form in secondary processes from pyrolysis products in the atmosphere. The authors assumed that the low volatility products of biomass pyrolysis undergo polymerization in multiphase reactions resulting in highly refractory carbonaceous particles [Tóth et al., 2014].

2.5.7 Particles from coal combustion

The combustion of coal leads to the emission of particulate matter to the environment. Particles from coal combustion can be divided into two categories, primary and secondary particles. Primary particles are formed at high temperatures in the combustion zone and secondary particles are formed in the flue gas plume or in the atmosphere. Generally, primary particles consist of inorganic or organic species or a combination of both. The particle size distribution in the primary and secondary particles consists of four modes: nuclei mode (particle diameter < 100 nm); Aitken mode (particle diameter < 0.1 µm); accumulation mode (particle diameter < 1 µm) and coarse mode (particle diameter > 1 µm). In epidemiological studies, particles are divided into the following classes: ultra-fine particles (particle diameter < 100 nm); fine particles (particle diameter ≤ 2.5 µm) and coarse thoracic particles (particle diameter ≤ 10 µm) [Uski, 2014; USEPA, 2004]. The ultra-fine particles (<100 nm) originate from high temperature processes, atmospheric transformation, and combustion sources [Uski, 2014] and are produced by gas-to-particle conversion or condensation [Wiinikka, 2005]. These particles then grow rapidly by coagulation and surface accretion. Most of the ultrafine particles gradually grow into accumulation particles [Uski, 2014].

Fine particles may be partly formed from ultrafine particles and these particles originate from processes, which include coal, wood, and oil combustion. Larger sub-micron particles are produced from inorganic matter in the fuel that remains chemically unaltered through the combustion process, but which may undergo physical change (melting, change in crystalline structure) [Wiinikka, 2005]. These particles may arise from re-suspended industrial and road dust, biogenic material (e.g. pollen and microbe filaments) [USEPA, 2009], and suspension from disturbed soil particles [Uski, 2014].

Particles emitted from coal combustion are usually in the fine and ultra-fine size range (i.e. particles with an aerodynamic diameter of less than 1 µm) [Hays et al., 2002; Kleeman et al., 1991]. Fresh coal emissions contain a large number of ultra-fine particles that condense rapidly as they cool and age. The emissions may include larger particles resulting from suspension of ash and solid fuel debris [IARC, 2010a].

When using small and simple household combustion devices, it is difficult to burn coal fuel without producing substantial amounts of smoke, principally due to the complexity of completely pre-mixing the air and evolved hydrocarbon gases fuel during the pyrolyzation stage of combustion [IARC, 2010a]. As a result, elevated levels of products of incomplete combustion (e.g. CO, PAHs and aldehydes) are released into the immediate environment. Studies in China and India have shown that household coal-burning devices convert about 10% to 30% of the carbon contained in the fuel into
products of incomplete combustion [Smith et al., 2000; Zhang et al., 2000]. The products formed can be present in the gas phase, the particle phase, or both, depending on their volatility. Hence, they represent a complex mixture of particulate and gaseous chemical species, including carbon monoxide, nitrogen dioxide and particulate matter (PM) [IARC, 2010a]. In addition, many coal types contain contaminants from their mineral deposits, such as sulphur, arsenic, silica, fluorine, lead or mercury. During combustion, these contaminants are released into the atmosphere in their original or oxidized state [IARC, 2010a].

2.5.8 Metals

Some carcinogenic substances are released during the combustion of lignites used in Shenyang City in northern China and smoky coals used in Xuanwei County, China. Lignites from a local Shenyang coal field had very high concentrations of nickel (75 ppm) and chromium (79 ppm) [Ren et al., 1999, 2004] when compared with the levels reported elsewhere in the world (0.5–50 ppm for nickel and 0.5–60 ppm for chromium) [Swaine, 1990]. Micro-fibrous quartz has been found in some smoky coals from Xuanwei County and the resulting coal emissions [Tian, 2005]. In Guizhou Province of China and other areas, particles emitted from burning coal have been reported to contain high levels of chemicals like fluorine, arsenic and mercury [Gu et al., 1990; Shraim et al., 2003; Yan et al., 2004].

2.6 Characterization of Combustion Aerosols

The most important physical properties of aerosol particles are size, number, mass, density, surface area, and morphology. According to Burtscher [2001], chemical analyses can focus on the elementary composition or on chemical compounds that constitute the particles. The analysis can “be done for of all particles, one size class, a single particle or may include the investigation of the chemical microstructure of a particle” [Burtscher, 2001:19].

Generally, there are two classes of methods used to characterize and investigate aerosol particles namely, filter sampling method and in situ methods. Filter sampling methods are employed for other techniques such as gravimetry, microscopy and chemical spectroscopy. However, filter sampling always include the possibilities of sampling artefacts and does not allow a good time resolution and real time analysis [Burtscher, 2001]. In situ methods on the other hand, allow for fast real time monitoring of aerosol particles.

2.6.1 Physical processes of aerosol particles

According to [Burtscher, 2001] most in situ methods for particle analysis are based either on the following processed: (i) interaction of particles with light, and (ii) interaction of the particles with the surrounding gas, mainly by collisions between particles and gas molecules.

The stationary motion of particles is determined by the Stokes law [Hinds, 1998] as presented in the following equation:

$$\vec{F} = 6\pi\eta d \vec{v}$$

Equation 25
where \( \vec{F} \) is the force, \( \eta \) is the viscosity, \( d_g \) is the diameter and \( \dot{\vec{v}} \) the particle velocity. The ratio \( \frac{\dot{\vec{v}}}{\vec{F}} \) is called mobility \( b \). However, Stokes law is valid for particles much larger than the mean free path \( \lambda_g \) in the gas. For smaller particles an empirical correction factor, the Stokes-Cunningham correction can be employed as follows:

\[
C_c = 1 + 1.275K_n + 0.4K_n \exp(-1.1K_n^{-1})
\]

Equation 26

where \( K_n \) is the Knudsen number \( \frac{2\lambda_g}{d} \). The mobility can be determined by measuring the motion of charged particles under the influence of an electrical field. By measuring the mobility \( b \), the mobility equivalent diameter \( d_e \) can be determined. For non-spherical particles, it is assumed that the irregular particle has the same diameter as that of a sphere and that it has the same mobility as the particle investigated [Burtscher, 2001]. The mobility is related to the diffusion coefficient as defined by the Einstein relation:

\[
D = b \cdot kT
\]

Equation 27.

This means that by measuring the diffusion coefficient of a particle one can yield the same particle properties as with mobility analysis. \( D \) is obtained by determining the particle precipitation due to the thermal motion in the measuring devices (a phenomenon referred to as ‘diffusion battery’) [Burtscher, 2001]. The diffusion coefficient \( D \) increases with decreasing particle size. Diffusion analysis therefore can be a useful method for very small particles (<300 nm). Mobility analysis methods are equally used for small particles. Impaction processes, on the other hand, gain importance with increasing particle size. Impactors therefore are more likely to be used for larger particles. To analyse small particle by impaction, the gas pressure has to be reduced [Burtscher, 2001].

Accelerated particle motion is described by:

\[
\vec{F} = \frac{\dot{\vec{v}}}{b} + m \frac{d\dot{\vec{v}}}{dt}
\]

Equation 28.

According Burtscher [2001] the solution of this equation yields a time constant \( \tau = mb \). This is a relaxation time constant, giving the time the particle needs to adapt to the new gas velocity. If the gas velocity is \( \nu \), a distance \( \nu \tau \) is required for this adaptation.

If an obstacle is in the gas flow, the ratio of \( \nu \tau \) to the characteristic dimension \( d \) of the obstacle helps to determine whether the particle will follow the gas flow or hit the obstacle (i.e. impaction). Figure 6 shows the relationship between \( \nu \), \( \nu \tau \) and the diameter \( d \) of a particle and impaction.

This relationship is commonly referred to as the Stokes number \( s \) and is represented by the following equation:
\[ s = \frac{mbv}{d} \]  

Equation 29.

Figure 6: **Particle motion in an accelerated (deflected) gas flow**

(Figure source: Burtscher, 2001)

## 2.6.2 Chemical processes of aerosol particles

Coal combustion has the potential to affect local, regional and global environments. At the local level, residential coal combustion is responsible for the release of significant amounts of fine PM [Hellén et al., 2008]. Many chemicals including polycyclic aromatic hydrocarbons (PAHs), chlorine and metals such as lead, calcium, and zinc, are bound to these particles [Mu et al., 2014; Molnar et al., 2005]. Coal smoke also contains volatile organic compounds [Hai et al., 2013; Chen et al., 2005], which may cause negative health effects. Residential wood/coal combustion increases exposure to 1,3-butadiene and benzene within households where coal is used for heating and cooking [Uski, 2014; Gustafson et al., 2007]. The regional environment is impacted by coal combustion especially from industries and power stations, as these tend to reduce the air quality greatly in the absence of pollution control mechanisms. Finally, coal combustion can affect the global environment through greenhouse gas emissions and particulate matter such as black and brown carbon [Fountoukis et al., 2014]. Black carbon has a large light absorption capacity [Andrea & Galencsér, 2006; Hansen & Nazarenko, 2004], and is considered the second-greatest global warming contributor after carbon dioxide [Ramanathan & Carmichael, 2008].

A single aerosol particle may be composed of many chemical compounds, and the entire aerosol may consist of mixed particles of different composition [Friedlander, 2000]. If all particles have the same chemical composition, they are *internally mixed*, while if the particles are segregated so that the particles are chemically different they are *externally mixed*. These factors can be distinguished by measuring the chemical composition of the individual particles. The mixing state of the aerosol particle has important implications for aerosol behaviour such as optical properties, and health effects [Friedlander, 2000].

High efficiency filtration is the most common method of collecting PM for the determination of aerosol chemical composition. Chemical analysis of filter samples provides important information on the composition of the aerosol averaged over all particle sizes and over the time interval of sampling [Friedlander, 2000]. For a constant gas-sampling rate, the mass concentration of the species averaged over particle size and time is related to the size-composition probability density function as follows:
\[ \bar{\rho}_i = \frac{M_i}{t} \int_{0}^{\infty} N_s \left[ \int_{n_i}^{n_{i+1}} g_n dn_2 \ldots dn_{s-1} \right] dv \]  

Equation 30

where \( \bar{\rho}_i \) is the instantaneous mass concentration of species \( i \) per unit volume of gas averaged over particle sizes, and \( M_i \) is the molecular weight of species \( i \) [Friedlander, 2000].

The instantaneous concentration of species \( i \) in the particulate phase is given by the mass fraction:

\[ c_i = \frac{\rho_i}{\rho} \]  

Equation 31

where \( \rho \) is the total mass of PM per unit volume of gas. The time averaged value of \( c_i \) can in principle measured over the instantaneous values of \( c_i \) measured during the sampling period. However, instantaneous values of \( c_i \) cannot be obtained directly from the usual filtration measurements. Instead, the average mass fraction is usually reported as the ratio of the average values of \( \rho_i \) and \( \rho \), \( \bar{\rho}_i / \rho \) [Friedlander, 2000].

The effects of atmospheric aerosol are largely determined by the size and chemical composition of the individual particles and their morphology (shape or fractal character) [Friedlander, 2000].

**Effect of fuel chemistry on emissions**

The chemical composition of the fuel has a significant effect on the total emissions given off from coal combustion sources. The volatile matter content in low-grade coals is high in contrast to high-grade coals. Coal is composed mainly of carbon (constituting over 50% of total mass) with smaller percentages of hydrogen, oxygen, nitrogen and sulphur. Inorganic compounds such as aluminium and silicon oxides are mostly dominant in coal ash. Generally, the composition of bituminous coal by percentage is as follows: carbon (70–90%); hydrogen (4–6%); nitrogen (1–1.5%); sulphur (less than 1%); oxygen (5–20%); ash (2–10%); and moisture (2–10%). There are other organic and inorganic elements and compounds, which are bound to the structure of the coal particles. The main elements are calcium, titanium, magnesium, manganese, sulphur, chlorine, phosphorus, iron, aluminium and zinc. However, the chemical composition of coal fuel varies depending on the geological origin, maturity and petrographic parameters.

**Effect of combustion conditions on emissions**

There is currently a lack of sufficient and reliable data, especially for emission factors (EFs) leading to uncertainties and bias in most emission inventories due to influence of a variety of parameters [Shen et al., 2013]. For example, combustion technology and operational practice of appliances have a major influence on the physico-chemical properties of the emitted particles [Uski, 2014; Tissari et al., 2008; Bølling et al., 2009]. Emission factors reported in the literature often vary due to differences in the following parameters:

- fuel properties (e.g. moisture and volatile matter content),
- stove design,
- fire ignition methods (BLUD versus TLUD),
• fire management and ventilation (e.g. air supply amount and fuel-air mixing condition), and
• experimental methods (e.g. laboratory chamber, simulated stove/open burning, and field measurement) [Shen et al., 2013; Chen et al., 2012; Jetter et al., 2012; Johnson et al., 2010; Jetter & Kariher, 2009].

In the low-income communities of South Africa and certain parts of the world where there are slums or squatter-type developments, residential coal stoves are mostly utilised for purposes of heating and cooking. In some developing countries in Europe and Asia, manually loaded boilers are used in apartments and by industry. It is an undisputed fact that both stoves and hand-loaded boilers are low efficiency, high-polluting systems. Erdöl et al. [1999] reported that, the Greater Metropolitan Municipality of Istanbul attempted to impose quality limitations for coals used in the domestic sector and industry in terms of calorific value, sulphur content, size and moisture. However, there were disagreements between the Municipality and coal producers on the effect of moisture on the coal smoke emissions. The difference of opinion could not be resolved by the available information in the literature.

In a quest to address such anomalies, some research studies have been conducted on how fuel moisture content affects the performance of the stoves [Huangfu et al., 2014; Kumar et al., 2013; Shen et al., 2013, Chen et al., 2010; Grandesso et al., 2011; Lu et al., 2009; Hays et al., 2003, Bhattacharya et al., 2002]. However, none of these involved a packed-bed residential coal stove. For example, Bignal et al. [2008] reported that emission factors of CO and PAHs for high moisture fuel were in the order 2 to 5 times higher than of those measured for low moisture wood logs. Chomanee et al. [2009] observed an increase on PM and PAH emission with the increase in wood moisture content. They further showed that PAH concentration exhibits a non-linear dependence on smoke particle concentration, underscoring the significance of wood moisture content and burning period with respect to both physical and chemical characteristics of smoke particles [Chomanee et al., 2009].

Shen et al. [2013] found a positive correlation between fuel wood moisture and emission factors of incomplete combustion pollutants. In controlled burning experiments, Grandesso et al. [2011] did not find significant impacts from wood moisture on the emissions of PCDD/Fs. In a field measurement, Roden et al. [2006] reported a statistically insignificant dependence of PM emission factors on fuel moisture, probably due to the interacting influence of other factors.

Genceli [1998] measured CO, CO₂, excess air concentrations for Yenikoy–Agacli lignite with varying moisture and reported similar CO behaviour to particulate emissions as reported in Erdöl et al., [1999]. The CO emissions were highest for the fuel sample with 24.6% moisture content followed by 21.6%, 37.3% and 17.4%, respectively.

2.7 Characterization of Gaseous and Particle Emissions from Residential Coal Smoke

It is now known that residential coal combustion can be a major source of gaseous and particulate matter emissions in environments where the fuel is extensively used for heating and cooking needs. The emissions from different kinds of residential coal combustion systems can vary significantly both
qualitatively and quantitatively, depending on a number of factors, e.g. appliance type, fuel properties and operation [Boman, 2005]. Despite the previously well-documented evidence on the effects of coal smoke on morbidity, relatively limited information is, however, available concerning detailed emission characteristics and quantification for different coal/stove combinations. The following sections highlight evidence from literature on the characterization of gas and particulate matter emissions from residential coal smoke.

2.7.1 Gaseous and PM emissions factors and emission rates from residential coal smoke

There seems to be limited data available on emission rates for hand-fired coal stoves in both the developed and the developing world. Studies on detailed emission factors from domestic coal combustion in small appliances are scarce. Such emission factors and their time variability are very critical parameters for any model assessment of the air quality and its relation to standards in areas with massive use of residential coal stoves. The use of atmospheric dispersion models to predict ground level pollutants concentrations has been on an increase in South Africa in the last decade. Much of the required input data for such models are not readily available and calculations have been conducted to make up for the shortfall. For domestic emissions, quantifying the emission factors for a variety of pollutants is proving to be a challenge for modellers [Mkhonto, 2013].

In 1997, the Atomic Energy Corporation of South Africa Limited (AEC) characterized ten low-smoke fuels and one standard coal sample for physical, chemical and pollutant emission factors. Emission factors were defined as expressing the masses of particular pollutants that form per mass of fuel burned [van Niekerk et al., 1997]. The authors contended that it is possible to use the emission factor data from a particular fuel, together with the energy usage, to predict total concentrations of pollutants in the air during combustion. However, during the experiments only a single representative brazier was used without specifications of the ventilation rates. The purpose of the report was not to compare efficiencies of a wide range of appliances, but to compare combustion emissions between the different low smoke fuels, in typical domestic appliances. The fuel quality was carefully articulated in the report with details on ash content, moisture content, volatile matter, sulphur and calorific value. They reported that in the brazier, coal fuel produced more particulates, carbon monoxide, and volatile phenols compared to any of the fuels analysed [van Niekerk et al., 1997]. The authors identified that there was a need to carry out a systematic assessment of different brazier configurations to have more accurate emission factors. They concluded that there are many different stoves and braziers in use in South Africa and that emission factor of pollutants should depend on brazier designs. As such, it is likely that a particular fuel would have different emission profiles from different braziers [van Niekerk et al., 1997].

Graham and Dutkiewicz [1999] evaluated the thermal and emissions performance of a suite of fuel/stove combinations in use in most residential set-ups of South Africa. These stoves included the (i) LPG has stove, (ii) kerosene primus stove, (iii) kerosene wick stove, (iv) three stone wood fire, (v) coal brazier, (vi) wood stove and, (vii) the cast-iron coal stove. The stoves were evaluated using the water boiling test (WBT) V 3.0, which required the stoves to be lit from a cold start. During the first
high power phase, 3 L of water were taken to a boil as quickly as possible. During the low power phase, the stove was kept at the lowest possible fire-power needed to maintain the boiling temperature for about an hour. Graham & Dutkiewicz [1999] did not report on the overall efficiency or calculate emission factors in units [g MJ⁻¹] of coal brazier to allow for the comparison of the devices. The fire-ignition method employed in igniting the coal in the brazier was not specified. The cast-iron coal stove was found to have an overall thermal efficiency of 28%. The combustion efficiency (measured as ratio of CO/CO₂) for the coal braziers was reported to be 6% compared to 64% for the cast-iron coal stove. The coal brazier gave out higher emissions of PM2.5 compared to the coal stove and the three stone wood fires, respectively.

Apart from doing a technical evaluation of the different fuel/stove combinations, Graham & Dutkiewicz [1999] calculated the cost-effectiveness of each appliance during a typical water boiling task. They showed that a coal stove or brazier is more cost effective than electricity on the Highveld but this would not be the case in Cape Town. Using a Rand/MJ metric, the coal stoves and coal braziers are much more cost effective compared to LPG and Kerosene [Graham & Dutkiewicz, 1999]. They concluded that in domestic fuel choices a fuel cost/ fuel convenience compromise is made by households. As a result households may use grid electricity, LPG and Kerosene to meet their basic energy needs (e.g. short cooking operations) in the summer months but burn wood or coal during the winter months [Graham & Dutkiewicz, 1999].

The Department of Minerals and Energy (DME), now Department of Energy (DoE), piloted the top-lit updraft (TLUD) fire ignition method, colloquially known as the Basa njengo Magogo at Orange Farm during the winter of 2003. Le Roux [2009] found that 76% of the interviewed households reported less smoke in the homes, while 67% reported less smoke in the streets after just one month of using the method. Work by Nova in eMbalenhle indicated that the Basa njengo Magogo reduced smoke by up to 60% compared with the conventional method of igniting a coal fire. To validate findings of these field surveys, the CSIR were appointed by the DME to conduct experiments under controlled laboratory conditions to gather quantitative data on the reduction in particulate emissions associated with the Basa njengo Magogo method of igniting coal fires [Le Roux, 2009].

The chief purpose of this study was to compare the fire-ignition methods. They used a single lab-designed brazier, with an experienced user confirming that it was representative of the braziers in the field. A D-grade coal with the bottom-lit updraft (BLUD) method was used as a reference case. The other coals namely Anthracite UG, Anthracite OC and Slater, were used only with a TLUD method. In all cases, the authors were using a chimney in the form of a second brazier with an open base, place on top of the fire. The purpose of the chimney is to induce draft and to improve the efficiency of the ignition phase. However, neither in the Le Roux [2009] report nor in this thesis is the effect of the chimney on combustion efficiency and emissions performance tested.

After conducting the technical experiments Le Roux et al. [2009] found that, the gaseous and particle emissions were dependent on the fire ignition method and coal type. Overall emission results were lower, which could be ascribed to the use of the chimney. In real world scenarios, the chimney is
seldom used by the communities. Again, the anthracite coals used in the study are high-grade fuels, are expensive relative to the bituminous D-grade coal, and thus are not highly used in the target markets. Emission factors in units of \([\text{mg MJ}^{-1}]\) were calculated for each fuel, enabling the comparison of emission factors. They noted that the average reduction in PM was 87% and ranged between 72% and 92% for the various fuels. \(\text{SO}_2\) emissions were not affected by the fire-ignition method. The authors found that the temperature curves are remarkably similar between the four tested *Basa njengo Magogo* fires; all peaked within a few minutes of each other, within the first five minutes of ignition. The coal using the bottom-up ignition method peaks later. Two hours after ignition, the temperature from all of the fires was very similar.

Pemberton-Pigott *et al.* [2009] focussed on the practical application of combustion principles to coal burning technologies including the braziers. The authors argued that little research has been carried out to understand the scientific basis behind the *Basa njengo Magogo* method, and how it could be optimised by rational design principles to produce more efficient and cleaner burning stoves/braziers [Pemberton-Pigott *et al.*, 2009]. The results from this work showed that when using the *Basa njengo Magogo* method there is a considerable reduction of visible smoke but no other major change in the basic operation of the coal stove or brazier. Although the *Basa njengo Magogo* method is generally assumed to burn much cleaner during the entire burn cycle, the authors noted that once the coal is coked there is no difference at all in emissions between the *Basa njengo Magogo* and the conventional fire ignition method. They noted that when employing the *Basa njengo Magogo*, the top coals will ignite first and will burn to ash before the bottom coals in the brazier. The formation of a top layer of ash above the hot burning coked coal appears to cause the CO output to increase (i.e. relative to the conventional bottom-up method). A possible reason for the increase in CO emissions is that the brazier may be lacking a CO top flame for a longer period during the smouldering phase of the fire. Since the ash forms around the coked coal, oxygen adsorption on to the fuel becomes a limiting factor for complete combustion; bare coke plus sufficient airflow is required to maintain a flame. Without the hot coke to sustain a CO burning flame, the device emits CO in large quantities, posing an immediate danger to anyone who takes the brazier into a poorly ventilated room for space heating or even persons who stand near it while in operation outdoors [Pemberton-Pigott *et al.*, 2009].

Makonese [2011] evaluated the thermal and emissions performance of braziers using the Heterogeneous stove Testing Protocol (HTP). He investigated the effect of fire ignition method (i.e. the traditional/conventional vs the *Basa njengo Magogo* method) on the thermal and combustion efficiency of the devices. For the technical experiments, ~5 kg of coal fuel was used in each brazier. Results showed that the traditional fire ignition method (BLUD) gave a higher average CO/\(\text{CO}_2\) ratio over a full combustion cycle compared to the *Basa njengo Magogo* ignition method. The average CO/\(\text{CO}_2\) for the BLUD was found to be 5% and that for the *Basa njengo Magogo* method was found to be 2% with the CO/\(\text{CO}_2\) ratio remaining stable until the fire begins to die down. The author concluded that the *Basa njengo Magogo* method is a better method of igniting a coal fire in a brazier, both in terms of reduced smoke generation (an indication of good combustion), and fuel savings. This result is similar to that of Anderson [2011], Le Roux *et al.* [2009; 2005], and Bhattacharya *et al.*
[2002] who found that the TLUD method had a better emissions performance compared to the BLUD method [Makonese, 2011].

Kimemia et al. [2011] set out to develop an optimised brazier/imbaula in terms of size and distribution of primary and secondary air holes, and the height of the fire grate. The experimental particulars of the study were guided and informed by field brazier characterisation data that was gathered in Setswetla informal settlement, Johannesburg, from June 2009 to March 2010. In their premise, the authors contended that optimisation of a domestic wood or coal stove involves attaining a fine-balance between combustion efficiency and thermal efficiency. In some cases (depending on the configuration of the brazier), high excess air in a brazier may result in better combustion efficiency but this may lead to a high specific fuel consumption rate and thus poor thermal efficiency. On the other hand, decreasing the excess air in a brazier results in increased emissions of products of incomplete combustion (due to starving the fire of oxygen) and higher fuel efficiency [Kimemia et al., 2011]. The 20 L metal drums were marked and perforated using 18 mm and 20 mm drill-bits and a total of four braziers were constructed and tested for thermal and emissions performance using the SeTAR Heterogeneous stove Testing Protocol (HTP) [Makonese, 2011]. Instead of using coal, pinewood was used as it is commonly used for cooking in Setswetla where information about the configuration of the braziers in use was collected. The first three braziers depicted the average maximum, middle and minimum number of air holes above and below the fire grate, as observed in the field study sample, while the fourth brazier was the first optimised brazier design [Kimemia et al., 2011]. Table 1 shows the characteristics of the four braziers.

<table>
<thead>
<tr>
<th>Design</th>
<th>No. of Holes</th>
<th>Grate height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Above the grate</td>
<td>Below the grate</td>
</tr>
<tr>
<td>Imb01w (High holes)</td>
<td>40</td>
<td>44</td>
</tr>
<tr>
<td>Imb02w (Min holes)</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>Imb03w (Med holes)</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>Imb04w (Improved)</td>
<td>32</td>
<td>16</td>
</tr>
</tbody>
</table>

The results of this study showed that the brazier with high holes had better combustion efficiency compared with the other designs, with the CO/CO$_2$ ratio reaching a low of 1.3% ± 0.1% in the middle phase of the burn cycle. The brazier with minimum holes had poor combustion efficiency than the rest of the stoves tested and this was attributed to lack of primary air supply in the device, resulting in a slow and inefficient combustion process. The authors concluded that design modifications to traditional wood burning devices (e.g. brazier) can lead to significant improvement in terms of CO and CO$_2$ emissions and thermal properties without necessarily incurring additional costs [Kimemia et al., 2011]. However, the authors did not explicitly articulate the effects of ventilation rates on the emissions of CO, CO$_2$ and particulate matter (PM2.5 or PM10) per MJ of useful energy. In their work, the authors recommended further investigations on additional improved configurations for wood and
coal burning braziers, which include comparing the different fire ignition methods (TLUD and BLUD) and varying grate height in the devices.

2.7.2 Determination of emission factors

There are different emission factors and quantification methodologies used around for the evaluation of pollution sources. These emission estimates are important for developing emission control strategies; determining applicability of permitting and control programmes; ascertaining the effects of sources and appropriate mitigation strategies; and a number of other related applications by an array of users including federal, state, and local agencies, consultants, and industry [Karademir, 2006]. A mass specific emission factor \( E_m \) for a pollutant can be defined as the mass of emitted pollutant per unit mass of fuel burned [Zhang et al., 2000] or per defined task performed [Mitra et al., 2002]. Energy specific emission factors are defined as the mass of emitted pollutant per useful energy released, and are given in units \( (g \text{ MJ}^{-1}) \) [Makonese, 2011]. An emission factors is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant [Karademir, 2006]. In stove analysis, an emissions factor is a term given to a gas concentration that has been normalised for any dilution by excess air. It can be mass based or task based. Hildemann et al. (1991) refers to task based emission factors as emission rates. Mass based emission factors, on the other hand, can be used readily for the development of emission inventories where the amount of fuel used is available.

For fuel consumption, published emission factors based on fuel energy content are more accurate compared to mass or volume based emission factors, except when mass-based or volume-based factors have been measured at a source-specific level [EPA, 2005]. In a study carried out by Zhang et al. [1999] on emission factors for 56 fuel/stove combinations in China and India, a carbon balance approach was used for the determination of the emission factors and were reported in grammes of pollutant per kilogramme of fuel consumed \( (g \text{ kg}^{-1}) \). Because airflow rates vary greatly in actual homes, the authors applied a carbon balance approach to measure emission factors. This approach does not require the measurement of airflow rate but requires a complete carbon analysis in the fuel, ash and unburned residues, and all airborne emissions. Since different amounts of fuel are needed for the same cooking task for each fuel/stove combination, task based emission factors rather than the fuel mass based are a better performance index to compare the pollution potential of different fuel/stove combinations [Zhang et al., 1999; Zhang & Smith, 1996; Joshi et al., 1989]. The simplest task measure is the release per unit energy delivered to the pot \( (g \text{kJ}^{-1}) \) [Zhang et al., 1999].

If the emission rate and the fuel burn rate for a combustion source were both constants, the emission rate would be the product of the emission factor and the burn rate. The emission rate, fuel mass based emission factors, and task based emission factors can be inter-converted if the necessary parameters are known [Mitra et al., 2002]. Zhang et al. [2000:4541] contends that: “…emission factor per delivered energy, rather than per cooking task as used conventionally, is more appropriate to use for the comparison of emissions among different stove”. The relationship between a mass-based emission factor \( E_m \) and the task-based emission factor \( E_e \) in domestic stoves or boilers can be described
mathematically. The conversion from emissions per kg of fuel to emissions per MJ delivered energy can be achieved using the following equation:

$$E_e = \frac{E_m}{H \eta}$$  \hspace{1cm} \text{Equation 32}

where $H$ is the fuel energy content or calorific value (MJ kg\(^{-1}\)) and $\eta$ is the thermal efficiency (%) of the stove [Zhang et al., 2000:4541].

Emission mass per task relate directly to human exposure and is calculated using the following equation:

$$M_E = \int_{t=0}^{T} C_M v_{\text{flue}} dt$$  \hspace{1cm} \text{Equation 33}

where $M_E$ is the mass of the pollutant (g), $T$ is the test duration (s), $C_M$ is the pollutant concentration (g m\(^{-3}\)) at time $t$ and $v_{\text{flue}}$ is the flue extraction rate (m\(^3\) s\(^{-1}\)) [Ballard-Tremeer, 1997].

From this calculation, emission factors, defined as the ratio of the mass of pollutant to the mass of fuel burned, can be calculated. Emission factors can be calculated using the equation used, for example, by Macumber & Jaasma [198]:

$$E = \frac{M_E}{M_f - M_c}$$  \hspace{1cm} \text{Equation 34}

where $(M_f - M_c)$ is the mass of the fuel burned. This emission factor is not exactly the same as the emission factor used by some researchers [Joshi et al., 1991; Joshi et al., 1989; Ahuja et al., 1987] where the denominator $M_f - h^o_c M_c$ is used [Ballard-Tremeer, 1997]. However, to relate the emission of a pollutant to the ‘equivalent wood consumed’ defined according to the enthalpy of combustion of the fuel and char is deceptive from a mass balance perspective and would lead to higher factors - generally about 25% [Ballard-Tremeer, 1997].

The results need to be presented in a way that allows for comparison between fuel/stove combinations. An alternative approach to the carbon balance is the oxygen mass balance model. The method requires taking the chemistry of the stack gases into consideration to determine what the actual level of excess air in the stack is. The approach is to measure the total oxygen content in the air stream and correct it to zero excess air by measuring the residual oxygen in the air stream [Makonese et al., 2011]. This method is further discussed in section 3.4.8.

2.7.3 Use of denuders for polycyclic aromatic hydrocarbon (PAHs)

Residential coal combustion is a potential source of PAHs in South Africa. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants with potential environmental persistence, toxicity, bioaccumulation and health effects on humans [Forbes et al., 2012; Giesy et al., 2010]. Once released into the atmosphere, PAHs are subject to transport and transformation
processes. The gas–particle partitioning of PAHs plays a key role in their global atmospheric distribution and long-range transport potential [Giesy et al., 2010].

PAHs consists of aggregates of condensed aromatic rings (Figure 7) which may be formed from low molar mass hydrocarbons via pyro-synthesis at temperatures above 500 ºC, under oxygen deficient conditions [Forbes, 2010]. During pyro-synthesis free radical are formed upon cleavage of the carbon-carbon and carbon-hydrogen bonds of hydrogen precursors. The radicals further undergo dehydrogenation and combine to form aromatic ring structures. The larger ring structures (>5 rings) are predominantly particle bound under ambient conditions, whilst the smaller species (< 3 rings) are usually in the gas phase, with 4-ringed species dominant in both the gas and the particle phase [Forbes, 2010].

![Figure 7: Structure of selected PAHs](image)

[Adopted from: Patricia Forbes, 2010]

PAHs are derived from a number of sources and specific PAHs present in the atmosphere have been used as source fingerprints (Table 2).

### Table 2: Main PAHs emitted from various sources, used as source fingerprints [Forbes, 2010]

<table>
<thead>
<tr>
<th>Source</th>
<th>PAH markers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal combustion</td>
<td>Anthracene; phenanthrene; fluoranthene; pyrene; ( \text{benzo(a)} )anthracene; chrysene</td>
</tr>
<tr>
<td>Coke production</td>
<td>Anthracene; phenanthrene; ( \text{benzo(a)} )pyrene; ( \text{benzo(ghi)} )perylene</td>
</tr>
<tr>
<td>Incineration</td>
<td>Phenanthrene; fluoranthene; pyrene</td>
</tr>
<tr>
<td>Wood combustion</td>
<td>Anthracene; phenanthrene; fluoranthene; pyrene</td>
</tr>
<tr>
<td>Oil burning</td>
<td>Fluoranthene; pyrene</td>
</tr>
<tr>
<td>Petrol fueled</td>
<td>Fluoranthene; pyrene; ( \text{benzo(ghi)} )perylene; coronene</td>
</tr>
<tr>
<td>Diesel fueled</td>
<td>Similar to petrol fueled automobiles</td>
</tr>
</tbody>
</table>
Understanding of organic carbon (OC) is complicated by the volatility and semi-volatility of many organic compounds, as they tend to change phase readily depending upon atmospheric conditions (e.g. ambient temperature) [Fan et al., 2003]. Furthermore, commonly used measurement techniques tend to alter the true ratio of particle-bound to gas-phase OC, potentially leading to substantial sampling artefacts [Fan et al., 2003]. As a result, several approaches have been employed, which use a diffusion-based denuder for semi-volatile organic compounds (SOVs) prior to the collection of particles.

Recent developments in analytical methods for the measurement and characterization of carbonyls entails the use of O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) to produce oxime derivatives ideal for GC-FID and GC-MS analyses [Temime et al., 2007:6514; Yu et al., 1997]. This method has been used for a variety of sampling techniques including impingers [Yu et al., 1997], filters [Jang & Kamens, 2001], and PFBHA-coated SPME fibres [Reisen et al., 2003]. This approach offers several advantages, which include better chromatographic separation, higher sensitivity, and the identification of unknown carbonyls using mass spectra [Temime et al., 2007]. However, this method does not provide simultaneous measurements of the gas and particle phase carbonyls. Furthermore, filter-sampling methods are prone to both positive and negative artefacts due to the deposition and evaporation of semi-volatile compounds [Temime et al., 2007:6514].

Over the last 20 years, the denuder filter sampling method [Forbes et al., 2012] has grown in popularity and has proved to be effective in providing accurate measurements of the gas-particle distribution of semi-volatile organic compounds [Temime et al., 2007]. The use of denuders has mainly been confined to nonpolar species (such as polycyclic aromatic hydrocarbons) as the denuders are usually coated with a nonpolar XAD-4 resin [Temime et al., 2007]. A novel and miniature denuder has been developed and tested at the University of Pretoria, Chemistry Department to investigate the gas-particle partitioning behaviour of airborne carbonyls [Forbes et al., 2012].

2.7.4 Diffusion denuder techniques

During the last three decades, diffusion denuder techniques have been employed to eliminate artefacts during ambient particulate sampling [Pang et al., 2002]. To date the most successful denuder systems for the removal of gas-phase organic compounds include the Brigham Young University organic sampling system (BOSS), the integrated organic vapour-particle sampler (IOVPS), and the larger integrated organic gas and particulate sampler (IOGAPS). Most denuder systems in use today are variants of the above three.

The real time ambient mass sampler (RAMS)

The Real-time total Ambient Mass Sampler (RAMS), based on diffusion denuder, Nafion dryer and TEOM monitor technology, is the state-of-the-art sampler being used for the real-time determination of total PM2.5 mass, including semi-volatile material (SVM). The RAMS measures total PM2.5 mass with a TEOM monitor using a “sandwich” filter to retain SVM, which would be lost from particles in a conventional TEOM monitor. The sandwich filter consists of Teflon-coated particle collection filter
(R&P TX40) followed by a recently developed charcoal-impregnated glass fibre filter (CIG, Schleicher and Schuell) to collect any semi-volatile compounds lost from the particles on the TX40 filter during sampling. Care must be taken to remove from the sample stream all gas phase species that can be absorbed by the CIG filter in order to prevent over determination of PM2.5 mass.

The RAMS has a dual inlet system consisting of a 2.5 µm cut-point cyclone inlet followed by a particle concentrator. A BOSS diffusion denuder, packed with charcoal-impregnated cellulose fibre (CIF) strips, serves to remove gas phase organic and other species. Gas-phase species such as NO₂ and O₃ are removed by a triethanolamine coated annular denuders. Gas-phase water is removed by Nafion Dryers, located before and after the BOSS and annular denuders. To correct for any gas phase species not removed by the denuders and dryers but absorbed by the sandwich filter, a second system similar to the one described above is employed. A quartz filter is placed immediately after the first Nafion Dryer on the second system to remove all particles. The second system is then used as a blank to correct the data obtained with the RAMS. Total PM2.5 data are being collected on a one-hour basis with the RAMS.

**Integrated organic vapour-particle sampler (IOVPS)**

The IOVPS involves a quantitative integrated organic vapour-particle sampler (IOVPS) comprising a resin-coated annular denuder and filter, which enable organic vapour/particle compositions to be efficiently phase separated and quantitatively measured using a unique sorbent resin coating. The sampler of the present invention comprises:

- A tubular device having an inlet at one end through which organic vapour and particles are introduced,
- An outlet at the other end through which gases exit,
- At least one annular denuder coated on the inside surfaces of the annulus with a specially prepared resin absorbent which selectively absorbs organic vapours contained in the gases introduced into the inlet,
- A filter, which traps and collects the particulate components.

The IOVPS is designed to measure directly semi-volatile organic species in both the gas-phase and particle-phase. Since lung deposition patterns of polycyclic aromatic hydrocarbons (PAH) depend on the distribution of PAH between the gas and particle phases, accurate measurements of phase distributions of PAH are needed in order to assess exposure to carcinogenic compounds [Forbes et al., 2012]. This design represents a significant improvement on conventional filter-sorbent bed samplers designed to sample gas-phase semi-volatile organic compounds.

The IOVPS was design principally to address conventional samplers’ inherent problems, such as positive and negative artefacts and the inability to recover quantitatively gas-phase species. The gas-phase species are stripped from the air stream before particle collection by a filter. Although volatilization losses of semi-volatile species from particles are possible if the IOVPS is operated at a
high face velocity, the system can be configured to correct for ‘blow-off’ from the filters, by placing a denuder or sorbent bed downstream of the filter.

**The integrated organic gas and particulate sampler (IOGAPS)**

The integrated organic gas and particulate sampler (IOGAPS) is a diffusion-based air sampler, which consists of an XAD-4 resin-coated denuder [Gundel *et al.*, 1995]. This denuder system samples particle-bound OC on a quartz filter downstream of a denuder that removes gas-phase organic compounds [Fan *et al.*, 2003]. This prevents artefacts arising from interaction of gas-phase chemicals with the particle-laden filter. XAD-4-impregnated filters designed to retain the off-gassing organic compounds, are used to quantify SVOCs evaporated from the particle-laden filter [Fan *et al.*, 2003].

The normal configuration of the IOGAPS consists of a cyclone inlet with 2.5 µm size cut to remove coarse particles followed by a denuder to retain gas-phase organic compounds. The IOGAPS is operated at a rate of 16.7 L min\(^{-1}\) and particulate matter (PM) is collected on a quartz filter placed downstream of the denuder. Three stages of XAD-4 resin-impregnated quartz filters (SIFs) are placed after the quartz filter to capture SVOCs that evaporate off the particles collected on the quartz filter [Fan *et al.*, 2003].

Like any other novel technique, the IOGAPS has technical, operational and user limitations. Fan *et al.* [2003] contends that further investigation into the use of IOGAPS is required for thorough evaluation since desorption of SVOC during the transit in the denuder tube is not known. They believe that when using this denuder system SVOC off-gassing tend to occur during transit in the denuder consequently resulting in underestimation of the SVOC captured by the SIFs and the total particle-phase OC. In addition, the capacity and collection efficiency of the SIF toward SVOC is not fully understood. Thus, a better collection medium, with the potential to capture evaporating SVOC from the front particle-laden filter, may be required to replace the SIF [Fan *et al.*, 2003:3150].

**2.7.5 Theory of denuder applications**

PAHs may be present in air samples as both in the gaseous phase as well as being adsorbed on the surface of other particles [Forbes, 2010]. The relative contribution of each phase is of importance to human health exposure and toxicity studies.

The gas–particle phase PAHs are typically separated using filter/sorbent samplers [Mader *et al.*, 2001]. The adsorption of gaseous semi-volatile organic compounds to filter surfaces has the potential to cause a positive bias in the measured particle-phase concentration and a negative bias in the measured gas-phase concentration of that compound [Mader *et al.*, 2001]. The resultant positive artefact may have an effect on the accurate determination of the gas–particle partitioning coefficient (\(K_p\)). A positive sampling artefact results from the adsorption of vapour-phase semi-volatile organic compounds (SVOC) onto the filter or onto collected particles; whereas a negative sampling artefact occurs when SVOC desorb or volatilize from the particles [Pang *et al.*, 2002:5205]. According to Ahrens *et al.* [2012], calculation of the gas–particle partitioning coefficient (\(K_p\)) from measurements
of ambient is dependent on accurate determinations of the gas- and particle-phase concentrations. The gas–particle partitioning coefficient is given by:

\[ K_p = \frac{C_p}{C_g} \]

Equation 35

where \( C_p \) is the concentration of the particle-phase measured in ng \( \mu g^{-1} \) and \( C_g \) is the concentration of the gas-phase measured in ng m\(^{-3} \) [Mader et al., 2001].

A common method used in correcting positive biases in filter pack samplers, involves the use of backup filters where a second filter (i.e. backup filter) is placed downstream of the front filter [Mader et al., 2001]. Semi-volatile organic compounds (SVOC) measured on the downstream filter originate only from the gas phase since the filter is exposed only to particle-free air [Mader et al., 2001]. To correct for positive artefacts, “the mass of the given SVOC measured on the backup filter is subtracted from the mass observed on the particle-loaded front filter.” [Mader et al., 2001:4857]. The correction assumes that (i) both filters have adsorbed the same amount of SVOC from the gas phase [Mader & Pankow, 2001], (ii) the gas adsorption capacity of the front and backup filter are equal, and (iii) the SVOC observed on the backup filter did not result from evaporation of particles collected on the front filter [Mader et al., 2001:4857]. However, this correction approach poses a significant problem because a non-zero volume of air is required to reach gas/filter equilibrium with the two filters, and the front filter will reach equilibrium before the backup filter. Therefore, if sampling ends before equilibrium is attained on both filters, the correction will underestimate the extent of the gas adsorption to the front filter since the mass amount subtracted from the front filter amount will be significantly small [Mader & Pankow, 2001; Mader et al., 2001].

During standard partitioning measurements based on conventional high volume samplers, analytical artefacts may be introduced through use of glass fibre filters, which remove particles from the sample flow prior to adsorption of the gas-phase analytes onto selected adsorbents. The artefacts are ideally from sorption of gas-phase analytes onto the filter or collected particles and desorption of analytes from these particles [Forbes et al., 2012]. Conventional air samplers are susceptible to potential blow-off sampling artefacts resulting from the volatilization of VOCs from filtered particles, and are then collected on the backup filter [Ahrens et al., 2012]. Thus, the measurement of the gas- and particle-phase using conventional high volume air samplers can lead to biased results [Ahrens et al., 2012]. This means that the diffusion denuder samplers should be designed and developed to avoid these sampling artefacts by collecting the gas-phase first, followed by the particle-phase. This is because accurate measurement of personal exposure to particulate matter (PM) and its constituents contributes to knowledge of the health effects associated with exposure and also to the identification of the sources of the PM to which humans are exposed [Pang et al., 2002].
2.7.6 Determination of the laminar flow

Laminar flow is a critical parameter for denudation [Forbes, 2010]. The Reynolds number ($R_e$) relating to the gas flow in the silicone rubber tubes was calculated as follows:

$$R_e = \frac{VD}{\nu}$$

Equation 36

where $V$ is the velocity; $D$ is the internal diameter of the silicone tubes; and $\nu$ is the kinematic viscosity.

The kinematic viscosity can be determined by:

$$\nu = \frac{\mu}{\rho}$$

Equation 37

where $\mu$ is the dynamic viscosity and $\rho$ is the gas density.

Using the equations above Forbes [2010] found $R_e$ values $<< 2300$ indicating that the gas flow in the silicone rubber traps is laminar. A low $R_e$ would minimize impaction of large particles on the walls of the denuder.

According to Ali et al. [1989], laminar flow conditions are only achieved at a short distance $l$, from the trap inlet. For a tube diameter $d$, $l$ is defined as:

$$l = 0.07dR_e$$

Equation 38.

Forbes [2010] discovered that with the silicone rubber tubes, the non-laminar portion accounts for $<5\%$ of the total length of the silicone tubes.

**Verification of the negligible linear velocity**

The Peclet number ($P_e$) is used to verify whether the contribution of longitudinal diffusion to linear velocity is negligible compared to the linear velocity arising from the pumping of sampled gas through the denuder. According to Kloskowski et al. [2002], $P_e$ has to meet the following requirements:

$$P_e = \frac{2R\nu}{D_A} > 10$$

Equation 39

where $R$ is the internal radius of the silicone rubber tube; $\nu$ is the actual linear velocity of airflow (cm s$^{-1}$) at a given distance from the centre; and $D_A$ is the diffusion coefficient of the analyte $A$ in the gas sample (cm$^2$ s$^{-1}$).

Further, for laminar flow the linear profile in an open tube is shown in Figure 8 and can be given by:

$$\nu = 2\nu_0\left(1 - \frac{r^2}{R^2}\right)$$

Equation 40
where $v_{av}$ is the linear velocity of the sample gas flow (cm s$^{-1}$); and $r$ is the distance from the longitudinal axis of the silicone tube (cm) [Forbes, 2010].

Results obtained during the validation of the silicone rubber traps met the requirements for the Peclet number ($P_e$), which was found to be greater than 10. Hence, the contribution to the linear velocity from longitudinal diffusion is indeed negligible. However, it was shown that close to the silicone walls, the linear flow rate would be less than the average value, indicating longitudinal diffusion may become important [Forbes, 2010].

### 2.7.7 Efficiency of collection of gaseous components by the denuder

In order to calculate the efficiency of analyte removal by the denuder, there is a need to make valid assumptions and simplify the mass balance equation for $A$ in a cylindrical, sorption denuder described by Katsanos & Roubani-Kalantzopoulou [1995], for a solution to be found. The first of these assumptions is to assume steady state conditions, where the composition of the air does not change during its flow along the denuder. Furthermore, it can be assumed that the linear velocity of analyte $A$ resulting from longitudinal diffusion is negligible compared with the linear velocity resulting from pumped sample airflow [Forbes, 2010].

If it is further assumed that no homogeneous reactions occur in the denuder, the mass balance method suggested by Katsanos & Roubani-Kalantzopoulou [1995] can be simplified to the following equation:

$$v = \frac{\partial c_A}{\partial z} = D_A \left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r}\right)$$

Equation 41,

which leads to the Gormley-Kennedy [1949] solution for this equation given as follows:

$$\frac{c_{av}}{c_0} = 0.8191 \exp\left(-7.314z^*\right) + 0.0975 \exp\left(-44.61z^*\right) + 0.0325 \exp\left(-113.9z^*\right) + \ldots$$  Equation 42

where $c_0$ is the gas concentration entering the denuder; $c_{av}$ is the average gas concentration leaving the tube; and $z^*$ is the dimensionless factor [Forbes, 2010].

The assumptions made in this solution are as follows: that analyte $A$ is a trace gas; laminar is developed with constant viscosity; the temperature is constant; and the amount of analyte collected on
the tube wall is small compared with the available capacity of the denuder [Katsanos & Roubani-Kalantzopoulou, 1995].

For the multi-channel silicone rubber traps, the Gormley-Kennedy approximation is valid for analytes of lower volatility (i.e. with higher retention volumes) but not so for more volatile analytes with lower retention volumes such as naphthalene. Forbes [2010] contends that in cases like this, a chromatographic model is more appropriate due to continuous partitioning behaviour, where the PDMS-air partitioning coefficients are expected to be proportional to the octanol-air partition coefficients [De Coensel et al., 2007] and experimentally derived breakthrough volumes for each analyte give an indication of the efficiency of the removal of gaseous components.

**Denuder collection efficiency**

The gaseous organics retention efficiency \( E \) of the annular denuder can be estimated using Possanzini’s model [Possanzini et al., 1983]:

\[
E = \left(1 - \frac{C}{C_0}\right) \times 100\% 
\]

Equation 43

\[
\frac{C}{C_0} = 0.82 \exp(-22.53 \Delta_a) 
\]

Equation 44

\[
\Delta_a = \frac{\pi DL (d_1+d_2)}{4F (d_1-d_2)} 
\]

Equation 45

where \( E \) is the collection efficiency of a single annulus for a given gaseous species; \( C_0 \) and \( C \) are the concentrations (µg m\(^{-3}\)) of organic species at the inlet and outlet of the denuder; \( \Delta_a \) is a first-order decay constant. \( D \) is the gas-phase diffusion coefficient (cm\(^2\) s\(^{-1}\)); \( L \) is the length of coated denuder (cm); \( F \) is the gas flow rate (cm\(^3\) s\(^{-1}\)) and; \( d_1 \) and \( d_2 \) are the outside and inside diameter (cm) of the annulus [Fan et al., 2003:3148]. According to Fan et al. [2003], this model is based on the assumption that the surface of the denuder annulus is a perfect sink for gas–phase organics. The denuder efficiency depends on the denuder capacity and the vapour pressure of a chemical species. Therefore, it is important for the denuder collection efficiency to be evaluated for performance prior to field application.

Forbes [2010] contends that higher particle transmission losses are experienced in denuders for smaller particles, due to their higher diffusion coefficients. Again, loss of charged particles may be eminent due to localised electrostatic fields of the denuder wall as a function of low humidity or because of handling. It is important that the movement of particles through the denuder is sufficiently fast to prevent re-equilibration of particle bound analyte to the gas phase during transit, as this would produce a gas phase concentration positive bias [Forbes, 2010]. In the case of silicone rubber traps used in this study a transit time of less than 0.03 s would occur at 500 ml min\(^{-1}\) sampling flow rate,
thus re-equilibration during transit was deemed not to be significant especially as the target PAHs are found predominantly in the gas phase under normal sampling conditions [Forbes, 2010].

2.7.8 Multi-channel silicone rubber traps

According to Forbes [2010], there is a need for the pre-concentration of the analytes prior to analyses due to the generally low environmental levels of organic air pollutants. This can be achieved by means of rubber traps, which extract the analytes of interest, by adsorption and sorption processes [Forbes, 2010; Baltussen et al., 1997]. Common adsorptive traps are based on Tenax TA, XAD-2, and polyurethane foam (PUF). According to Wauters et al. [2008] polydimethylsiloxane (PDMS) has been used in various configurations to in sorptive samples such as mixed bag traps containing PDMS, and Tenax TA and PDMS particles for sampling of PAHs in air. Although adsorptive traps have high capacities, they have the disadvantages of artefact formation, high background concentrations, and irreversible analyte loading [Forbes, 2010].

Sorptive samplers are based on the reversible transfer of the analyte into the sorptive medium (PDMS) and as such breakthrough volumes are an important consideration in the utilization of these traps [Forbes, 2010; Baltussen et al., 1997]. Silicon degradation products are usually evident in the chromatograms obtained upon sample analysis, and can be easily identified by mass spectrometry [Forbes, 2010].

Principle of operation

The operation of the trap can be viewed as a chromatography column, where the gas phase organic analyte partitions between the stationary phase (PDMS) and the air flowing through the trap [Forbes, 2010]. The breakthrough volume ($V_b$) of the trap may be defined as the sample volume at a particular flow rate whereby 10% of the total concentration of the analyte entering the trap is exiting the trap at the outlet. Generally, the breakthrough volume is smaller for high sampling flow rates due to the smaller number of theoretical plates ($N$) generated under these conditions, and higher for lower sampling flow rates [Forbes, 2010]. The retention volume ($V_R$) is independent of the flow rate:

$$V_b = V_R \left(1 - \frac{2}{\sqrt{N}}\right)$$

(Equation 46.)

According to Forbes [2010], more volatile analytes such as naphthalene will have lower $V_b$ than the less volatile compounds, such as pyrene.

2.8 Dilution Sampling Techniques and Applications

The current literature review serves as a background in facilitating efforts to develop an appropriate aerosol source emissions measurement methodology (i.e. hardware and procedures) that can be applied for expanding key areas of particulate emissions database [Chang & England, 2004].
The particles emitted from combustion sources are usually small (tens to a few hundred nm in diameter) and their concentration in the exhaust is generally high [Uski, 2014] especially at ignition where smouldering conditions are prevalent. Furthermore, emissions collected directly from combustion sources are extremely hot and are under constant change. In order to overcome these problems, the emissions need to be diluted and homogenised before collection [Giechaskiel et al., 2014; Uski, 2014]. Dilution sampling is a technique that has been developed to examine the influence of rapid cooling and dilution on PM from combustion sources. When sampling from stationary sources (e.g. small coal-fired devices), dilution sampling is employed to simulate atmospheric conditions by diluting, cooling, and ageing the hot exhaust. A dilution sampler rapidly mixes hot exhaust gases with a specified amount of conditioned/compressed dry air allowing for processes such as nucleation, condensation, and coagulation to occur [Lipsky et al., 2004]. Aerosol dilution is useful in preventing adsorption or condensation of volatile compounds, and to suppress chemical reactions, which can change the composition of the aerosol [Hueglin et al., 1997]. The rapid cooling and dilution promote gases to nucleate or condense on pre-existing particles, as in the ambient environment [Lee, 2010]. Although dilution sampling cannot simulate the complexity of actual plume mixing, it allows for systematic examination of the effects of rapid cooling and dilution on PM emissions to understand PM transformations that occur in plumes [Lipsky et al., 2004].

Scientific evidence has shown that sampler design and dilution conditions can significantly affect measurements of fine particulate matter [Lipsky & Robinson, 2006; Lipsky & Robinson, 2005; Lyryranen et al., 2004; Maricq et al., 1999]. Hildemann et al. [1989] contends that “Filtering of hot and undiluted exhaust has been shown to underestimate the amount of organic particulate matter present, while filtering and cold-trapping leads to overestimation of the organic mass present in the aerosol phase in the ambient atmosphere” [Hildemann et al., 1989:193]. According to Lee [2010], “growth of particles in a diluted plume depends on temperature, relative humidity, ageing time, mixing rate, and partitioning of species between the gaseous and solid phases. Design and construction of dilution samplers, therefore, require integration and optimisation of these features while ensuring unit performance reliability, data integrity, and easy adaptability to field applications...” [Lee, 2010:877]. Again, the system must be free of plastic materials that may leach organics into the system or lead to adsorption of analytes on the plastic surface [Forbes, 2012: personal communication], and that would prevent thorough cleaning and heat treatment of the system between tests to lower the system’s organics blank [Hildemann et al., 1989].

The size and complexity of dilution samplers in use for source characterization has been reported to be a major barrier to more widespread application of these systems [Lipsky & Robinson, 2005]. Many scholars and researchers have attempted to build more portable and cost effective dilution samplers that can be used in field studies [Lipsky & Robinson, 2005; Lyryranen et al., 2004]. However, the majority of dilution samplers designed for stationary sources are cumbersome, complex machines compared to conventional stack sampling techniques [Lipsky & Robinson, 2005]. For example, the widely cited American Society for Testing and Materials (ASTM) and Caltech designs consist of a large mixing tunnel and a large residence tank [Lipsky & Robinson, 2005; Hildemann et al., 1989].
Recent research has focussed on the design of portable and smaller dilution systems [Lipsky & Robinson, 2005; Lyryranen et al., 2004].

Traditionally, emission sampling has been performed from undiluted, hot (120–180°C) flue gases. This method has been reported to suffer from drawbacks related to transient conditions with varying flue gas flows and the condensable nature of many of the semi-volatile organic compounds [Boman, 2005]. As such, sampling at lower temperatures, to simulate atmospheric dilution, is therefore desirable. The most extensively used sampling method is based on whole flow dilution in a dilution tunnel where a constant flow of diluted flue gases enables constant volume sampling (CVS).

According to Boman [2005], the methodology of CVS system was first designed for gasoline-fuelled vehicles in the beginning of the 1970s and since then it has been widely used and evaluated. “While this kind of dilution sampling has become the standard reference method for internal engine emission measurements, the experiences of such methods for stationary sources and solid fuel combustion are more limited although some work have been performed” [Boman, 2005:16]. A dilution sampling system for stationary sources has been defined and used by England et al. [2007] and a more portable standardized dilution system has been used for determination of particulate emissions from a pilot-scale pulverized coal combustor. There is, however, still a need for detailed characterization and quantification of residential coal combustion emissions under controlled and standardized conditions, using different fuels and combustion techniques. The purpose of this section is to discuss the design and performance of a small and portable state-of-the-art dilution system that can be used for characterization of aerosols from small-scale coal-burning devices.

2.8.1 A review of past and existing dilution systems

Dilution samplers have been used vastly in the past by a number of research groups to collect particulate matter from combustion sources. However, errors may occur when sampling is not isokinetic (i.e. when the gas velocity of the main stream and the sampling flow do not match). These errors are large for large particles (>1 µm), but are not significant for submicron particles [Burtscher, 2001]. The Stokes number can be useful in calculating/estimating errors due to non-isokinetic sampling [Hinds, 1998].

Ideally, there are several reasons for diluting the exhaust before sampling. According to Burtscher [2001], the following are some of the reasons for the exhaust gas to be diluted:
- Adaptation to the sensitivity range of the instruments used for sampling
- Cooling
- Prevent condensation of water and other species.

History of dilution samplers

A number of techniques are available, including full flow and partial flow dilution tunnels, which are mainly used for car emissions [Burtscher, 2001]. Other techniques used include the ejector dilution and the rotating disk dilution. The ejector dilution has a constant dilution ratio, which usually is in the
order of tens. To obtain higher dilution several dilutors can be cascaded [Burtscher, 2001]. Figure 9 shows the schematic diagram of the ejector dilution system.

**Figure 9: Schematic diagram of the ejector dilution system**

[Picture source: Burtscher, 2001]

In this dilution system, the compressed air flow creates a pressure difference $\Delta P$ at the nozzle. $\Delta P$ controls the inlet flow of the exhaust gas. The dilution ratio is calculated as the ratio of the inlet flow rate versus the compressed air flow rate and can be varied by the pressure of the compressed air [Burtscher, 2001]. The dilution ratio of the rotating disk dilutor can be varied from 30–1000. However, this system can only be applied for submicron particles [Hueglin et al., 1997].

In 1975, Bradway and Cass [1975] used an extractive technique for sampling at a gas-fired power plant, which employed a cyclone pre-separator to remove large particles greater than 15 μm before dilution. Such large particles had the potential to clog orifices and capillary tubes. Bradway and Cass took several approaches to diluting the sample, including an air ejector, a capillary tube system and a pump system. Large particles were removed in the particle sizing dilution system described by Ensor et al. [1975] using an in-stack impactor sized to cut particles larger than 2.7 μm. Flow control was accomplished by manipulating dilution air control valves, whereas dilution was determined as the ratio of total flow to stack gas flow [Chang & England, 2004].

Schmidt et al., 1976 used a two-stage dilution system in which the first dilution occurred in the stack, downstream of a pre-cutting cyclone to reduce submicron aerosol fumes; the second stage occurred out of stack. Flow through the cyclone was measured using a venturi at the cyclone outlet. The dilution ratio was determined by dividing total flow rate by sample flow through the cyclone venturi.

Baladi and Stultz [1977] employed an in-stack single stage dilution system with eductors to achieve controlled turbulent mixing between the sample and dilution air. The sample flow and the dilution streams intersect at right angles, causing turbulent mixing before passing through a straight section producing laminar flow. The advantages of this system are its compactness, and the ability of the pressure-induced sampling and mixing principle to produce a diluted sample at atmospheric pressure; however, under low dilution conditions fume condensation is likely [Chang & England, 2004].
Felix et al. [1981] incorporated charge neutralization in two locations, upstream of an out-of-stack cyclone inside the dilution chamber. An optional bank of SOx absorbers was included in the system to eliminate acid mists prior to dilution. Highly turbulent mixing conditions were created by introducing cooled, desiccated dilution air through perforations in a cone, whereas the stack gas was injected through the cone’s apex. Dilution ratios and dilution flow rates were adjusted using two bleed valves on the dilution air pump. The manipulation of the valves changed pressure in the dilutor, which in turn set the sampling rate. Gross changes in sample flow were accomplished by changing orifice meters. Preliminary results with this system revealed that particle loss became significant as the dilution ratio dropped below 50:1 [Chang & England, 2004].

The original dilution stack sampler design as reported by Houck et al. [1982] was made of plastic material that had the potential to leach organics into the system. The materials prevented thorough cleaning and heat treatment of the system between tests to lower the organics blank of the system [Hildeman et al., 1989]. While this design is useful for collecting samples for inorganic analyses and bulk organics mass concentration determination, the chance of cross-contamination of individual organic compounds from one test to the next cannot be ignored. Hildeman et al. [1989] contends that while the dilution system had size-fractionation capabilities using a dichotomous sampler, the inherent low sample flow rate of 17 L min\(^{-1}\) severely limited the quantity of organic material that could be collected.

A dilution system designed for a fixed dilution factor of 10 was developed by Koch et al. [1988]. This product is commercially available as a Palas, VKL-10 model [Hueglin et al., 1997]. The dilution system is used for vertical operation of particle size ranges up to 20 µm. Dilution factors of up to 1:100 000 are achieved by cascading several VKL systems.

Hueglin and co-workers developed a continuously adjustable dilution system (with a dilution ratio that ranges from 1:10 to 1:10000) for submicron aerosols [Hueglin et al., 1997]. The dilution system was designed for the treatment of exhaust gas samples in order to use a photoelectric aerosol sensor (PAS) as detector for particle-bound polycyclic aromatic hydrocarbons (PPAHs). The system was small and portable, easy to use and required little maintenance. The designers contended that the system was not limited to applications with PAS but could be used in conjunction with other devices for monitoring the production of nanoparticles in material science [Hueglin et al., 1997]. Experiments carried out with this system showed that dilution ratios were independent of particle size in the fine particle size region. The authors argued that the penetration characteristics of larger particles could be pronounced since particle loss due to impaction increase with size.

Particle impaction could cause altered dilution ratios of this system by changing the effective volume of the cavities responsible for dilution. Although contamination can be neglected for short-term measurements, it can be important for measurements over an extended period of time [Hueglin et al., 1997:1053]. Hueglin and co-workers discovered that first experiences with the dilution method showed that the level of contamination varies for different aerosol particles. They concluded that the long-term stability of the dilution system due to contamination is mainly affected by particle
composition; where the exhaust gas sample cooled down forming condensable particles, the sampling line was clogged after a short time, interrupting the flow in the aerosol channel [Hueglin et al., 1997].

Liu and co-workers designed a source dilution sampling system (SDS) for use in the evaluation of aerosol particle from diesel engines. The system has the ability to operate under transient or steady state conditions simultaneously simulating atmospheric dilution and ageing conditions, and maintaining proportional sampling conditions during changes in temperature [Liu et al., 2008]. The system prevents particle loss and secondary reactions by reducing wall effects, use of inert materials, optimisation of a smooth flow transition, and minimising thermophoretic and electrostatic forces [Liu et al., 2008:271].

The full exhaust flow was first piped into the CFV-CVS tunnel where it was mixed with filtered, dry dilution air. The CFV-CVS tunnel combines primary dilution and ageing in one stage to allow particles to grow into size ranges encountered in the atmosphere [Liu et al., 2008; Kittelson et al., 2002]. A partial sample of the diluted engine exhaust was then isokinetically extracted into the secondary micro-dilutor where more dilution air was added. The diluted air was introduced to a residence time chamber where individual samples were collected through isokinetic sampling probes. Liu and co-workers concluded that the SDS system was suitable for collecting representative samples from an exhaust flow under transient or steady state conditions while simulating atmospheric dilution and ageing, maintaining proportional sampling during temperature excursions, and minimizing particle loss and alteration [Liu et al., 2008].

The University Research Glassware (URG) dilution sampler
The University Research Glassware (URG) dilution sampler was designed to simulate far-field plume aerosol chemistry involving condensation and coagulation of reactants [Myers & Logan, 2002]. The semi-portable inverse U-shaped modular system is divided into four major components: (i) probe/dilution air interface, (ii) mixing chamber; (iii) time-delay module; and (iv) sampling manifold module.

Probe/dilution air interface: Stack gas is extracted from the source isokinetically through an in-stack cyclone. Particles and gases are moved through the heated probe to the interface of the dilution air. Purified dilution air is introduced concurrent with the flow of hot stack gas through holes drilled in concentric circles at the back of the probe to facilitate thorough mixing. Typically, depending upon isokinetic flow rate, a side stream of the stack gas is extracted at a gas flow rate of 1–5 L min$^{-1}$ with the dilution flow rate of 40 L min$^{-1}$, to yield dilution ratios ranging from 8:1 to 40:1 [Myers & Logan, 2002].

Mixing chamber: The mixing chamber is approximately 910 mm long, made of Teflon coated glass to minimize the loss of reactants. The chamber is heated to ensure that water remains in the vapour state.

Time-delay module: The time-delay module allows the diluted stack gas to react and simulate plume chemistry reactions. The time-delay module is made of both interior coated Teflon® glass and interior coated Teflon® aluminium. The module can extend the residence time of the reactive stack gas to up
to several minutes. The time-delay module is designed to provide the diluted stack gas at ambient air conditions involving temperature, pressure and humidity to the sampling module representing a 5-40 second residence time. **Sampling module:** The sampling module is attached to the end of the time-delay module and allows up to 10 sampling ports. Depending upon the analytes of interest, the sampling ports allow the user to attach different systems to quantify simulated plume constituents. Each sampler would be equipped with a pump, flow controllers etc. [Myers & Logan, 2002].

The basic URG system has been used extensively by various researchers for source profile studies both in Canada and in the US. The design is based on earlier work by Houck *et al.*, [1982] aimed at obtaining source signatures for receptor model validations [Chang & England, 2004]. Internal surfaces of this system are coated with Teflon®. After extraction through an in-stack cyclone, the sample passes through a heated probe upon which it is injected through a venturi-type nozzle into a mixing chamber. Dilution air is injected radially from an air source situated upstream of the mixing chamber, before passing through holes drilled in a concentric circle around the heated sample probe. Stack sample flowing at 1 to 2 L min⁻¹ is thus mixed in a coflow arrangement with dilution air at approximately 40 L min⁻¹. System residence time is ~20 to 30 s but can be extended by adding more sections onto the sampler upstream of the sample collection point. System flows are controlled by adjusting valves connected to the sampling pumps and varying the size of dilution air orifice plates [Myers & Logan, 2002]. Limitations of the URG dilution sampler include leak check difficulties - in past testing, there has been a need to use silicone rubber sealants between the sampler sections, posing sample contamination problems. On the other hand, the means for adjusting the dilution ratio and residence time could result in considerable down time in field applications [Chang & England, 2004].

**The Brigham Young University (BYU) dilution system**

The design and construction of the Brigham Young University (BYU) Dilution System is similar to the URG Dilution System. The main body of the BYU dilution system is the inversed U-shaped dilution chamber, internally coated with Teflon®. The stack gas is extracted isokinetically from the source through a nozzle attached to a 3–5 m long, 10 mm diameter stainless steel probe. At the exit of the probe is an elutriator-impactor assembly to remove particles larger than 2.5 μm at a flow rate of 18 L min⁻¹. Upon exiting the probe, the stack gas is mixed with dry, filtered and purified dilution air, at a ratio of 1:6 to 1:45, in the mixing chamber of the inversed U-shaped dilution system. After the mixing chamber, the diluted stack gas is further cooled and equilibrated. The equilibrium time of the diluted stack gas in the dilution system is about 4 min with a total flow of 0.75 cubic meters per minute (m³ min⁻¹) or 30 min with a total flow of 0.1 m³ min⁻¹. Parallel sampling ports are positioned at the exit of the dilution system, similar to the other described dilution systems [Myers & Logan, 2002].

**The Carnegie Mellon University (CMU) dilution system**

At the Carnegie Mellon University (CMU), Lipsky and Robinson [2005] designed and built a portable dilution system for measuring fine particle emissions. The design is based on the Caltech dilution sampler with improvements that allow for the independent control of dilution ratio and residence time. The CMU was primarily designed to investigate how the dilution processes, i.e., dilution air ratio and
residence time, affect the size distribution of PM emitted from pilot-scale coal-fired boilers [Chang & England, 2004]. The primary objective of the dilution sampler was to create a system that reproduces the results of the Caltech design. Compared to the Caltech design, this new design reduces the size of the dilution tunnel and associated flow system (i.e. operating at lower flow rates). However, the total residence time within the new tunnel is similar to the Caltech tunnel, both around 2.5 s. The residence time tank was eliminated to reduce the size and complexity of the new dilution sampler. In the Caltech design and its variants, diluted exhaust passes through a large residence time tank before filter sampling or aerosol characterization [Lipsky & Robinson, 2005:543]. Initial experiments with this system revealed that no difference was observed in simultaneous measurements made at 2.5 and 40 s after dilution. The authors concluded that the conditions of the experiments allowed the aerosols to achieve phase equilibrium in less than one second [Lipsky & Robinson, 2005].

Figure 10 shows a schematic of the dilution sampler. In this case, the exhaust is sampled isokinetically into a heated inlet line maintained at temperatures about 10 °C above the exhaust temperature to minimize thermophoretic losses [Chang & England, 2004]. The sampled exhaust is then rapidly mixed by turbulence with filtered (HEPA and activated carbon) dilution air inside a 0.9 m long and 0.15 m diameter stainless steel dilution tunnel. The dilutor sampler is constructed out of stainless steel to avoid contamination. The total flow rate through the system is 174 L min⁻¹ and the dilution ratio is varied by changing the relative exhaust and dilution airflow [Lipsky & Robinson, 2005].

![Figure 10: Schematic of field tunnel sampler. Not drawn to scale](Figure credit: Lipsky & Robinson, 2005)
The Desert Research Institute (DRI) dilution sampler

The Desert Research Institute (DRI) dilution sampler is very similar in construction and operation to the CalTech dilution sampler, except for a few differences. Like the CalTech dilution system, the DRI dilution system uses a U-shaped configuration [Myers & Logan, 2002]. In operation, the stack gas is extracted at a rate of 20–30 L min⁻¹ through a heated probe without having to pass through a separation cyclone. The exhaust is further channelled through a heated venturi located at the entrance of a 150 mm diameter, mixing chamber. Dry and purified dilution air is introduced at a 90° angle to the stack gas in the mixing chamber at a dilution ratio that ranges from 25:1 to 50:1 [Myers & Logan, 2002]. From the mixing chamber, the diluted exhaust flows down the U-shaped dilution tunnel at a rate of 1 200 L min⁻¹ for ~2.4 s. As the exhaust flows through the dilution channel, a portion is extracted into residence time chamber where an additional 80 s of residence time is provided to simulate plume conditions before being passed onto sampling ports at the end of the dilution tunnel. External sensors are used to monitor and record stack and dilution flow rates, ambient and dilution tunnel temperatures, relative humidity, and other system variables [Myers & Logan, 2002]. As with the CalTech dilution system, the DRI dilution system is constructed entirely of stainless steel and Teflon® to facilitate cleaning of the system between runs and to prevent cross-contamination. The system is relatively portable, compact, and can be easily disassembled and re-assembled by two persons [Chang & England, 2004]

The Nuclear Environmental Analysis Inc. (NEA) dilution sampler

The Nuclear Environmental Analysis Inc. (NEA) was designed by Houck et al., [1982] to simulate the effects of plume dilution and cooling on stack emission. The dilution sampler is linear in design compared to the U-shaped construction archetypal of the CalTech and the DRI dilution systems. In operation, the flue exhaust is isokinetically sampled through a traditional EPA Method 5 button-hook nozzle down a heated stainless probe to the entrance of the mixing chamber [Myers & Logan, 2002]. The unfiltered stack gas stream enters the mixing chamber at a 90° angle to the dilution gas like in the CalTech and DRI dilution samplers. The dilution gas is first cryogenically dried, filtered using HEPA filters, and purified of organics by passage through activated carbon. The mixing of the dilution gas with the unfiltered stack gas stream provides a diluted sample of the sample gas at near ambient temperature and low relative humidity (i.e., less than 30%) within a residence time of 2s [Chang & England, 2004]. The diluted stack gas sample is then passed through and filtered by a quartz filter for mass determination. If particulate sizing is needed, a parallel port attached to the mixing chamber is used for cascade impactor sampling. Following the removal of particles, gas phase samples can be collected through a downstream six-port manifold [Chang & England, 2004; Myers & Logan, 2002]. Potential limitations of the NEA design are as follows:

- Involves an indirect method of controlling flows and dilution ratio - this flow could introduce a potential error to the final sample results due to differences in the field pressure drop characteristics relative to those in the calibration laboratory;
- Short residence time; and
- The system is cumbersome prohibiting representative (traversing) sampling [Chang & England, 2004].

**The Southern Research Institute (SRI) dilution sampler**

Similar to the NEA Dilution System, the Southern Research Institute (SRI) dilution sampler is linear in construction. All active components of the dilution system are made of glass or Teflon® coated aluminium to maintain the integrity of the extracted sample by avoiding cross-contamination of the sample [Myers & Logan, 2002]. For removing primary particles, the dilution sampler employs an 8 μm in-stack cyclone, heated probe and an external EPA Method 5 filter. Similar with other systems detailed above, the dilution air used in the system is first cooled, dried, scrubbed through activated carbon, and finally filtered before delivery to the mixing chamber. The dry dilution gas enters the mixing chamber through a cone assembly containing 82 perforations, which create a well-mixed, stable velocity profile at the exit of the mixing chamber [Myers & Logan, 2002]. The SRI dilution sampler can reach dilution ratios of up to 20:1 and achieve a residence time of ~2 seconds. The dilution ratio is set to provide a diluted stack gas stream at near ambient temperature, with moisture remaining in the vapour state. To quantify condensables, the diluted exhaust is then passed through and filtered by a quartz filter maintained at about 20°C at the exit of the mixing chamber. Dilution ratios can be varied through adjustments of the mixing chamber pump and dilution airflow rate to simulate plume chemistry [Chang & England, 2004; Myers & Logan, 2002]. However, the highly turbulent mixing chamber provides qualitatively different mixing than that in an actual plume. Again, improvements to the portability of the system at stack level would facilitate representative (traversing) sampling [Chang & England, 2004].

### 2.8.2 Insights and implications for future designs

In conclusion, it is appropriate to make use of others’ successes and to make adjustments as necessary to enhance future testing activities. Recent successful source-testing hardware (dilution) systems are adaptations of the Caltech dilution stack sampler developed by Hildemann et al. [1989]. These sampling systems and methodologies have been employed in the developed of the majority of the current fine particulate emissions database [Chang & England, 2004]. However, the only major drawback to the Hildemann design and the later systems (e.g. the DRI system and other systems) is that the equipment is large and cumbersome to apply in many stack applications. Inasmuch as the Caltech and DRI systems have been successfully employed in numerous field applications, there still exists a need for more compact hardware that will enhance future testing efforts. Most importantly, when designing a new hardware or when carrying out a revision of an existing hardware for source testing, it is critical for the design to be subjected to extensive performance evaluation exercises to ascertain that the results are consistent with the existing database [Chang & England, 2004]. Based on the literature presented herein, there appear to be opportunities for improving on the practical aspects of dilution sampler design. We recommended that a more compact system be designed, constructed and then thoroughly evaluated for data comparability. After successful validation, the new hardware...
and associated measurement protocols can be used to fill critical gaps in the existing PM2.5 database [Chang & England, 2004].

2.9 Microscopy and Coal Combustion Particle Morphology

Aerosol particles are ubiquitous in the troposphere and due to their shapes and sizes can influence the global climate and the environment [Buseck & Pósfai, 1999]. Aerosol particles affect the climate by acting as cloud condensation nuclei, scattering light, transmission and absorption of radiation. The magnitude of the radiative effects of aerosol particles depends on the following properties: composition, size and size distribution, abundance, hygroscopic properties, surface properties, aerosol density, and refractive indices [Buseck & Pósfai, 1999:3373]. The traditional method of studying the physico-chemical properties of aerosol particles is through bulk methods. This enables large numbers of particles to be analysed en masse [Buseck & Pósfai, 1999]. However, the resultant data does not provide information about individual aerosol species and mixing states. In order to enhance our understanding of how particles transform during atmospheric transport, there is a need to study individual particles using electron microscope techniques.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are very powerful tools to study the shape and morphology of aerosol particles. Equipped with energy dispersive X-ray (EDX) or electron energy loss (ELL) spectroscopy they give information on the elemental composition of the particles of interest [Burtscher, 2001]. While TEM allow a higher resolution down to the nano- and atomic scale, SEM usually has a better contrast. For TEM, very thin grids (often copper) coated with a carbon film, are used. The quality of this film is extremely important to obtain a good resolution. If samples are used for quantitative analysis (e.g. of the size distribution) care has to be taken to have a well-defined size dependence of the sampling process [Burtscher, 2001].

Microscopy techniques have become the most ‘sought after’ and effective tools in coal combustion and atmospheric research, particularly the use of beam microscopes which include Scanning and Transmission Microscopes [Li et al., 2012; Silva & da Boit, 2011; Fryda et al., 2010; Silva et al., 2009; Zhu et al., 2008; Zhang & Ninomiya, 2006; Smith et al., 2005; Buhre et al., 2005]. Microscopy techniques can be useful in the study of a range of particle properties since important information on particles resides in the morphology and chemical composition of individual particles [Gwaze, 2007; Fletcher et al., 2001]. High Resolution Scanning Electron Microscope (HRSEM) has been used to a lesser extent in coal combustion research [Silva et al., 2012; Mhlaba et al., 2011; Ribeiro et al., 2010; Lu et al., 2007; Zhang & Ninomiya, 2006]. In published and peer reviewed literature there is limited information with regards to characterising emissions from residential coal combustion processes using an Ultra-High Resolution Field Emission Gun Scanning Electron Microscope except for the work of Wentzel et al. [1999] who characterized aerosols from the Soweto atmosphere and Gwaze [2007] who characterized aerosols from coal combustion. Unfortunately, their work has not been followed up although it is vital to understand the modes of formation and transformation of conglomerates originating from low temperature coal combustion. This study proposes the use of a high resolution
SEM for characterising and assessing the morphology and characteristics of coarse (>10 µm) and fine particles (< 2.5 µm).

### 2.9.1 Fractal analysis of particles using SEM images

The severity of the impacts of particulate matter on human health and the environment is determined by chemical and physical properties of the PM [Arora & Jain, 2015; Pöschl, 2005]. The physical properties include size and morphology, while chemical characterization in terms of organic and elemental composition is significant in assessing overall impact of the PM [Arora & Jain, 2015; McDonald & Biswas, 2004]. During combustion of fuels such as coal, primary particles aggregate to form clusters, with some clusters over 100 µm in length [Wentzel et al., 1999]. These agglomerates have morphologies that can be measured using electron microscopy techniques [Chakrabarty et al., 2014; China et al., 2014]. For example, fractal dimensions of particles including other shape descriptors such as aspect ratio, roundness of particles and root form factor are used to characterize the morphological properties of agglomerates instead of using conventional optical (light scattering and absorption) methods [Arora & Jain, 2015; Chakrabarty et al., 2014; Chakrabarty et al., 2006].

### 2.9.2 Fractal analysis

The concept of fractal dimension was first introduced by Mandelbrot in 1982. The concept has been extensively used in atmospheric sciences in describing complex particulate matter morphologies resulting from random aggregation of fine aerosol particles [Chakrabarty et al., 2006]. The fractal dimension ($D_f$) of individual particles can be calculated using a number of methods [Arora & Jain, 2015]. Fractal dimensions can be calculated based on the perimeter or the density of the aggregates [Chakrabarty et al., 2006].

The density method is deemed the most accurate method for calculating $D_f$ of an aggregate [Chakrabarty et al., 2014]. The method has been used to calculate the fractal dimension of soot particles from different fuels and combustion conditions [Chakrabarty et al., 2014; China et al., 2013; Chakrabarty et al., 2006]. According to Kiselev et al. [2010], soot aggregates are often characterized according to the radius of gyration $R_g$, which is defined as the mass-weighted root mean square of distances of the primary particles relative to the centre of mass of the aggregate. Consequently, the structure of the soot aggregates can be described statistically by a power law relationship between the number of primary particles $N_{pp}$ and $R_g$ normalized to the diameter of the primary particle $d_{pp}$ [Thajudeen et al., 2015; China et al., 2013; Kiselev et al., 2010; Chakrabarty et al., 2006; Schmidt-Ott, 1988].

$$N_{pp} = k_f \left( \frac{2 \cdot R_g}{d_{pp}} \right)^{D_f}$$

**Equation 47**

where $D_f$ is the average fractal dimension and $k_f$ is the fractal prefactor of the system of agglomerates. For a given $R_g$, the fractal dimension is proportional to the number of primary particles. For example,
the higher the fractal dimension, the higher is the number of primary particles in agglomerate, resulting in increased particle numbers or mass densities [Chakrabarty et al., 2006].

The perimeter method entails drawing grids of different box sizes upon a 2-D image of a fractal aggregate [Gwaze et al., 2006]. When considering a grid with a certain box size, the number of grid boxes covered by the perimeter of the aggregate is counted [Arora & Jain, 2015; Chakrabarty et al., 2014; 2006]. Once the perimeter is established, another grid with a different box size is drawn over the aggregate, and the number of grid boxes through which the perimeter passes is counted once again. This process is repeated, upon which the logarithm of the box size is plotted against the logarithm of the box count, providing $d_{pp}$ as the slope [Chakrabarty et al., 2014].

The aggregate simulation method involves generating a 3-D fractal aggregate by the particle-cluster aggregation technique [Chakrabarty et al., 2009] with an algorithm that satisfies the fundamental fractal equation given in equation 44 [Arora & Jain, 2015; Chakrabarty et al., 2014, Sorensen, 2001].

**Image processing and thresholding**

The ImageJ software package (free-online graphics software), is often used for image processing and analysis [Arora & Jain, 2015; Gwaze, 2007; Gwaze et al., 2006] although other software packages such as Digital Micrograph 3 are useful [Chakrabarty et al., 2006]. Images are typically binarised by selecting brightness thresholds to ascertain entire particles. According to Gwaze [2007] using, the automatic thresholding tends to give hollow primary particles due to its high sensitivity to particle boundaries. Because of this, it is advisable that thresholding is selected manually for each aggregate. ImageJ uses a nested square method [Dye et al., 2000] to measure the 2-D density fractal dimension of the aggregate. The software contains a customized macro customized for implementing this algorithm. The macro first threshes the image to be analysed by converting the imaging into black and white pixels where the black pixels represent part of the particle and white represents everything else not part of the analysed particles [Chakrabarty et al., 2006]. After threshing the aggregate of interest, primary particles are selected using the elliptical marquee tool to obtain the result in calibrated units (nm or µm) [Arora & Jain, 2015]. Finally, the ‘measure’ macro provides results for diameter and projected area for each selected aggregate and this allows further calculations to be made to determine the average diameter and area of primary particles in a particular aggregate [Arora & Jain, 2015].
CHAPTER THREE

This chapter discusses the design of a small and portable state-of-the-art dilution system that can be used for characterization of aerosols from small-scale coal-burning devices. A range of six coal braziers and an innovative bottom-lit downdraft stove developed at the SeTAR lab were evaluated for gaseous and particulate emissions. Innovative developments in polycyclic aromatic hydrocarbon (PAHs) monitoring are motivated and apparatus used to carry out these experiments are described in detail. The elements of the test procedure making up a full test protocol are identified and discussed including emission factors, thermal performance and fuel consumption. Scanning electron microscope (SEM) techniques employed in this study to characterize condensed matter/smoke emissions are described in detail. Aspects of quality control and documentation of protocols and standards are presented herein.

3. Materials and Methodology

3.1 Design Considerations for the SeTAR Portable Dilution System

The preceding chapters explicitly presented limitations of previous and existing in-use dilution systems. From the critical evaluation of existing dilution systems, including the CALTECH and the Hildeman designs, a need to develop an alternative, robust, portable and easy to use dilution system for use in the evaluation of residential coal combustion devices in the South African context was established. In conceptualising and designing the new dilution system, several objectives were identified. The primary design objective was to design a system that is simple and portable. Several aspects that would preclude widespread use of the existing dilution sampling systems include the size, weight and complexity of the systems. While the existing dilution sampling systems were used principally in the development of fingerprints for use in receptor modelling [Myers & Logan, 2002], we wanted a method that would additionally quantify the total fine particulate emissions. We sought to maximize the total flow rate of diluted exhaust based on the requirements for filter packs and other instrumentation to be used during the source characterization to minimize exhaust vented to the atmosphere [Lipsky & Robinson, 2005]. This design consideration has an effect of reducing the size of the dilution system and the associated flow control system.

The following design concerns were considered for our dilution sampler:

- To simulate atmospheric dilution
- To minimize contamination of the sample
- To provide enough residence time to allow condensation processes to occur
- To eliminate the need of a residence time tank – this reduces the size and complexity of the new dilution system.
- To minimize particle and vapour losses in the system
- To eliminate chemical reactions in water by rapid dilution to below the saturation vapour density of water [Myers & Logan, 2002]
- To provide samples suitable for scanning electron microscope (SEM)/transmission electron microscope (TEM) analysis.

To achieve these goals, design concepts used in past and currently used dilution sampling systems were adopted. However, some design concepts used by most of the existing dilution sampling systems were not compatible with achieving the above-mentioned goals. Most of the sampling dilution systems developed over the past years have fixed dilution factors. In such systems, high dilution factors can be achieved by using the two dilutors or more in a tandem set up [Hueglin et al., 1997]. For our purposes, a dilution system for continuous selection of dilution factors over a wide range was needed due to the broad range of concentrations of coal smoke aerosols emitted across a full burn cycle. The new dilution system is expected to be small and portable, easy to use and should require little maintenance. Because of the venturi flow required in most dilution systems, clean pressurized air is required for operation.

In this design, carbon dioxide mixing ratios of the diluted and undiluted exhaust were measured to determine the dilution ratio. This eliminates the need for a venturi flow meter on the inlet, which has been shown to be a significant factor of particle losses [Lipsky and Robinson, 2005; Hildeman, 1989]. For purposes of this study, dilution ratio (DR) is defined and calculated by the following equation:

$$DR = \frac{CO_{2\text{meas\_undil}} - CO_{2\text{amb}}}{CO_{2\text{meas\_dil}} - CO_{2\text{amb}}}$$

Equation 48

where $CO_{2\text{meas\_undil}}$ is the CO$_2$ measured from the undiluted exhaust, $CO_{2\text{meas\_dil}}$ is the CO$_2$ concentration measured from the diluted exhaust, and $CO_{2\text{amb}}$ is the CO$_2$ concentration of the ambient environment. The CO$_2$ mixing ratio of the exhaust is measured at the sample inlet location. The diluted exhaust CO$_2$ mixing ratio is monitored at the end of the tunnel after the sample is well mixed. Two separate CO$_2$ analysers were used to monitor continuously the dilution ratio of the system. Variations in the CO$_2$ of dilution air were negligible and did not influence the calculation of dilution levels based on Equation 45 [Lipsky & Robinson, 2005].

### 3.1.1 Components of the SeTAR Dilution System

The design specifications for the unit include the following: (i) a dilution/mixing chamber with dilution ratios of 100:1; (ii) a residence tunnel with residence time of at least 2 s; (iii) a high-efficiency particulate air (HEPA) filter with a carbon adsorption canister to remove fine particles and VOCs from ambient dilution air to minimize contamination. The operational performance of the SeTAR dilutor was determined from the results of a series of laboratory and field-simulated tests. The volume of dry CO$_2$-free air supplied through the jet can be controlled by using a Rotameter with a needle valve flow controller. The gap between the nozzle and the conical receiver can be varied by turning the Carrier (Figure 11), which varies the gap between them. The dilution level can be pre-set
or can be changed by continuously varying the volume of dry air depending on need. By recording diluted CO\textsubscript{2} and undiluted CO\textsubscript{2}, the dilution ratio can be calculated for each 10 s interval. As such, there is no need for flow monitoring or calibration of flow meters.

The SeTAR dilutor (Figure 11) is designed and made out of stainless steel and Teflon\textregistered tubing to avoid contamination and leaching of organics.

![Image of the SeTAR dilutor](Photo credit: Crispin Pemberton-Pigott)

The sampling nozzle is placed in the stack gas but is not equipped with a PM2.5 fractionating cyclone inlet. This part is followed by a mixing section where hot stack aerosol is diluted with filtered air. The mixed aerosol stream then passes through an ageing section (mixing chamber), followed by sampling ports for gaseous and particle emissions monitoring.

### 3.2 Fuel Characterization

Coal was purchased from local coal merchants and compared with coal sourced directly from a colliery (Slater Coal Mine) in Witbank Emalahleni coalfield. Batches of coal were purchased sufficient to conduct a range of comparative tests, and were further characterized for thermal content, major elemental (proximate) analysis, moisture and ash content by an independent laboratory (Bureau Veritas Inspectorate Laboratories (Pty) Ltd). The fuel samples were analysed on an air-dried basis (Table 3). Experimental results presented in this thesis are based on the proximate and ultimate analysis results for the D-grade and A-grade coals used in making the fires.

The coal was crushed and sieved to maintain a mean size diameter of 20 mm – 40 mm. Uniform coal sizes were used in our experiments to minimise errors inherent in the use of different coal sizes. The fuel was then stored in moisture free containers. Each batch of fuel was analysed for moisture content prior to testing.
Table 3: Proximate and ultimate analysis data for the A-grade and D-grade coals used in the experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard Method</th>
<th>Slater Coal A-Grade</th>
<th>Slater Coal D-Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Air Dried Basis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>ISO 5925</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Volatiles (%)</td>
<td>ISO 562</td>
<td>25.4</td>
<td>20.3</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>ISO 1171</td>
<td>14.0</td>
<td>24.2</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>By difference</td>
<td>56.8</td>
<td>52.0</td>
</tr>
<tr>
<td>Calorific value (MJ kg⁻¹)</td>
<td>ISO 1928</td>
<td>27.0</td>
<td>23.4</td>
</tr>
<tr>
<td>Calorific value (Kcal kg⁻¹)</td>
<td>ISO 1928</td>
<td>6440</td>
<td>5590</td>
</tr>
<tr>
<td>Total sulphur (%)</td>
<td>ASTM D4239</td>
<td>0.66</td>
<td>0.63</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>ASTM D5373</td>
<td>72.4</td>
<td>62.6</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>ASTM D5373</td>
<td>3.26</td>
<td>2.72</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>ASTM D5373</td>
<td>1.61</td>
<td>1.43</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>By difference</td>
<td>4.41</td>
<td>4.96</td>
</tr>
<tr>
<td>Total Silica as SiO₂ (%)</td>
<td>ASTM D4326</td>
<td>54.9</td>
<td>58.6</td>
</tr>
<tr>
<td>Aluminium as Al₂O₃ (%)</td>
<td>ASTM D4326</td>
<td>24.7</td>
<td>27.6</td>
</tr>
<tr>
<td>Total Iron as Fe₂O₃ (%)</td>
<td>ASTM D4326</td>
<td>5.77</td>
<td>6.63</td>
</tr>
<tr>
<td>Titanium as TiO₂ (%)</td>
<td>ASTM D4326</td>
<td>1.13</td>
<td>0.82</td>
</tr>
<tr>
<td>Phosphorous as P₂O₅ (%)</td>
<td>ASTM D4326</td>
<td>0.23</td>
<td>0.55</td>
</tr>
<tr>
<td>Calcium as CaO (%)</td>
<td>ASTM D4326</td>
<td>4.27</td>
<td>2.30</td>
</tr>
<tr>
<td>Magnesium as MgO (%)</td>
<td>ASTM D4326</td>
<td>1.34</td>
<td>0.83</td>
</tr>
<tr>
<td>Sodium as Na₂O (%)</td>
<td>ASTM D4326</td>
<td>0.49</td>
<td>0.42</td>
</tr>
<tr>
<td>Potassium as K₂O (%)</td>
<td>ASTM D4326</td>
<td>0.89</td>
<td>0.79</td>
</tr>
<tr>
<td>Sulphur as SO₃ (%)</td>
<td>ASTM D4326</td>
<td>5.77</td>
<td>1.10</td>
</tr>
<tr>
<td>Manganese as MnO₂ (%)</td>
<td>ASTM D4326</td>
<td>0.08</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.3 Devices and Ignition Methodologies

3.3.1 Experimental combustion devices

Three stoves procured from users in communities (referred to hereafter as field stoves) and three stoves designed and built at the SeTAR laboratory (hereafter referred to lab stoves) were tested for thermal performance, emissions of gases and particles. Tests were conducted under laboratory conditions at the SeTAR Centre situated at the University of Johannesburg. *Imbaula* stoves are handmade out of metal drums with perforations of varying sizes punched around the sides, and a wire grate across the middle of the container to hold the solid fuel. The *imbaulas* are found in three characteristic sizes, determined by three commonly available metal drums: 20 L metal paint drums for domestic use; 70 litre metal dustbins, or sectioned 200 L oil drums for commercial purposes and typically used in street-side restaurants. Typical 20 L *imbaulas*, procured from users for testing are illustrated in Figure 12.
Imbaulas commonly have a fuel support grate, made of wire or a perforated plate, but some are operated without a fire grate. With a fire grate in place the rate of burning is increased. It should be noted that there is no standard imbula, as the devices vary greatly in terms of the number and sizes of the side holes (i.e. affecting ventilation rates), the presence of a grate and its position in the metal drum. The stoves can burn wood, coal, or a combination of both, and often rubbish, which can include waste plastic.

![Illustration of field procured braziers used in the experiment: (a) high ventilation; (b) medium ventilation; and (c) low ventilation](image)

**Figure 12:** Illustration of field procured braziers used in the experiment: (a) high ventilation; (b) medium ventilation; and (c) low ventilation

A photographic catalogue of the lab-designed stoves is presented in Figure 13.

![Lab designed imbaulas: (a) high ventilation case; (b) medium ventilation case; and (c) low ventilation case](image)

**Figure 13:** Lab designed imbaulas: (a) high ventilation case; (b) medium ventilation case; and (c) low ventilation case

Ventilation rates affect the overall performance of the stove and these rates differ significantly from one device to the other. To evaluate realistically and compare the performance of two or more braziers, ventilation rates need to be specified. The total hole areas, which are indicative of the ventilation rates for the three field obtained braziers used in the experiments are given in Table 4, and the total hole areas for the lab-designed braziers are given in Table 5.
Table 4: Area of holes for each of the field procured stoves

<table>
<thead>
<tr>
<th>Stove Type</th>
<th>Area of holes above the grate (\text{cm}^2)</th>
<th>Area of holes below the grate (\text{cm}^2)</th>
<th>Total hole area (\text{cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field: High ventilation</td>
<td>159</td>
<td>248</td>
<td>407</td>
</tr>
<tr>
<td>Field: Medium ventilation</td>
<td>166</td>
<td>189</td>
<td>355</td>
</tr>
<tr>
<td>Field: Low ventilation</td>
<td>91</td>
<td>63</td>
<td>154</td>
</tr>
</tbody>
</table>

The fabrication process of the lab stoves involved marking and perforating the air holes on standard 20 L metal drums with a height of 360 mm and diameter of 295 mm, and then setting the fire grate in place. In total, three brazier designs were constructed and tested for emissions and fuel efficiency. The fabricated brazier stoves depicted the maximum (high), medium, and minimum (low) number of air holes above and below the fire grate. For the three designs, the fire grate was set at one-third of the device height from the base, in keeping with common practice for coal/wood brazier burners in the study area where the initial designs were collected [Kimemia et al., 2011]. All three designs had a uniform hole-diameter of 20 mm below and above the grate. Primary air was supplied into the brazier through air holes below the fire grate, whereas secondary air was introduced through air holes above the grate.

Table 5: Area of holes for each for the lab-designed stoves

<table>
<thead>
<tr>
<th>Stove Type</th>
<th>Area of holes above the grate (\text{cm}^2)</th>
<th>Area of holes below the grate (\text{cm}^2)</th>
<th>Total hole area (\text{cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab: High ventilation</td>
<td>126</td>
<td>138</td>
<td>264</td>
</tr>
<tr>
<td>Lab: Medium ventilation</td>
<td>101</td>
<td>50</td>
<td>151</td>
</tr>
<tr>
<td>Lab: Low ventilation</td>
<td>63</td>
<td>38</td>
<td>101</td>
</tr>
</tbody>
</table>

3.3.2 Fire-ignition methods

There are two ignition methods used for igniting a coal fire in a brazier— the traditional, BLUD, method, and the top-lit, TLUD method, known colloquially as the Basa njengo Magogo method. The order of laying the fire in the conventional method is as follows: a few lumps of coal, paper, wood, ignition, after which the bulk of the coal is added at an appropriate time after the wood fire is established. As such, 1 000 g of coal were placed onto the grate at the bottom of the brazier followed by 36 g of rolled paper and 360 g of pine wood kindling. After ignition, ~2 000 g of coal was added on top of the already burning kindling.

In the TLUD, the order of laying the fire is reversed—first the major portion of the coal load, and then paper and wood kindling, with a few lumps of coal added at an appropriate time after the fire has been lit. In our experiments, 2 000 g of coal were added to the bottom of the brazier onto a fuel grate followed by 36 g of paper and 360 g of kindling. After ignition of the kindling, ~1 000 g of coal was added to the brazier above the kindling.
Fire-ignition techniques for electron microscope samples

Since domestic coal combustion is usually initiated with some type of kindling (e.g. wood, paper, kerosene) there is a need to separate coal combustion emissions from emissions due to the combustion of the kindling. When two fuels are burned together, it is a challenge to separate the emissions from each fuel [Bond et al., 2002]. One suggested approach is to start combustion with the kindling that is normally used for igniting the coal, since the total emission from both fuels can be attributed to the use of the coal in real-world scenarios. However, this approach has the potential to overestimate total emissions, especially in situations where emission factors are applied to fuel use databases where coal consumption and wood consumption are reported separately [Bond et al., 2002]. Furthermore, the measurement would not be representative of continuously burning fires used for heating or prolonged (commercial) cooking purposes with intermittent refuelling [Bond et al., 2002].

An alternative method, and the one used in this study, was first used by Bond et al. [2002] and entailed starting the combustion using a clean burning, low-smoke fuel. The authors reported the use of Kingsford® barbeque briquettes, which have low particulate emissions during combustion. It was assumed that the emissions from the barbeque briquettes would cease before the first coal is burned. Wood kindling, on the other hand, showed high emissions that persisted into subsequent coal cycles. In our preliminary experiments, we found that pinewood had high particulate emissions at the start of ignition, but the emissions did not persist into subsequent coal cycles. Pinewood as a kindling was faster at igniting the coal compared to locally available barbeque compressed briquettes. We therefore used pinewood to initiate combustion so that the coal emissions could be isolated. Thus, the particle morphologies presented herein are representative of coal combustion smoke without being influenced by the kindling. However, to determine the total particulate matter attributable to coal combustion (e.g., to assess health effects or net effect of fuel switching) one should consider kindling emissions [Bond et al., 2002].

For electron microscope sampling using the Basa njengo Magogo method, a special ignition strategy was needed to obtain kindling-free emissions: A test brazier was prepared with 2 000 g of coal placed directly on the grate. In a second, similar brazier, 1 000 g of coal was ignited using 150 g of pine wood and 20 g paper used as kindling. After ignition, the coal was allowed to coke until red-hot, whereupon the burning coke was transferred to the test brazier and placed on top of the previously loaded 2 000 g of coal. As soon as the hot red embers had been transferred to the test brazier, particulate sampling would commence.

For the BLUD (traditional fire ignition) method, 1 000 g of coal was added to a coal brazier with similar configurations as the test brazier. A similar amount of kindling as in the TLUD method was added and the fire started until the coals turned red-hot. The red ambers were then transferred to the test braziers onto the grate; where upon 2 000 g of fresh coal was added on top of the burning red coal ambers. This marked the onset of particulate sampling for microscopy examination.
### 3.4 The Heterogeneous Stove Testing Protocols

The experimental procedures to be described in this chapter cover the tests for thermal efficiency, particle and gaseous emissions performance, fire-power, and fuel burn rate. Overview procedures are presented in the text; standard operating procedures, with detailed task and instrument descriptions are presented elsewhere [Makonese, 2011]. This overall collection of tests and methods is what we have termed the Heterogeneous Stove Testing Protocols (HTP). The practical methods of the tests are presented in this chapter. As the description and discussion of the full protocol is not one of the outputs of this thesis, focus will be on the use of the protocols to assess performance of domestic coal burning braziers.

Specifically, the protocols will be used to describe three sets of experiments that were carried out as part of the practical tasks of this research programme:

- **A comparative evaluation of gas and particulate emissions from a suite of coal-burning braziers in use in the low-income urban stratum of South Africa**
- **Measurement and comparison of the thermal performance and heat transfer efficiencies of a suite of coal-burning braziers.**
- **Characterisation of system and combustion efficiencies from top-lit updraft (TLUD), bottom-lit updraft (BLUD) coal-burning braziers.**

The HTP data processing methodologies are embedded in the SeTAR data calculation sheet, a tool used to capture and process raw data from gas analysers, PM monitors and temperature loggers. The raw data is captured at ten second intervals for the entire duration of the testing and measurement period. Data from the flue gas analysers are given in [ppm(v)] for all the gases monitored, while the data from the PM monitor are given in [mg m\(^{-3}\)] for the size ranges monitored, the fuel and system masses are in [grams], and temperatures are given in [°C]. On completion of a text cycle, data are transferred manually from the data logging computer into the data calculation tool, in the relevant sections and columns. The following sections contain a description of the metrics that are calculated using this tool.

#### 3.4.1 Choice of cooking pots

The pots used in this study are Hart™ aluminium 6 L capacity pots, commercially available and widely used for cooking in South Africa and regionally. For the water heating tasks, an amount of water (5 L for the large pots) was heated from ambient temperature to the target temperature (about 70°C), not higher, to prevent losses through evaporation [Makonese, 2011]. A pot was used together with the lid it was designed for to minimize evaporative losses. It is important to minimise or divert the steam from the combustion flow because it would complicate the analysis of the combustion gases. Excess water vapour has the potential to render the drier on the flue gas analyser less effective than it should be [Makonese, 2011].
3.4.2 Thermal performance evaluation

Thermal efficiency (\(\eta\)) is the ratio of work done by heating and evaporating water, to the thermal energy that is generated by burning fuel, and is mathematically represented as:

\[
\eta = \frac{C_p M_w (\Delta T) + M_e L_v}{M_f (LHV_f) - M_c (LHV_c)}
\]

Equation 49

where \(M_w\) is the mass of the water in the pot at the start of the test, \(C_p\) is the specific heat capacity of water, \((\Delta T)\) rise in the water temperature in °C, \(M_e\) is the mass of the evaporated water, \(L_v\) is the latent heat of vaporisation of water, \(M_f\) is the mass of the raw fuel burned, \(M_c\) is the mass of the remaining charcoal, \(LHV_f\) is the lower heating value of the fuel, and \(LHV_c\) is the lower heating value of the residual charcoal (if any).

The formula given in Equation 49 does not account for excess ash, which is formed in high ash containing fuels such as coal. This could result in an error in the evaluation of thermal performance of fuel/stove combinations [Makonese, 2011]. “For relatively short tests with most woods, this will not be a large source of error, but with dung or agricultural residue, or with long tests in stoves that are very effective at burning up their char, the counting of ash as char could introduce a serious error” [Taylor, 2009:53]. The ash may be accounted for by calculating the change in char mass \((M_c)\) as:

\[
M_{\text{corrected}} = M_c - (M_f - M_e) A_{\text{fuel}}
\]

Equation 50

where \(M_{\text{corrected}}\) is the mass of the charcoal corrected, \(M_c\) is the mass of the charcoal, \(M_f\) is the mass of raw fuel, and \(A_{\text{fuel}}\) is the ash content of the fuel on a wet mass basis.

Efficiency can only be determined by separating the fuel, char, and ash, measuring the proportions of each, and then calculating the energy content of each. It should be noted that although the method shown in Equation 50 is not recommended as a standard way of determining thermal efficiency, it has the advantage of addressing the influence of ash content in the material removed from a stove at the end of a test, thereby minimising error. There is a deduction for the mass of free ash that should be present in addition to the char. The energy accounting error (due to ash content) can be avoided and is an important result in terms of test metrics since the error may greatly affect most other outputs of the test. As a result, thermal efficiency will be calculated using the following equation:

\[
\eta = \frac{C_p M_w \Delta T + M_e L_v}{M_f (LHV_f) - M_{\text{corrected}} (LHV_c)}
\]

Equation 51.

To obtain a good indication of the energy released from the fuel it is better to batch load the stoves with fuel and operate them in such a way that only char and ash remain at the end of an experiment (or heating phase) [Bhattacharya et al., 2002]. This means operating the stove in a way that does not entirely reflect real-world uses of stoves. However, the equivalent mass of fuel burned, on an energy
basis (with reference to the unburned fuel), can thus be calculated with reasonable accuracy [Makonese, 2011].

### 3.4.3 Fire-power for fuel/stove combinations

The test procedure for determining the power settings used was similar to that advocated by Prasad et al. [1983], but with minor changes. It is important to note that burn rate can be regarded as comparable to fire-power [Bhattacharya et al., 2002]. The stove was filled with fuel and the mass of the stove and fuel were recorded. The mass of a stove was measured by means of a mass balance on which the stove rested. The mass balance recorded the mass loss due to the fuel’s consumption as a function of time. The instantaneous power output of the stove is defined as the mass loss rate multiplied by the lower heating value of the fuel, assuming complete combustion (i.e. products of incomplete combustion are minimal):

\[
P = \frac{(LHV \times \Delta m)}{\Delta t}
\]

where \( P \) is the fire-power of the stove at a specified power setting; \( \Delta t \) is the time interval; \( \Delta m \) is the mass loss in a specified time interval; and \( LHV \) is the lower heating value of the fuel.

### 3.4.4 Measurement of fuel burn rate and water evaporated

“Fuel burn rate is calculated as an overall figure during the heating up phase and the simmering phase. Having the stove resting on the scale suggests that the burn rate can be measured continuously.” [Ballard-Tremeer, 1997:23]. The difficulty is that both water mass in the pot and fuel mass decrease at different rates, neither of which is constant [Ballard-Tremeer, 1997]. Since the mass of the stove and pots are known, lifting the pot from the fire for a few a seconds (until the scale has become stable) makes it possible to calculate the interim fuel and water masses and hence to be able to calculate separately the fuel and water loss rates. In the SeTAR data calculation sheet, the pot-lift test requires that the mass of fuel burned and the mass of water evaporated are determined periodically by recording the system mass (\( M_1 \)); and then lifting the pot slightly for a few seconds to get the system mass without the pot mass (\( M_2 \)). By subtraction, the mass of fuel burned and the mass of water evaporated can be determined. From simultaneous recordings of the water temperature, the system efficiency can be calculated.

The SeTAR data calculation sheet, allows for the pot-swapping test, in which the system mass change is restricted to the combustion of fuel only. When the pot containing water reaches 70°C (before much evaporation takes place), the pot is swapped for another identical one containing cold water. The water can be taken through a 40°C to 50°C rise, say from 20°C to 70°C. In this case, it is assumed that evaporative losses are negligible if the water is not taken above 70°C. Any mass change is ‘missing fuel’ only. The water temperature change is monitored in order to calculate the total heat gained. All tests in this study were conducted with the pots being swapped in this manner.
For solid fuel burning stoves, “the burn rate was determined by burning a known amount of fuel in a test and measuring the time for 90% of the fuel to be consumed. It was done by putting the stove on a weighing scale and the time was noted when 10% of the initial fuel weight was left” [Bhattacharya et al., 2002:390]. This strategy, which we adopted, avoids the uncertainty of deciding when the fire has reached smouldering stage or has died out. The fuel burn rate was determined in real time by placing the stove system on a scale and recording the instantaneous change of mass as the fuel burns. For a selected power level, a separate calculation of the elemental composition of the fuel burned was made in order to determine the mole mass of the combustion products. From these values, the volume of emissions was calculated and, based on a sample of those emissions total gaseous and particulate sample masses were estimated.

### 3.4.5 Moisture content (MC) determinations

Each batch of fuel was determined for moisture content (MC) prior to each test. The moisture content was determined from the batches of fuel as received from the field. Two distinct moisture content values for two batches of coal fuel were used in this study (2.4% MC and 8.6% MC, respectively). To determine the MC in the fuel, a small sample (~50 g) of the coal was weighed on a calibrated scale with 0.1 g resolution and dried in an oven at 100ºC for about 24 hours. The sample was taken out and weighed again after a day. To check that the coal fuel had attained dry mass, the exercise was repeated every 3 hours. Steady weight without further decrease confirms that the coal has attained dry mass. The percentage moisture content was calculated on wet basis using the following equation:

$$MC_{wet} = \frac{MF_{wet} - MF_{dry}}{MF_{wet}} \times 100$$

where $MF_{wet}$ is the mass of the wet fuel and $MF_{dry}$ is the mass of the dry fuel.

### 3.4.6 Gaseous emissions performance test

The characteristics and quantities of gaseous and particulate emissions from residential coal combustion in typical braziers were determined and emission factors reported in an extensive experimental study. A large number of gaseous and particulate components were studied for the experimental fuels and devices with systematic variations in the following characteristics: (i) for fuel quality, A-grade and D-grade; (ii) moisture content – 2.4% MC and 8.6% MC; (iii) ventilation rates of braziers – high, medium and low ventilation rated for field procured and lab designed devices; and (iv) operational properties – bottom lit and top lit ignition. Special focus was on detailed characterization of the emissions of CO, CO$_2$, NOx and particulate matter. Statistical analyses were used to determine if there are significant differences in emission factors due to varying these parameters. A two-tailed student T-test at the 95% confidence level was used for statistical evaluation of the thermal and PM data.

The hood method was used for evaluating emissions. Since the experimental stoves did not have a flue, the stoves were placed under a collection hood attached to the dilution system, which was
responsible for the ducting and dilution of the exhaust gas stream (Figure 14). Since a high extraction rate may influence the combustion characteristics of the stove [Bhattacharya et al., 2002], an extractor fan was not used for drawing air through the hood and duct. The hood method can be used simultaneously with that for the determination of thermal parameters, (procedures for thermal parameters are described in Section 3.4.2). This has the added advantage of enabling simultaneous measurements of emissions and thermal parameters in a systematic and standard manner [Zhang et al., 1999].

Figure 14: Schematic illustration of the experimental dilution set-up for the SeTAR dilutor, showing the mixing point (A) and the sampling point (B)

[Not drawn to scale]

The sampling configuration for gases included, in sequence, a stainless steel channel, a filter holder, and a flue gas analyser (Testo® 350XL/454) for the undiluted flue gas channel. For the diluted channel, the sampling configuration included, in sequence, the dilution system, a Teflon tube channel, and a flow splitter to take gas samples to the DustTrak aerosol monitor and to a second Testo® flue gas analyser. The Testo® measures CO₂, CO, NOₓ, NO₂, H₂, H₂S, S, SO₂ and O₂. The monitor is equipped with measurement modules for O₂, CO, NO and NO₂ as standard. In addition to this, measurement modules for CₓHᵧ, NOₓ, CO, CO₂, SO₂, H₂S or CO₂ by infrared absorption are optionally available. The monitor uses electrochemical cells for CₓHᵧ, H₂S and NOₓ gas measurements. CO₂ is determined using a non-dispersive infrared cell and is normally depicted as CO₂ IR. Oxygen balance is used for the calculation of excess air.

The Testo® XL 350/454 comprises a control unit, an attached box with gas analysis cells and an integrated differential pressure probe. Up to six measuring channels can be shown simultaneously on
the graphic display and the unit is able to save up to 250,000 readings. This enables documentation and analysis to be made on site with an integrated printer. The measurement data can be stored in the system’s internal memory or it can be transferred to a computer via the serial interface.

The flue gas is drawn into the flue gas probe when the gas pump is started manually or automatically. The measuring gas is suddenly cooled to 4–8°C to precipitate condensates, with minimal absorption of NO₂ and SO₂. The unit is equipped with a Peltier gas box, which has a peristaltic hose pump for the controlled removal of condensate, and a fresh air valve for providing automatic zero-calibrations during long-term measurements. The dry gas passes through a particle filter, which traps particles before the gas passes through the sensors.

The minimum system requirements for Testo® software include a PC with operating system Microsoft Windows 95® or higher, CD-ROM drive, Pentium 100 MHz, 32 MB Ram, 15 MB unused hard drive capacity, an available serial interface port (COM) or corresponding adapter for test 1, and USB port in a laptop or corresponding PC module for test 2. The computer is used for both data logging and storage.

**Carbon mass balance method**

For the determination of gaseous emission factors, our system relies on the carbon mass balance method, which has been previously employed for sampling open biomass combustion sources [Ward et al., 1996] and biofuels [Bertschi et al., 2003]. This method relies on the ratio between pollutants and a fuel proxy (e.g. CO plus CO₂) in the exhaust gas to determine an emission factor [Roden et al., 2008; 2006]. This approach requires a representative sample, so multiple points in the plume must be sampled equally, or the entire plume must be collected and well mixed before sampling [Roden et al., 2008]. For our experiments, samples from the braziers were taken at ~1.0 m above the fire so that initial dilution occurred through natural plume rise and entrainment.

**3.4.7 Particle mass concentration**

The particle mass concentration is determined from the unfiltered, diluted air stream. The sampling configuration for particulate matter included the SeTAR dilutor and the particulate monitor (DustTrak DRX 8533 aerosol monitor), connected by Teflon tubing. The DustTrak DRX Model 8533 is a desktop instrument that simultaneously measures size segregated mass fraction concentrations (PM1, PM2.5, PM4, PM10, and Total Particle Mass -TPM) in real time over a wide concentration range (0.001–150 mg m⁻³).

When operating the instrument, aerosol particles are continuously drawn into the sensing chamber using a diaphragm pump. The aerosol stream is split ahead of the sensing chamber and part of it is passed through a HEPA filter before being injected back into chamber around the inlet nozzle as sheath flow. The remaining flow (sample flow) passes directly through the inlet into the sensing chamber where it is illuminated by a sheet of class 1 laser light formed from a laser diode. The emitted laser beam initially passes through a collimating lens, and a cylindrical lens to create a thin sheet of light. The sampled aerosol particles will then scatter this light, upon which a significant
fraction is captured on a gold-coated spherical mirror before it is focused onto a photo-detector. Figure 15 shows a schematic of the aerosol measurement, signal acquisition, and signal processing which occurs in a DustTrak monitor.

**Figure 15: Schematic showing aerosol measurement and signal acquisition processing in the DustTrak DRX model 8533**

[Diagram source: www.tsi.com]

The instrument compensates for coincidence error using dead-time correction algorithms. To reduce mass calculation errors due to particle density and refractive index, the instrument converts particle pulses to aerodynamic size through factory/custom calibrations. An advantage of using the DustTrak DRX monitor is the lack of a need for a size-selective inlet conditioner; PM1, PM2.5, PM4, PM10 and TPM fractions are simultaneously measured without the use of size-selective inlet conditioners.

The unit can be calibrated using gravimetric samples, which require the side-to-side monitoring of the monitor readings, and gravimetric samples to determine the accuracy of mass measurements. For gravimetric analysis, a 37 mm filter cassette sampler is inserted in-line with the aerosol stream at the outlet of the optics chamber (Figure 15) allowing for gravimetric analysis without the need of an external pump and filter holder.

### 3.4.8 Emission factors

In stove analysis, an emission factor (EF) is the term given to a gas concentration that has been normalised for dilution by excess air, to some reference value of residual oxygen [Makonese, 2011]. It is not valid to compare gas emissions from two stoves if each sample has been diluted by a different or unknown quantity of air, which is related to the design or operation of that stove. It is essential to adjust the concentrations in the gas sample by post hoc calculation to a reference dilution, at standard
temperature and pressure, so that the stoves that have high excess air are not rated as ‘cleaner’. The amount of excess air flowing through a stove is quantified (by measurement of the residual oxygen) and then factored out of the emissions measurement to yield a portable figure that makes possible meaningful comparison between stoves.

In this thesis, the term emission factor is defined as concentration of a gas or particulate matter emitted by the stove, expressed in g MJ\(^{-1}\) or mg MJ\(^{-1}\), normalised to 0% excess air (oxygen). This provides the concentrations in undiluted air (i.e. sufficient air to provide stoichiometric combustion). It is common practice to normalise stack emission concentrations to some standard dilution factor. For example, EPA Method 5 stack testing method requires adjustment to 15% residual oxygen content. In the case of non-ducted stove emissions, variable amounts of dilution air cause uncontrolled dilution of the stack gases, hence direct measurement of volume flow rates of primary and post dilution is impractical [Makonese, 2011]. For simplicity in representing the results of mass balance of all emissions from complete and partial combustion of the fuel, we have chosen zero per cent excess air as a reference value for emission factor reporting. Emission factors can also be presented in units grammes of pollutant per kilogramme of fuel consumed (g kg\(^{-1}\))

Emission rates and properties can be impacted by factors such as type and chemical composition of the fuel, ignition method, fuel feeding practice, stove type and design, and combustion temperature [Roden et al., 2008; Rau, 1989; Butcher & Ellenbecker, 1982]. In most of the emission tests, we tested stoves as used by local residents. We preferred beginning each test with a cold stove, as a warm start has the potential to affect the emission rates and properties of a fuel/stove combination. If a stove was in use at the beginning of the test, the user extinguished the burning coal ambers, removed the coals and ash, and then relit the stove after equipment setup and re-calibrations (45–60 min).

**Excess air**

Excess air (EA), denoted by the symbol \(\lambda\) expresses the factor by which the amount of air supplied to the stove is larger than the minimum amount that is theoretically necessary to burn the fuel completely. The air supplied to the stove and passed through the fire may be considered notionally as comprising two components: the quantity of air containing exactly the amount of oxygen needed to combust the fuel; plus the residual air containing oxygen not used. This latter fraction is what is called excess air. In the design and intended operation of stoves, excess air is an important indicator when optimising for low pollution emissions, required fuel burn rate, and high fuel efficiency (minimum unburnt fuel at end of cycle).

Many systems calculate the \(\lambda\) factor based on CO\(_2\) concentrations in the exhaust stream (Equation 51):

\[
\lambda = \frac{CO_{2\text{max}}}{CO_{2\text{meas}}} \quad \text{Equation 54}
\]

where \(CO_{2\text{max}}\) is the maximum possible concentration of CO\(_2\) in the stack and \(CO_{2\text{meas}}\) is the measured concentration of CO\(_2\) in the combustion gases.

Equation 54 can be transformed into the form:
\[ \lambda = \frac{20.95\%}{20.95\% - \text{O}_2\text{meas}} \]  

Equation 55.

where \( \text{O}_2\text{meas} \) is the measured concentration of oxygen in the combustion gases and 20.95\% is the atmospheric concentration of \( \text{O}_2 \).

In other contexts, the term emission factor is used to describe the specific emissions from a stove or other combustion process over a certain period or cycle, for example, the ratio of total quantity of carbon monoxide emitted per ton of fuel burned. This parameter is useful in studies of atmospheric dispersion and ambient air quality. This example of an alternate definition of the term emission factor is a caution that in every report or publication dealing with emissions factors, the exact meaning and mathematical formulation of the term needs to be stated explicitly, to avoid confusion and error [Makonese, 2011].

The SeTAR data calculation sheet uses a chemically balanced approach for the determination of Excess Air (EA). The determination of the total volume of emissions from the fire is affected by the volume of diluting air in the sample. The calculation of the total air demand (\( \lambda \)) is made in the following manner:

\[ \lambda = 1 + \frac{\text{O}_2\text{meas} - \text{O}_2\text{oxid}}{\text{O}_2\text{det} - (\text{O}_2\text{meas} - \text{O}_2\text{oxid})} \]  

Equation 56

where \( \text{O}_2\text{meas} \) is the measured \( \text{O}_2 \); \( \text{O}_2\text{oxid} \) is the \( \text{O}_2 \) required to complete the oxidisation of incompletely burned gases and \( \text{O}_2\text{det} \) is the total \( \text{O}_2 \) in all detected gases. This method can determine \( \lambda \) even when a water gas shift reaction is taking place in the fire (the water gas shift reaction splits water into \( \text{H}_2 \) and \( \text{O} \)).

**Calculating the volume of emissions**

Based on the chemistry of the burned fuel (raw fuel corrected for remaining materials) the stoichiometric volume of the combustion products was estimated. A gas sample was drawn from the emission stream. As many gases as possible are measured using the Testo gas analysers, typically \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{CO} \), \( \text{NO} \), \( \text{H}_2 \), \( \text{H}_2\text{O} \), \( \text{SO}_2 \) and \( \text{H}_2\text{S} \). The value of \( \lambda \) is calculated as in Equation 56. The volumetric concentration of each gas is multiplied by \( \lambda \) to derive a total number of moles from which a total mass of each gas is calculated.

**Determination of energy specific emission factors in [g MJ\(^{-1}\)] or [mg MJ\(^{-1}\)]**

It is possible to convert emissions in ppmv to other units, such as energy specific emission factors referenced to the energy content in the fuel consumed –[g MJ\(^{-1}\)] or [mg MJ\(^{-1}\)]. First, there is a need to determine Net Heat Gained (\( \text{H}_{\text{NET}} \)) from the fuel. This is the heat retained by a cooking vessel during a burn cycle and is expressed in units of MegaJoules [MJ]. It includes the heating of the pot and its contents plus the heat of evaporation of water, but excludes other heat flows through the pot, specifically radiative and convective losses from the pot sides and top.
The mass of detected PM2.5 or PM10 is first multiplied by any dilution applied by the equipment, then multiplied by $\lambda$ to obtain a total mass emitted. This approach is based on the foreknowledge that any missing fuel has been turned into combustion products of some type. This method is able to track and correctly determine the performance of the stove in real time while burning fuels in an inhomogeneous manner, as is often the case with biomass and coal fuels. At a minimum, the standard reporting metrics for the particle mass concentration include mass of PM emitted per MegaJoule$_{\text{NET}}$ of energy delivered into the pot, or mass of PM emitted per MegaJoule$_{\text{NET}}$ of energy delivered from the fire. For example, the mass of CO$_2$, CO, PM2.5 and PM10 in grams; NOx in milligrams emitted during a burn cycle are determined and divided by the net heat gained H$_{\text{NET}}$, yielding emission factors units mass of emissions per net Mega Joule [g MJ$^{-1}$ or mg MJ$^{-1}$]. For example:

$$CO_{\text{EF}} = \frac{CO [g]}{H_{\text{NET}} [MJ]}$$  
Equation 57

$$PM10_{\text{EF}} = \frac{PM10 [g]}{H_{\text{NET}} [MJ]}$$  
Equation 58

$$NOx_{\text{EF}} = \frac{NOx [mg]}{H_{\text{NET}} [MJ]}$$  
Equation 59.

**Determination of emission rates**

Emission rates [g s$^{-1}$] for PM and gaseous emissions were determined, averaged per hour for each hour of a maximum three-hour burn cycle, and also for the entire three-hour cycles. Hourly emission rates were estimated from the maximum number of grams of pollutant emitted during any hour when the release is occurring divided by 3 600 s. Three-hour average emission rates were calculated by dividing the integrated emissions over the first three hours of combustion by 10 800 s.

**Statistical analysis**

An F-test for the null hypothesis that two normal populations have the same variance was used in our data analyses. This test can be used in practice, with care, particularly where a quick check is required, and subject to associated diagnostic checking. We used large alpha levels (at least 0.05) and balanced layouts as the F-Test is relatively robust. The F-Test is used to determine the type of T-test to use (i.e. T-test: Two sample assuming equal variances or T-test: Two sample assuming unequal variances).

A two-tailed student T-test at the 95% confidence level is used for statistical evaluation of the thermal and emissions data. Note that for the purposes of this study, a statistically significant number means that the p-value is less than 5% (p<0.05); a number that is not statistically significant means that the p-value is greater than 5% (p>0.05).

### 3.5 Monitoring of Temperature Profiles in Braziers during Different Burn Cycles

Bed temperatures were measured by introducing 5 mm K-type thermocouples at specific intervals along the depth of the stove as shown in Figure 16. This set up allows one to create temperature profiles, which show the propagation of the combustion front through the packed bed. In the TLUD
fires, the reaction front migrates from the top of the packed-bed downwards, and for the BLUD fires, the combustion front migrates from the bottom of the packed-bed upwards.

Figure 16: Schematic diagram showing the set-up for monitoring temperature profiles in a brazier during different ignition methods. T1, T2, T3, T4, T5 refer to temperature thermocouples

[Not drawn to scale]

3.6 Monitoring of PAHs Emissions

The objective of this section is to show the application of a novel denuder-filter sampling technique for the collection of carbonyl compounds (polycyclic aromatic hydrocarbons) from domestic coal-combustion devices. The approach involves the combined use of two multi-channel silicone rubber traps (178 mm long, 6 mm o.d., containing 22 silicone tubes), separated by a quartz fibre filter for removal of condensed phase (particles) organic matter [Forbes et al., 2012].

3.6.1 Filter and PDMS Trap Preparation

6 mm quartz fibre filter punches were prepared and then placed in a vial to which methanol was added and swirled for one minute before being decanted. The same procedure was repeated with dichloromethane. The cleaned filter punches were then placed in an oven to dry for 30 min at 100°C and were then stored in a desiccator. Quartz was used due to its well-known transparency in the UV-visible region. The fibre punches were used in SEM analysis of the collected particles.

Multi-channel silicone rubber traps were prepared in 178 mm long quartz tubes of 4 mm i.d. and 6 mm o.d., according to the method described by Ortner [1996]. The traps were heat in a GC oven at 300°C for ~24 h, with a hydrogen carrier gas flow of ~60 ml min⁻¹. After use, the traps were reconditioned at 250°C under nitrogen gas flow for two hours in a Gerstel Tube Conditioner (TCI) [Forbes, 2010]. Figure 17 shows a schematic of the multi-channel silicone rubber traps and quartz fibre filter employed in the denuder configuration.
Figure 17: Schematic of the multi-channel silicone rubber traps and quartz fibre filter employed in the denuder configuration
[Figure credit: Forbes et al., 2012]

PDMS was found to absorb at wavelengths below 300 nm, which may affect the excitation process but should not affect the sensitivity of the method as fluorescence emission wavelengths longer than this can be selected for the PAHs of interest [Forbes, 2010]. Gas phase organic emissions were sampled for 10 min onto three polydimethylsiloxane (PDMS) multi-channel rubber traps [Forbes et al., 2012] in series (primary and secondary traps, respectively), starting 5 min after ignition. These samples were taken in addition to denuder samples.

**Experimental Set-up**

In all cases, sampling started about 5 min after ignition. The sampler location was 1 m from the combustion device, in the stream of effluent gases. Air samples were taken by means of a portable sampling pump at a flow rate of 0.5 L min⁻¹ (Figure 18).

Figure 18: Experimental set-up for monitoring of PAH emissions from braziers
[Photo credit: Patricia Forbes]
Teflon tubing connections were used in each case to avoid contamination of the sample by leaching organics into the denuder system, or absorption or reaction on the tubing. After sampling, the traps were end-capped and wrapped in aluminium foil. Samples were then refrigerated prior to analysis by two-dimensional gas chromatography with time-of-flight mass spectrometric detection.

3.6.2 Analysis of PAHs

The analysis was carried out according to methods described by Forbes et al. [2012]. Two-dimensional gas chromatography with time-of-flight mass spectrometric detection (Leco Pegasus 4D GCxGC-TOFMS equipped with an Agilent 6890 GC) was employed in the analysis of thermally desorbed (Gerstel 3 TDS) filter samples (particle associated organic emissions) and silicone rubber traps (gas phase organic emissions). The primary column was a 30 m RTx 5SilMS (0.25 mm id; 0.25 μm film thickness) and the secondary column was a 1.5 m RTx 200 (0.1 mm id; 0.1 μm film thickness). The modulation period was 4 s.

Calibrations were performed by the analysis of 1 μL injections of mixed PAH standard in toluene (1, 2, 10, 20 and 30 ng for naphthalene, and 1, 2, 10, 20 and 40 ng for phenanthrene, anthracene, fluorene, and pyrene) onto blank traps or clean filters [Forbes, 2010].

3.6.3 Limitations of monitoring PAHs from real-world use scenarios

The research is limited to uncontrolled sampling environments and the experiments were carried out in an open environment prone to wind drafts. Drafts are known to affect the combustion efficiency of a fuel/stove combination, and affect the dispersion of emissions, and therefore the sampling efficiency. No efforts were made to repeat the same experiments under controlled environments. The idea behind these experiments was to simulate real-life use scenarios of the heating devices and to monitor what users may be exposed to during the ignition phase, which is normally characterized by high smoke emissions. Monitoring of PAH emissions was carried out during the ignition phase only, which is for the first ten minutes after ignition–no attempt was made to characterize emissions across an entire burn cycle. Results presented herein are considered illustrative and indicative of possible PAH pollutant emissions from coal combustion in selected braziers. Because the experiments were uncontrolled, it was not intended to calculate emission factors for individual PAH compounds; instead, relative peak areas of each compound are reported. Extensive tests comparing the laboratory evaluations with field-based tests is an important future task, but will not be considered in this thesis.

3.7 Electron Microscopy Techniques

Electron microscopy techniques are widely used to image the shape and structure (i.e. morphology) of solid surfaces or particles. By using the reflection (scattering) of electrons instead of light, as in ordinary microscopy, resolution in the nanometre scale can be obtained [Boman, 2005]. In the present work the JSM 5800LV SEM at the University of Pretoria and the Vega3 LM at the University of Johannesburg were used to observe particle morphologies from coal-burning fires. Both instruments were equipped with energy dispersive spectroscopy (EDS), which provides the possibility to analyse
particle chemical compositions. The samples from real-world uses of braziers were collected on quartz fibre filters; samples from laboratory tests were collected on polycarbonate membrane filters using suction sampling.

The three most common modes of operation in SEM analysis are (i) backscattered electron imaging (BSE), (ii) secondary electron imaging (SEI), and (iii) electron dispersive spectroscopy EDS [Kutchko & Kim, 2006]. The SEM is not without its limitations; there is evidence that suggests that the samples under observation in SEM are susceptible to mass loss of adsorbed water or volatiles due to the necessity of operating in vacuum and possible damage by electron beam heating or electrostatic disruption [Gwaze, 2007]. Therefore, only non-volatile particle components can be characterized with the SEM [Chakrabarty et al., 2006]. The influence of the accelerating voltage of the electron beam on the shape on the aerosol particles was characterized by varying the accelerating voltages between 10 and 20 kV. Within this voltage range, there was found to be little or no change in the shape of the aggregates. In this study, a moderate accelerating voltage of 20 kV was used for most images. Compared to lower accelerating voltages (e.g. 10 kV), the use of 20 kV improves imaging of the surface and internal structure of the particles [Chakrabarty et al., 2006].

In addition to particle damage when using the SEM, there is lack of 3D information, which may lead to biases in sizing measurements of particles that could orient on during deposition on the filter material. Gwaze [2007] suggested that it is possible to tilt the sample support and measure particle sizes in several electron beam projections, which can then be computed to particle volumes. However, the author contends that the procedure is rather complex, laborious and tedious; as such, this procedure was not adopted in this study.

Analytical elemental measurements were performed evaluating the X-rays emitted during electron bombardment on particles to determine elements with an atomic number greater than five using EDS. According to Goldstein et al. [1992], the interaction volume of the sample with the energy beam is a function of the atomic number of the sample and the electron beam energy. For accelerating voltages of 15 and 20 kV used in this study, the interaction volume could be of the order of a few micrometres for low atomic number samples, thus negatively biasing bulk analyses of Aitken and accumulation mode size particles [Gwaze, 2007]. The EDS analyses in this study were therefore useful for deriving elemental composition of coarse mode particles.

### 3.7.1 Sample preparation and analysis

Polycarbonate membrane filters with sample particles were cut and tapped onto a double-sided carbon tape mounted on a SEM stub. This mount enables the analyst to determine the particle morphology, external surface structure and external elemental distribution of individual aerosol particles. Filters were coated before sampling, just like in the Gwaze [2007] study, with a thin layer of gold (<10 nm) using an Emitech Sputter Coater in order to enhance contrast in SEM images and minimize electrostatic charging of particles. Some samples were analysed uncoated and we discovered that particles could “jump off” the filter or restructure due to charging, especially at high magnifications.
High magnifications were essential in this study because primary particles could be as small as 20 nm in diameter [Gwaze, 2007].

The elemental composition and morphology were noted for each particle and compiled for each sample. As in the Kutchko & Kim [2006] study, the elemental analysis was performed in a spot mode, in which the beam is localized on a single area manually chosen within the field of view. The EDS is not a quantitative measure of elemental concentration although Kutchko & Kim [2006] are of the opinion that relative amounts can be inferred from relative peak heights.

3.7.2 Electron Microscopy Imaging

Filters were analysed shortly after sampling and on subsequent days. Over the course of the days, there were no observable changes in the morphology of the particles. Aggregates were selected by changing the field of view and following random trajectories on the filter. All particles analysed in the field of view were photographed to avoid operator bias. Magnification was chosen to allocate an individual particle or aggregate to the whole scan area. Output images were acquired with a 1024 x 768 pixels and 256 grey scale levels [Gwaze, 2007].

3.8 Quality Control and System Evaluation

3.8.1 Instrument calibration and calibration of the burn cycle

For each fuel/stove combination, a series of preliminary burn cycles were carried out to standardise procedures and to minimize the natural variability due to differences in operator behaviour. In order to familiarize the operators with the testing procedure and with the characteristics of the stove, these trial runs were conducted repeatedly until a stable mode of operation was established. Thereafter three or more definitive tests were conducted for each fuel/stove combination. After each fuel/stove combination was tested, the probes were cleaned and the pumps and machines checked and zeroed.

Continuous gas and particle monitoring instruments are sent for calibration by the manufacturers prescribed intervals, or at least once in a year (See Appendix A for calibration certificates for gas and particle instruments used in the study), and need to be periodically verified with laboratory standards. Zero and span calibration were performed on all analysers before and after every test run in order to account for small variations in the dilution ratio. For example, the DustTrak DRX was zeroed with filtered air before each test run.

3.8.2 Instrument delay and response times

The response time of monitoring instruments can be affected by the time the exhaust takes to travel from the inlet probe to the instrument and through the sensing volume within the instrument. The instrument response time may vary from test to test depending on the length and diameter of the transfer line and the flow rate. These differences need to be accounted for in order to synchronize the real-time data so that differences in pollutant release time from the source can be examined. In this study, synchronisation of instrument response times to pollutant emissions was carried out according
to the careful steps outlined in Wang et al. [2012]. The time lags were measured before and after a test by sampling smoke from a fire ignition torch lit at the inlet. The system was allowed to run on air for a few minutes first in order to sample ambient air for purposes of obtaining background readings. Then the ignition torch was lit near the inlet of the sampling probe. After the ignition torch was extinguished, the system sampled ambient air for a few more minutes to allow the instrument signals to return to background levels, after which the ignition torch was lit again. These time delays were noted and then corrected for in the spreadsheet when calculating pollutant emission factors for different fires. The particulate matter analyser (DustTrak DRX 8533) model was found to have the fastest response time of less than 5 s compared to 15–30 s for the Testo XL gas analysers.

3.8.3 Quality control for the dilution system

In order to ensure repeatability and reproducibility of results, a precise set of standard operating procedures were followed before, during, and after testing. Before tests were conducted, the sampling dilution system components were cleaned, assembled, and tested for leaks to prevent contamination from the surrounding air. A calibration was performed to check the accuracy of the flow rates through each of the critical flow orifices. The sampling dilution system was cleaned prior to testing to minimize pre-existing organic and metal compounds, including the use of high power compressed air and water to remove large particles. The collection trains, including the stainless steel piping and sampling nozzles, were cleaned with soap and water and air dried with compressed air. Similar to Liu et al. [2008], the sampling trains and pipes used to collect trace metals were rinsed in a 5% HNO₃ solution to detach contaminants and then rinsed with water followed by acetone.

System reproducibility

System reproducibility and the impact of the sampling methodology were examined with tests of three identically designed, improved paraffin cookstoves measured at the SeTAR Centre, University of Johannesburg under similar operating conditions. For these tests, three with the direct sampling probe and three with the dilution sampling system, the coefficient of variation was found to be 10% for PM emission factors and 7% for CO emission factors, respectively. Instantaneous dilution levels across the entire burn cycle were multiplied with the instantaneous emission rates to convert the rates to equivalent exhaust concentrations [Lipsky & Robinson, 2005].

3.8.4 Quality control for gas sampling and monitoring procedure

The sum of the emission factor values of the oxygen-containing carbon gases (CO₂ and CO); represented by \([\Sigma \text{Carbon (EF)}]\) is the sum of \([\text{CO (EF)}]\) and \([\text{CO}_2 (EF)]\). The total oxygen, represented by \([\Sigma \text{O}_2 \text{ in all gases}]\) can be used as an instrument and data quality check. The pump flow rate was monitored (Figure 19).
Figure 19: Data quality check: total oxygen (ΣO₂), total carbon (ΣCarbon EF), and pump flow rate (instrument check)

The two Σ lines (total carbon and total oxygen) should track each other. With low hydrogen fuels, they overlap (i.e. no consumption of oxygen to form H₂O. H₂O is a component that was not monitored). Any departures from parallel tracking are indicators of deviant instrument behaviour and reason to discontinue the test or discard a particular data set. On the left axis is the sum of all detected oxygen (expressed as O₂ equivalent) and the sum of the carbon (EF) values. The instantaneous ΣO₂ level should be constant if the fuel is burned at a uniform rate and if all the combustion products are detected. The sum of the (EF) values of all oxygen-containing gases will be equal to the background atmospheric oxygen level of 209,480 ppm (and any O₂ released from the fuel at that time) [Makonese, 2011]. If the H₂O formed from combustion of any hydrogen in the fuel, the [ΣO₂ EF] value will be low by that amount. [H₂O (EF)] is not measured and not included in the calculation. Under poor combustion conditions, the water-shift gas reaction (a chemical reaction in which carbon monoxide reacts with water vapour to form carbon dioxide and hydrogen) can take place creating additional CO₂ without using any oxygen from the air supply. This CO₂ is detected and the additional oxygen added to the derived [ΣO₂]. This procedure uses an oxygen balance model at the beginning and end of the calculations to detect deviations from the expected values caused by possible instrument or calculation errors [Makonese, 2011].

3.8.5 Quality control during PAHs analysis

Quality control and quality assurance techniques, measurements, and materials used in these experiments are given in Section 3.5. The repeatability and sensitivity of the method (i.e. multichannel silicone rubber traps) employed for sampling PAHs from coal fires in this study is presented in more detail in Forbes [2010].
3.8.6 Calibration of the SEM

Calibration of the SEM was done similarly, to what is reported in Gwaze [2007]. The calibration of the instrument was verified by measuring standard grids of alternating SiO₂/Si surfaces with lateral (xy) dimensions between 0.9 and 15 µm, and polystyrene latex (PSL) spheres of diameters of 0.126 ± 0.001 µm and 0.600 ± 0.005 µm. Deviations between measured sizes of both the standard grids and PSL spheres and nominal specifications were below 7%. The X-ray detector was calibrated regularly with Cu standard sample.
CHAPTER FOUR

This chapter presents and discusses a motivation for the SeTAR dilutor, which was used in the characterisation of gaseous and particle emissions from residential coal combustion devices. Results from gas and particulate matter emissions from informal coal burning devices are presented in detail as examples of typical emissions performance results. Polycyclic aromatic hydrocarbon emissions from three informal field stoves are presented in some detail. SEM characterisation of condensed matter emissions from coal-burning devices is presented in detail as a function of ventilation rates and ignition method.

4. Results and Discussion

4.1 Introduction

In this chapter, we report on the results of the various experimental sections of this thesis, starting with a report on the development of what we have termed the SeTAR dilutor. Section 4.2 presents a motivation for the development of the SeTAR dilutor and a description of the design components and assembly of the system. This dilution system is an enabling component that facilitates measurements of very high concentration smoke, such as from coal-fired braziers that would otherwise saturate the particulate analysers.

Subsequent sections present results of gas and particulate emission performance of a range of coal burning braziers. Several other residential coal-fuelled stoves have been evaluated and presented in technical reports to clients; however, evaluation of these other stove designs is outside the scope of this thesis.

Polycyclic aromatic hydrocarbons (PAH) emissions were monitored from real-world uses of coal braziers for a few selected braziers–illustrative results are presented and discussed as a sub-section. We present results from microscopic examination of smoke particles from a few selected braziers. The aim of this section is to study and characterize individual particles from domestic coal combustion in typical residential braziers. The general approach in this study is similar to that of Buseck and Pósfai [1999], namely to emphasize the individual particles because the radiative, environmental, and health effects of particles depend on their speciation and morphology, rather than on their average bulk compositions. In this section, particles contained in the smouldering and flaming-phase of residential coal fires are investigated, and a report on the occurrence of giant soot particles presented. Based on the unique morphological properties of giant soot particles, we discuss their possible formation mechanism. We could not analyse for all test conditions in the brazier stoves due to the complexity and time-consuming nature of SEM analyses.

Thermal performance evaluation of the stove and the cooking efficiency are important topics to be discussed when doing fuel/stove combinations. However, these parameters are not discussed in detail.
in this thesis, save for sections that deal with effects of selected parameters (fuel moisture content, ventilation rates, fuel type) on the performance of coal braziers. Detailed analysis of thermal and cooking efficiencies are presented in a parallel thesis [Masekameni, 2015].

4.2 The SeTAR Dilution System

An appropriate dilution sampler for residential coal combustion appliances was designed, constructed and evaluated. The design of the SeTAR dilutor followed the basic principles used in earlier units, for example, built by Hildemann et al. [1989], the Desert Research Institute (DRI) and the Caltech design by Lipsky et al. [2002]. The design components of the dilution system include the following:

- A one-step dilution/mixing section using a parallel jet flow system to reduce the mixing time required for dilution ratios above 20:1;
- A dilution channel to allow the ageing and cooling of the mixed exhaust for at least 10 s;
- A high-efficiency particulate air filter canister to remove fine particles and VOCs from ambient dilution air to minimize contamination; and
- Accessible ports for sampling gases and particle emissions.

Combustion products are drawn from the exhaust duct through an inlet line heated to the exhaust temperature. The combustion products are then turbulently mixed with dry compressed air that has passed through a HEPA filter and an activated carbon bed in the dilution tunnel, through a venturi nozzle into a 22 mm diameter, 900 mm long tube. The flow rate of both the dilution air into the tunnel and the combustion products through the inlet line are controlled by manually operated rotameters and needle valves. At the end of the dilution tunnel, measurement ports draw the dilution mixture to a gas analyser (Testo® 350XL/454 flue gas analyser, which measures CO₂, CO, NOx, H₂, and O₂), a particle analyser (TSI DustTrak DRX model 8533, which measure particle mass in the range PM1, PM2.5, PM4 and PM10). The ports at the end of the dilution tunnel are considered to have zero residence time [Lipsky & Robinson, 2005]. All parts of the sampler in contact with the exhaust sample for gas analysis and are made of stainless steel and Teflon tubes to minimize reactions on the tube walls. Figure 20 shows a sectioned view of the SeTAR dilutor. Table 6 lists the specifications for the SeTAR dilution sampler and compares them with other recent designs.

![Figure 20: Sectioned view of the SeTAR dilutor assembly](image)

[Drawing credit: Crispin Pemberton-Pigott]
Table 6: Illustrative features of some recent dilution sampler designs against the SeTAR dilution sampler

<table>
<thead>
<tr>
<th>Unit</th>
<th>Sampler diam (cm)</th>
<th>Mixing length (diam)</th>
<th>Nominal residence time (sec)</th>
<th>Dilution Ratio</th>
<th>Mixing section Reynolds No.</th>
<th>Ageing section diam (cm)</th>
<th>Ageing section Reynolds No.</th>
<th>PM2.5 Cyclone in stack</th>
<th>PM2.5 cyclone after ageing</th>
<th>Sampler Material</th>
<th>Portable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caltecha</td>
<td>15</td>
<td>10</td>
<td>2 - 180</td>
<td>25:1 – 100:1</td>
<td>10 000</td>
<td>46</td>
<td>700</td>
<td>Yes</td>
<td>Yes</td>
<td>Stainless steel/ Teflon</td>
<td>Luggable</td>
</tr>
<tr>
<td>CARBb</td>
<td>15</td>
<td>12</td>
<td>1 - 5</td>
<td>1-5:10:1 – 1-50:1</td>
<td>10 000</td>
<td>N/A</td>
<td>N/A</td>
<td>No</td>
<td>No</td>
<td>Teflon-coated stainless steel</td>
<td>Yes</td>
</tr>
<tr>
<td>DRIc</td>
<td>15</td>
<td>18</td>
<td>~ 80</td>
<td>40:1 – 50:1</td>
<td>5 500</td>
<td>20</td>
<td>800</td>
<td>Yes</td>
<td>Yes</td>
<td>Stainless steel</td>
<td>Luggable</td>
</tr>
<tr>
<td>CDSd</td>
<td>20</td>
<td>1</td>
<td>10</td>
<td>15:1 – 50:1</td>
<td>5 500</td>
<td>20</td>
<td>800</td>
<td>Yes</td>
<td>Yes</td>
<td>Stainless steel</td>
<td>Yes</td>
</tr>
<tr>
<td>CMUE</td>
<td>15</td>
<td>15</td>
<td>0 - 720</td>
<td>20:1 – 200:1</td>
<td>3 000 – 13 000</td>
<td>No data</td>
<td>No data</td>
<td>Yes</td>
<td>Yes</td>
<td>Stainless steel</td>
<td>Luggable</td>
</tr>
<tr>
<td>CAN MET3f</td>
<td>5</td>
<td>40</td>
<td>10 - 40</td>
<td>40:1 – 80:1</td>
<td>11 000</td>
<td>27</td>
<td>170</td>
<td>Yes</td>
<td>Yes</td>
<td>Teflon-coated stainless steel</td>
<td>Yes</td>
</tr>
<tr>
<td>PEPRI-CANg</td>
<td>14.5</td>
<td>18</td>
<td>90</td>
<td>30:1(25:1 – 40:1)</td>
<td>11 000</td>
<td>27</td>
<td>170</td>
<td>Yes</td>
<td>Yes</td>
<td>Teflon-coated stainless steel</td>
<td>Luggable</td>
</tr>
<tr>
<td>EPAh</td>
<td>14</td>
<td>3.2</td>
<td>1</td>
<td>20:1 – 40:1</td>
<td>No data</td>
<td>N/A</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
<td>Teflon-coated aluminium and stainless steel</td>
<td>Yes</td>
</tr>
<tr>
<td>SeTARIi</td>
<td>2.2</td>
<td>2.2</td>
<td>2 - 20</td>
<td>2:1 - 150:1</td>
<td>No data</td>
<td>2.2</td>
<td>No data</td>
<td>No</td>
<td>No</td>
<td>Stainless steel/ Teflon</td>
<td>Yes</td>
</tr>
</tbody>
</table>

[Adopted and adapted from: Chang & England, 2004].
The overall goal of the SeTAR dilution sampler is to provide rapid mixing of the exhaust sample with the dilution air. With the exception of the EPA compact sampler, the other dilution systems require longer residence times for mixing with similar dilution ratios. The longer residence times require larger ageing chambers and bulkier units [England et al., 2007:67]. The SeTAR dilution sampler is similar in characteristics to the Caltech compact unit, which has, as an additional feature, two PM2.5 cyclones, one in stack at the sampling point and the second after the mixing and ageing tunnel. The Caltech samplers are equipped with conventional heated sampling stainless steel probes for the stack equipped with thermocouples to measure stack gas temperature.

For the SeTAR dilutor, the stack exhaust passes through a venturi constriction into the mixing tunnel. The mixing tunnel was designed to fully mix the undiluted stack gas and dilution air with minimal back mixing and with a low-pressure drop. The SeTAR design avoids high concentrations of exhaust gas sample along the walls to minimize wall losses and presents a relatively uniform velocity profile to the outlet ports where the stack gas is channelled to gas and particulate analysers for real-time monitoring. Wall losses in the SeTAR design were assumed to be similar to, or smaller than, those determined for larger samplers such as the Hildemann et al. [1989] dilution sampler; the SeTAR (straight) sampling section is 900 mm long compared with the curved, longer sampling section, estimated to be 1 800 mm in the England et al. [2007] dilution system.

Robustness of the dilution system

The SeTAR design is smaller than the bulkier laboratory-based units; it was constructed in modular units of less than 7 kg each for portability. According to England et al. [2007], the EPA Method 5 particulate sampler weighs ~113 kg. The SeTAR dilution sampler weighs ~5 kg plus ~40 kg of ancillary equipment (i.e. sampling pumps, analysers and a computer device for data capturing). Thus, the SeTAR design is relatively easy to handle; such small systems can be positioned easily in stack sampling locations, and the relatively lower weight allows them to be used on temporary scaffolding or space-restricted permanent platforms.

The SeTAR design is designed for easy assembly and disassembly to enable the operator to perform maintenance checks on the system. The design allows the operator to disassemble it to obtain filter samples and to recover deposits from the probe and internal surfaces.

Cost of fabricating the system

The current system is cheap to fabricate compared to dilution systems available on the open market, with some having price tags of more than R 50 000 per unit. The SeTAR dilutor is fabricated from steel at a cost of less than R 5 000 and can be easily assembled in the laboratory without requiring great expertise.

4.2.1 Variable dilution in the SeTAR dilution system

The majority of dilution samplers reported in literature and some currently on the market do not provide the option of varying the dilution during sampling. For example, the Palas VKL-10 model is a commercially available dilution system with a fixed dilution factor of 10. This dilution system is used
for powder and dust particles, with size ranges up to 20 µm. Dilution factors of up to 1:100 000 are achieved by cascading several VKL systems.

The SeTAR dilutor was designed to have a variable dilution system, which allows the operator to change the dilution ratio as required during normal sampling procedures. The conditions and variations in the current SeTAR dilutor with a lower variable dilution ratio (2 to 8 times) and ‘somewhat’ longer residence time (~20 s) are assumed to be appropriate to closely simulate conditions for residential coal combustion emissions. To minimize potential recovery losses (emanating from low temperature without water condensation) and maximize the detection possibilities (i.e. lowest detectable dilution rate), sampling at 45 ± 5°C with a variable dilution ratio of 2 to 8 times was determined to be the robust and applicable sampling conditions in the present emission sampling set-up. However, in situations where the smoke emitted from the tested devices was high (especially during the ignition and pyrolysis phase of BLUD fires), the dilution ratio was varied up to 120 times to avoid deposition of tarry condensates in the sampling channels and the inner surfaces of the particle analyser.

Emissions from braziers are typically high during the ignition and pyrolization phase of combustion and if the dilution ratio is not adjusted accordingly, there is a risk of clogging the sampling channels leading to gas sensors in the gas analysers and overloading the particle detection system. Consequently, the present dilution system has a variable dilution system, which can be adjusted at any given time during the course of the experiments. Figure 21 shows a time series graph of the dilution ratio and total suspended particulate matter (TSP) during a typical brazier fire. Notice how the trend for the particulate matter emissions follows closely the dilution ratio. After the pyrolization phase, the dilution ratio is lowered and kept constant at between two and ten times for the rest of the test. A minimum dilution ratio of 2 times is selected for small appliances that burn liquid fuels and some pellet stoves. For wood stoves and coal stoves, a dilution ratio of seven times is selected. However, this depends on the manner in which the fire progresses, sometimes requiring a higher dilution of ten times if the smoke emissions are still high but not high enough to overload the detection systems.

Figure 21: Time series graph of TSP [mg m⁻³] and dilution ratio in a typical brazier fire
The present SeTAR dilutor for residential coal combustion appliances was shown to be an appropriate sampling set-up for residential coal fires. A suite of coal braziers were evaluated for emissions performance using the dilution system (with related testing equipment) to illustrate how the system can be used to understand residential coal combustion processes.

4.3 Gas Emissions from Residential Coal Combustion

The general observations made during both fire ignition methods are as follows. For the BLUD method, when the kindling was lit the coal immediately began to give off sulphurous odours and dense whitish/yellowish smoke—a consequence of devolatilized organic matter that had not reached combustion temperature or had insufficient oxygen to oxidise fully. A few minutes elapsed before the coal could be considered ignited—taken as parts of the lowest lumps of coal glowing visibly red. However, the thick white smoke continued for up to thirty minutes as volatiles were evolved from the gradually heated coal above the rising combustion front. For the TLUD ignition method, there was considerably less smoke, with high flames above the coal bed resulting from ignition of the evolved devolatilized organic matter passing through the descending combustion front, with homogenous phase combustion continuing in the rising gas mixture above the coal bed.

Preliminary experiments on domestic coal burning braziers using the BLUD method showed that particulate matter emissions during the ignition phase are high compared to the pyrolysis and ‘coking’ phases of combustion (~80 times higher). Emission of particulate matter immediately ignition of the wood and charcoal can be up to 50 times higher than during later phases of combustion [Bond et al. 2002].

4.3.1 Gas emission factors for lab-stoves using D-grade coal

Gas emission factors for the laboratory designed stoves, using D-grade coal, for top-lit and bottom-lit ignition methods are presented in Table 7, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion cycle, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

When comparing the ignition methods, results show that there are no significant difference (p>0.05) CO, CO\textsubscript{2} and NOx emissions (Table 7). This implies that the fire-ignition method may not affect the combustion characteristics of CO, CO\textsubscript{2} and NOx in the experimental devices tested. Results show that there are no statistically significant differences in NOx emissions when varying the ignition method, although there is an average 16% decrease in the emissions for the TLUD method. Our results for NOx are expected; it is expected that NOx emissions do not vary significantly with the ignition method, when other parameters are held constant. Total NOx emissions are a function of the combustion temperatures and the residence time of nitrogen at that temperature. Fuel NOx is formed mainly from nitrogen in the fuel. At high temperatures above 1 200°C and at standard atmospheric pressure, molecular nitrogen (N\textsubscript{2}) and oxygen (O\textsubscript{2}) in the combustion air disassociate into their atomic states and participate in the Zeldovich mechanism (see section 2.3.6).
Table 7: Gas emission factors for the lab-designed coal braziers using D-grade coal, for the TLUD and the BLUD ignition methods

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>BLUD Method</th>
<th>TLUD Method</th>
<th>Statistical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission Factors</td>
<td>Stdev</td>
<td>Emission Factors</td>
<td>Stdev</td>
</tr>
<tr>
<td>CO</td>
<td>High</td>
<td>4.5 [g MJ⁻¹]</td>
<td>4.6 [g MJ⁻¹]</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>6.2 [g MJ⁻¹]</td>
<td>5.0 [g MJ⁻¹]</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>6.4 [g MJ⁻¹]</td>
<td>5.7 [g MJ⁻¹]</td>
<td>-11</td>
</tr>
<tr>
<td>CO₂</td>
<td>High</td>
<td>98 [mg MJ⁻¹]</td>
<td>99 [mg MJ⁻¹]</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>98 [mg MJ⁻¹]</td>
<td>96 [mg MJ⁻¹]</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>97 [mg MJ⁻¹]</td>
<td>102 [mg MJ⁻¹]</td>
<td>5</td>
</tr>
<tr>
<td>NOₓ</td>
<td>High</td>
<td>149 [mg MJ⁻¹]</td>
<td>126 [mg MJ⁻¹]</td>
<td>-16</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>118 [mg MJ⁻¹]</td>
<td>99 [mg MJ⁻¹]</td>
<td>-16</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>87 [mg MJ⁻¹]</td>
<td>75 [mg MJ⁻¹]</td>
<td>-13</td>
</tr>
</tbody>
</table>

CO₂ emissions do not show significant differences with a change in the ignition method. This is because CO₂ emissions are dependent on the carbon content of the coal, and since the fuel was taken from the same batch, no change in total CO₂ emissions is expected. CO is influenced by poor combustion conditions during initial phases of pyrolyzation, but the majority of CO arises during coking combustion (Figure 22: from 90 minutes).

Figure 22: Typical CO [ppm] time series plot from a TLUD ignition method, for the low ventilation, field brazier
4.3.2 Gas emission factors from field stoves using D-grade coal

Gas emission factors for the field designed stoves, using D-grade coal, for TLUD and BLUD ignition methods are presented in Table 8, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion cycle, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

Results show that there is no statistically significant difference between the TLUD method and the BLUD method for the CO emission factors at high and medium ventilation rates (p>0.05). However, there was a significant difference in CO EF between the fire-ignition methods at low ventilation rates (Table 8). At this ventilation rate, there is a 20% increase in CO when using the TLUD method. This result is rather counterintuitive—it is expected that CO emissions will increase with poor ventilation rates (typical of BLUD fires). In the absence of sufficient oxygen, CO$_2$ is reduced to CO. Thus, a lack of oxygen results in smouldering combustion conditions that favour emission of products of incomplete combustion, including CO. Further detailed explanations need to be sought to explain this anomaly. CO$_2$ EFs do not show any significant differences between fire-ignition methods as expected. The explanation for this result is given in the section 4.3.1.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>Emission Factors [g MJ$^{-1}$]</th>
<th>Stdev</th>
<th>Emission Factors [g MJ$^{-1}$]</th>
<th>Stdev</th>
<th>% diff. between BLUD and TLUD</th>
<th>T-Stat</th>
<th>P-Value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>High</td>
<td>4.1</td>
<td>0.3</td>
<td>4.0</td>
<td>0.2</td>
<td>-3%</td>
<td>1</td>
<td>0.568</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>4.2</td>
<td>0.4</td>
<td>4.1</td>
<td>0.4</td>
<td>-4%</td>
<td>1</td>
<td>0.567</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>4.6</td>
<td>0.3</td>
<td>5.5</td>
<td>0.2</td>
<td>20%</td>
<td>4</td>
<td>0.017</td>
<td>Yes</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>High</td>
<td>102</td>
<td>4</td>
<td>100</td>
<td>6</td>
<td>-2%</td>
<td>1</td>
<td>0.615</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>102</td>
<td>5</td>
<td>99</td>
<td>3</td>
<td>-3%</td>
<td>1</td>
<td>0.489</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>98</td>
<td>6</td>
<td>101</td>
<td>5</td>
<td>2%</td>
<td>0</td>
<td>0.652</td>
<td>No</td>
</tr>
<tr>
<td>NOx</td>
<td>High</td>
<td>195</td>
<td>8</td>
<td>168</td>
<td>10</td>
<td>-14%</td>
<td>4</td>
<td>0.021</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>188</td>
<td>10</td>
<td>163</td>
<td>4</td>
<td>-13%</td>
<td>4</td>
<td>0.015</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>187</td>
<td>11</td>
<td>161</td>
<td>9</td>
<td>-14%</td>
<td>3</td>
<td>0.036</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Emission factors of NOx show statistically significant differences between ignition methods. The use of the TLUD method resulted in a 13% decrease in NOx (Table 8). These results are rather counterintuitive as NOx emissions are expected not to change with a change in the ignition method. As such further explanations need to be sought.
4.3.3 Gas emission factors from field stoves using A-grade coal

Gas emission factors for the field designed stoves, using A-grade coal, for TLUD and BLUD ignition methods are presented in Table 9, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion cycle, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

Results show that there is no statistically significant difference (p>0.05) in the CO EF at the high and medium ventilation rates, between fire-ignition methods. However, there is a statistically significant (p<0.05) difference in the CO EF at low ventilation rates between the BLUD method to the TLUD ignition method (Table 9), with a 17% increase in CO when using the TLUD method. There is no statistically significant difference (p>0.05) in CO\textsubscript{2} emissions between the fire ignition methods across ventilation rates. Emissions of NO\textsubscript{x} are not significantly different between the fire ignition methods at the low and medium ventilation rates. However, there is a statistically significant difference (p<0.05) in the NO\textsubscript{x} emission factors between the BLUD method and the TLUD method at high ventilation rates. Emissions of NO\textsubscript{x} at high ventilation rates, when employing the BLUD method, were five-fold higher compared to the TLUD method (Table 9). This indicates that when using the field braziers, high ventilation rates may have an effect on the combustion characteristics of NO\textsubscript{x} emissions.

A comparison of fuel quality (A-grade and D-grade coals) effects on emission factors is presented in Section 4.5.3.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>BLUD Method</th>
<th>Emission Factors [g MJ\textsuperscript{-1}]</th>
<th>Stdev [g MJ\textsuperscript{-1}]</th>
<th>TLUD Method</th>
<th>Emission Factors [g MJ\textsuperscript{-1}]</th>
<th>Stdev [g MJ\textsuperscript{-1}]</th>
<th>% diff. between BLUD and TLUD</th>
<th>Statistical Analysis</th>
</tr>
</thead>
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4.3.4 Average emission rates from selected coal-burning braziers

The emission rates of CO, CO$_2$ and PM10 for selected braziers with three different ventilation rates, using D-grade coal, were calculated from measurements using the TLUD and BLUD ignition methods. Knowing the burn rate of the fuel (mass loss) and concentrations of the exhaust components, we determined the exhaust emission rates during the operation of the braziers, per hour of operation (Table 10) and for the full three-hour combustion cycle (Table 11). The emission rates are expressed in units [g s$^{-1}$], as required by dispersion model input specifications. Averages of three tests are given together with the standard deviation. Highest emission rates occur in the first hour of combustion (ignition and pyrolysis phases) compared to the second and third hours, associated with volatiles that are driven off from the kindling and during initial heating of the coal. Once all the volatiles are driven off, the emission rates decrease considerably, reaching lowest levels during last hour of the three-hour combustion cycle. In constructing realistic emission patterns for dispersion modelling of domestic combustion, the diurnal time evolution of emissions becomes an important factor to obtain representative dispersion patterns. Such hourly emission factors can be adapted to the lifestyle patterns of the modelled communities when conducting health risk assessments based on dispersion modelling and exposure assessments.

Table 11 presents a summary of three-hour (full burn cycle) emission rates for lab-designed and field-obtained braziers for each ventilation rate using the BLUD and the TLUD fire ignition methods, and the combined average emission rate over the three ventilation rates. There are no differences in the combined average CO$_2$ emission rates for the two ignition methods and between the lab and field stoves. The combined average CO$_2$ emission rates are determined in the range 0.54–0.64 g s$^{-1}$. There are differences in the combined average CO emission rates between the stoves and the ignition methods. The combined average CO emission rates are determined in the rage 0.20–0.26 g s$^{-1}$. The combined average PM10 emission rates are determined in the range 0.0028–0.012 g s$^{-1}$ (Table 11).

The data presented in Table 10 and Table 11 are useful for short-term modelling of pollutants where one-hour average emission rates are required inputs for standard dispersion models. Source input data requirements for air dispersion modelling include specific mass emission rates; physical stack measurements e.g. diameter, stack height, exit velocity and temperature of the exhaust gases, and dry and wet deposition settling parameters for PM. For domestic sources that are too numerous to model individually, emissions are treated as area sources, requiring a knowledge of the source density [number of homes/emission points per km$^2$] and the emission rate per source [g s$^{-1}$]. The source density can be derived from remote sensing images and GIS methods, or from census data. However, up to now there has been no systematic study to characterize emissions from a range of domestic coal stoves and braziers, including variability of stove design, fuel quality, and stage of the burn or user behaviour. Emission values presented in Table 10 and Table 11 may be used to construct better area source emission estimates than have been available up to now, in the absence of reliable emission factors of individual coal combustion devices, and the time variations of these emissions.
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<th>CO(_2) [g s(^{-1})]</th>
<th>Stdev [g s(^{-1})]</th>
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<td>Field</td>
<td>Avg</td>
<td>3.75</td>
<td>0.37</td>
<td>0.64</td>
<td>0.06</td>
<td>0.025</td>
<td>0.0029</td>
<td>1.2E-02</td>
<td>1.7E-03</td>
</tr>
<tr>
<td><strong>TLUD</strong></td>
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<td>Min</td>
<td>3.88</td>
<td>0.32</td>
<td>0.64</td>
<td>0.06</td>
<td>0.027</td>
<td>0.0027</td>
<td>4.2E-03</td>
<td>3.6E-04</td>
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<td></td>
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<td>Med</td>
<td>3.63</td>
<td>0.43</td>
<td>0.63</td>
<td>0.07</td>
<td>0.028</td>
<td>0.0037</td>
<td>3.8E-03</td>
<td>5.5E-04</td>
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<td></td>
<td>Max</td>
<td>3.67</td>
<td>0.59</td>
<td>0.41</td>
<td>0.09</td>
<td>0.022</td>
<td>0.0020</td>
<td>7.8E-04</td>
<td>3.4E-04</td>
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<tr>
<td></td>
<td>Field</td>
<td>Avg</td>
<td>3.73</td>
<td>0.45</td>
<td>0.56</td>
<td>0.08</td>
<td>0.026</td>
<td>0.0028</td>
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<td>4.2E-04</td>
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<tr>
<td></td>
<td></td>
<td>Min</td>
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<td>0.46</td>
<td>0.55</td>
<td>0.08</td>
<td>0.020</td>
<td>0.0037</td>
<td>4.7E-03</td>
<td>6.6E-04</td>
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<tr>
<td></td>
<td></td>
<td>Med</td>
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<td>0.51</td>
<td>0.06</td>
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<td>0.0021</td>
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<tr>
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<td>Max</td>
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<td>0.31</td>
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<td>0.05</td>
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</tr>
<tr>
<td></td>
<td>Field</td>
<td>Avg</td>
<td>3.04</td>
<td>0.37</td>
<td>0.50</td>
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<td>0.023</td>
<td>0.0026</td>
<td>2.8E-03</td>
<td>3.6E-04</td>
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</tbody>
</table>

4.3.5 Application of multi-channel silicone rubber traps in monitoring of PAH emissions from residential coal combustion

The effect of the fire-ignition method and ventilation rates on polycyclic aromatic hydrocarbon (PAH) emissions was investigated for the field braziers. Results presented herein are considered illustrative and indicative of possible PAH pollutant emissions from coal combustion in selected braziers. Because the sampling was uncontrolled (i.e. sampled in the open atmosphere rather than a capture hood), it was not intended to calculate emission factors for individual PAH compounds; instead only species and relative peak areas of PAHs are reported, which illustrate the relative abundances of each PAH compound in the sample.

**Observations and analytical results**

Much visible smoke was produced from the fire using the traditional BLUD method compared to the TLUD fire ignition method. Figure 23 shows relative peak areas of gas phase PAH emissions from the TLUD method using a high ventilation brazier; naphthalene, fluorene and phenanthrene appear to be predominant PAHs. Naphthalene had the highest peak area, followed by phenanthrene and fluorene with almost identical peak areas.
Figure 23: Gas phase PAH emissions detected on primary and secondary traps from a high ventilation using the TLUD ignition method

Figure 24 presents normalized PAH emissions from the high ventilation TLUD results presented in Figure 23. Results show that relative to naphthalene, fluorene and phenanthrene have similar abundance and are lower than naphthalene by a factor of two. Anthracene and fluoranthene are on average five times lower compared to naphthalene, whilst acenaphthene and pyrene are ten-fold lower relative to naphthalene.

Figure 25 shows relative emissions of PAHs from the BLUD fire-ignition method. Again, naphthalene, fluorene and phenanthrene seem to be dominant PAH emissions from this ignition method. In contrast to the TLUD, phenanthrene shows the highest peak area, followed by fluorene and naphthalene. It is evident upon comparing the peak areas from both ignition methods (Figure 23 & Figure 25) that higher level of gas phase PAHs and PAH derivatives were collected when employing the traditional fire ignition technique. This could be because of different temperature profiles during ignition.
Figure 24: Normalized gas phase PAH emissions detected on primary and secondary traps from a high ventilation case using the TLUD ignition method.

Figure 25: Gas phase PAH emissions detected on primary and secondary traps from the high ventilation brazier using the BLUD ignition method.

Figure 26 presents normalized PAH emissions from a high ventilation BLUD ignition method. In contrast to the TLUD ignition method profile shown in Figure 24, fluorene and phenanthrene are the dominant PAHs relative to naphthalene. Relative to naphthalene, acenaphthylene and pyrene are ten-fold lower; while acenaphthene and anthracene are five-fold lower. With the emissions normalized to naphthalene, the high ventilation BLUD ignition method shows a different profile to the high ventilation TLUD ignition method.
Emissions of PAHs from a low ventilation brazier showed a different profile compared to the high ventilation for both fire ignition methods. The dominant PAH compounds detected when employing the traditional fire ignition method in a poorly ventilated brazier appeared to be fluorene, naphthalene and fluoranthene (Figure 27). It should be noted that peak areas of the identified PAH compounds increased with a change in the fire ignition method (i.e. TLUD to BLUD) and a shift from using a highly ventilated brazier to a poorly ventilated brazier. Low ventilation rates result in poor combustion efficiency, which leads to high emissions of products of incomplete combustion. The higher PAH emissions may be due to the slower burning of coal and a higher volatile release. The increase in PAH emissions suggests less complete combustion compared to the TLUD method.

Figure 28 presents normalized PAH emissions from a high ventilation BLUD ignition method. In contrast to the TLUD ignition method profile shown in Figure 26, fluorene and fluoranthene are the dominant PAHs relative to naphthalene. Phenanthrene is greatly reduced in the primary traps but is more abundant in the secondary traps. Relative to naphthalene, pyrene is two-fold lower, with anthracene ~10 times lower. Compared to the other cases presented above, pyrene and fluoranthene are enhanced in a low ventilation BLUD ignition method.
Significant differences are observed in the devolatilization products of each ignition method. It is apparent that changes in the fire ignition method significantly affect the devolatilization profiles. To best illustrate the differences between the emissions from the two ignition methods, relative ratios are compared for each ignition method and bubble plots are employed as chemical fingerprints. For example, Figure 29 shows a relative ratios of normalised gas phase PAH emissions detected on primary traps when employing the TLUD and the BLUD ignition methods in a well-ventilated brazier, and the BLUD method in a poorly ventilated brazier. The BLUD ignition method in a poorly ventilated brazier produced high PAH emissions relative to the other tests.
The denuder system employed in this study performed well in that the gas phase naphthalene was successfully retained in the primary trap, thus less breakthrough occurred for this PAH, which is not particle bound at room temperature [Forbes, 2010]. Other PAHs were found to be dominant in the secondary traps compared to the primary traps. For example, phenanthrene and acenaphthylene were identified more in the secondary traps than in the primary traps for experiments involving a low ventilation brazier using the BLUD ignition method. A similar result is observed for fluoranthene and acenaphthylene for the high ventilation brazier using the BLUD ignition method (Figure 25). The presence of other PAHs in the secondary trap infers that they originated from blow off of PAHs from the particle phase collected on the filter given that naphthalene is the PAH with by far the lowest breakthrough volume [Forbes, 2010]. The results presented herein also demonstrate the importance of naphthalene as an indicator for PAHs, as it was present at highest levels, which is agreement with literature [Forbes, 2010; Viau et al., 2000]. Although the experiments were done outdoors, there is a need to carry out indoor samples from domestic fuel as household air pollution results in higher exposure levels.

**Implications of the results**

Due to the abundance of naphthalene, fluorene, phenanthrene and fluoranthene relative to other detected PAHs, these pollutants can be potential signatures for coal fires in source apportionment studies. The results reported herein should be taken as indicative, as they are only meant to illustrate PAH emissions during the ignition phase of coal combustion in braziers with various ventilation rates. Further controlled experiments are required to understand the impacts and contribution of each monitored parameter (i.e. fire ignition method and ventilation rate) on the resulting emissions and possibly calculation of related emission factors. However, we have shown that it is advisable to have a large hole-area in a brazier to improve stove ventilation rates and consequently the combustion. High
ventilation rates coupled with the TLUD fire ignition method hold a potential to reduce polycyclic aromatic hydrocarbon (PAH) emissions. The method is a low-cost option, as it does not require changes in the fuel or corresponding devices used but a change in user behaviour.

Although the *Basa njengo Magogo* (TLUD) fire ignition method performs better than the traditional (BLUD) fire ignition method, the method still produces substantial amounts of products of incomplete combustion. As such, the method does not totally solve the underlying problems (i.e. exposure to particulates and associated health risks) faced by the users. As a recommendation, there is need for an efficient and less polluting coal-burning device to replace these inefficient braziers. These preliminary results can be useful to organisations responsible for improving local ambient air quality in priority areas and governmental campaigns on the role-out of the TLUD fire ignition method. In past campaigns, focus was placed only on the fire ignition method and no attempt was made to highlight the importance of ventilation rates on the combustion efficiency of the braziers. In many instances, the *Basa njengo Magogo* ignition method was not readily adopted by households, as the emission reduction claims by campaign leaders and community champions could not be readily substantiated. The method was often demonstrated in poorly ventilated braziers resulting in elevated smoke emissions, in some cases worse compared to the traditional fire ignition method. Our thesis is that the *Basa njengo Magogo* fire ignition method coupled with an optimised well-ventilated brazier, results in improved combustion efficiency and reduced particle (visible smoke) emissions.

4.4 **Particle Emissions Factors [g MJ⁻¹] from Coal Braziers**

4.4.1 **PM emissions from lab-designed braziers with D-grade coal**

Particle emission factors for the laboratory designed stoves, using D-grade coal, for TLUD and BLUD ignition methods are presented in Table 12, together with a statistical evaluation of the differences. The emission factors, expressed as particulate mass per MegaJoule of energy in the combusted fuel, are based on integration over the combustion cycle from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>BLUD Method</th>
<th></th>
<th>Statistical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission Factors [g MJ⁻¹]</td>
<td>Stdev [g MJ⁻¹]</td>
<td>Emission Factors [g MJ⁻¹]</td>
<td>Stdev [g MJ⁻¹]</td>
</tr>
<tr>
<td><strong>PM2.5</strong></td>
<td>High</td>
<td>1.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>1.9</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.5</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>PM10</strong></td>
<td>High</td>
<td>1.3</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>1.9</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.5</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Results show that for the TLUD ignition method or the BLUD ignition method, PM2.5 and PM10 emissions are similar for any given ventilation rate. From Table 12 it can be seen that PM2.5 particles constitute more than 90% of PM10 emissions. There are statistically significant differences (p<0.05) in particle emissions between the BLUD and TLUD methods, for all three ventilations rates (Table 12). The top-lit ignition method reduces PM10/PM2.5 by 76% to 80% compared to the BLUD method. This result is similar to assertions made by Le Roux [2009] who found a reduction in particulate emissions of between 78% and 92% when using the TLUD ignition method.

4.4.2 PM emissions from field stoves with D-grade coal

Particle emission factors for the field procured stoves using D-grade coal, for top- and bottom ignition methods are presented in Table 13, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion cycle, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

Table 13: Particle emission factors for the field-designed coal braziers using D-grade coal in both the BLUD and the TLUD fires

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rate</th>
<th>BLUD Method</th>
<th>TLUD Method</th>
<th>Statistical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission Factors [g MJ⁻¹]</td>
<td>Stdev [g MJ⁻¹]</td>
<td>Emission Factors [g MJ⁻¹]</td>
<td>Stdev [g MJ⁻¹]</td>
</tr>
<tr>
<td>PM2.5</td>
<td>High</td>
<td>1.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.9</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.3</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>PM10</td>
<td>High</td>
<td>1.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.9</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.3</td>
<td>0.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Results show that there are statistically significant differences (p<0.05) in PM2.5 and PM10 emission factors between the fire-ignition methods. Emissions of PM2.5 and PM10 from the TLUD ignition method are five-fold lower (80% reduction) than those from the BLUD method, across all ventilation rates. These results confirm results presented in Table 12 for the lab-designed stoves.

The effects of ventilation rate, based on the total area of ventilation holes in the braziers, and based on the information in Table 12 and Table 13, are presented in Figure 30. The trends are that the more air holes there are in a brazier, the less the particulate emissions. An increase in ventilation rate from low to high results in a 50% reduction of particulate emissions. However, the reduction due to increased ventilation is not as great as the reduction due to the top-lit ignition. A well-ventilated brazier when used in conjunction with the TLUD ignition method has the potential to have the maximum reduction of PM emissions from coal fires in informal braziers. A detailed presentation and statistical evaluation of the trends of emissions of particles and gases with ventilation rates is presented in Section 4.5.1.
4.4.3 PM emissions from A-grade coal fires (field stoves)

Particle emission factors for the field designed stoves, using A-grade coal, for top- and bottom-lit ignition methods are presented in Table 14, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion cycle, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

Table 14: Particle emission factors for the field-designed coal braziers using A-grade coal in the BLUD and TLUD fires

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rate</th>
<th>BLUD Method</th>
<th>TLUD Method</th>
<th>Statistical Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission Factor</td>
<td>Stdev</td>
<td>Emission Factor</td>
<td>Stdev</td>
</tr>
<tr>
<td></td>
<td>[g MJ⁻¹]</td>
<td>[g MJ⁻¹]</td>
<td>[g MJ⁻¹]</td>
<td>[g MJ⁻¹]</td>
</tr>
<tr>
<td>PM2.5</td>
<td>High</td>
<td>2.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>3.3</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.6</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>PM10</td>
<td>High</td>
<td>2.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>3.3</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.6</td>
<td>0.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Results show that there is a statistically significant difference (p<0.05) in PM emission factors between the BLUD method and the TLUD method at any given ventilation rate. Emissions of PM when employing the BLUD method were seven-fold higher compared to emissions from the TLUD method at high ventilation rates. At medium and low ventilation rates, PM emission factors are reduced five-fold when using the TLUD method (Table 14). For the A-grade coal, we found that use of the TLUD method resulted in an 80% decrease in PM2.5 and PM10 emission factors, similar to the case for the D-grade coal. Furthermore, results show that on average there is a 50% reduction in
PM2.5 and PM10 emissions from low to high ventilation rates. It should be noted that the range of ventilation areas as defined in this study were based on representative samples collected from field observations and as such, these potential reductions can be applied in estimating benefits that could be obtained in implementation campaigns.

4.4.4 Dynamical effects of ignition method

In the preceding sections (Sections 4.3 and 4.4), the emission factors are given for the integrated measurements over the combustion cycle. In this section, consideration is given to the time-varying differential emissions of particles and gases to understand the dynamics of combustion, and gain insight into which stages of the combustion cycle give rise to greater or lesser emissions. We present temperature, CO and PM10 emission time plots for the BLUD and TLUD ignition method. By way of tables and representative illustrations, we discuss the influence of fire-ignition method on the characteristics of emissions from residential coal combustion. Results are presented for selected braziers, and it is not intended to give a detailed systematic analysis of emission and temperature time plots for all the braziers evaluated in this study.

To understand the changes in integrated emissions discussed in the preceding sections, there is a need to refer to the dynamics of condensed matter formation during the various stages of the combustion cycle, making use of the temperature time plots at various depths in the fuel bed, for the respective fire-ignition methods. As the purpose is to compare the ignition methods, only one ventilation rate (high ventilation) is chosen for discussion.

**Temperature profile for the BLUD method**

The temperature and CO time plots from a typical BLUD combustion cycle are shown in the Figure 31. The behaviour of the temperature and CO emission curves can be explained more readily by reference to observations made during each fire ignition method.

For the BLUD, ignition at the bottom creates an upward migrating pyrolytic zone that is starved of oxygen, generating a pyrolytic gas, char and low flame temperatures (indicated by curve T5 from 0 to 30 min after ignition) (Figure 31). Temperature T3 (indicated by the red line) is the initial hot zone where the coal undergoes thermal decomposition. The coal swells, resulting in the breaking of weaker bridges in its macro-structure, which produces tars and semi-volatile organic compounds (SVOCs) in a process known as devolatilization [Makonese, 2011]. The removal of these volatiles increases the pore volume in the coal structure. The tars and semi-volatile organic compounds become pre-mixed with air around the surface of the coal macromolecules. Homogenous gas phase combustion of this pre-mixed fuel/air mixture occurs. The combusting gas mixture rises, using up available oxygen, and passes through the cooler coal above (indicated by T4). The lump coal around T4 may undergo some pyrolysis, but initially there is not enough oxygen or heat to sustain combustion [Makonese, 2011]. The semi-volatiles subsequently condense into droplets as the cooling gas mixture passes through T5 (area above the top brim of the brazier) into the atmosphere, resulting in the formation of a dense plume of white smoke.
This poor combustion efficiency is indicated by high PM10 concentration for the first hour of combustion (Figure 32). The stove at this stage does not produce sufficient heat for cooking and has to be kept outdoors because of the excessive smoke. It could take up to sixty minutes for the combustion to improve to the stage when the device could be taken indoors safely for cooking or space heating.
This initial poor combustion are indicated by high CO emissions (above 4 500 ppm) during the first thirty minutes after ignition. The high concentration of hydrocarbons vaporised from heating the coal nuggets and the relatively low temperature at ignition favour incomplete combustion, resulting in high concentrations of CO (Figure 31). The temperature at T3 rises rapidly after ignition, as the combustion gases from the kindling rise through the coal bed. In contrast, the temperature at T2 (blue line), located just above the grate and separated from the kindling by a layer of coal ~100 mm deep, rises slowly—the downward moving combustion front is driven only by radiation. With continued combustion, volatile hydrocarbons are depleted and CO emissions decrease sharply (at ~30 minutes).

In our experiments, we conceptually divided the pyrolysis phase of a coal brazier fire into two stages: stage I and stage II. We hypothesize that particle formation during pyrolysis differs between the two phases, where the separation between these stages is defined by the temperature of the exit gases reaching ignition point for the emitted organic gases. This transition point may be observed as the point at which visible flames are sustained above the coal bed and instrumentally as the point at which the CO and PM concentrations drop sharply. During pyrolysis stage I, devolatilization of the coal occurs upon heating, resulting in the release of SVOCs. In BLUD ignition, these gases are low in free oxygen, and cool rapidly when passing through the coal bed above the combustion zone. Under these conditions, much of the evolved SVOCs escape before combusting and condense to form the dense white smoke characteristic of coal-fired braziers. Attempts to collect filter samples during this pyrolysis phase stage I results in filters becoming blocked rapidly as the condensed liquid droplets merge into a continuous viscous layer.

During pyrolysis stage II, visible flames begin to emerge above the fuel bed and the gas temperature (T5) confirms that the gas mixture is above the ignition temperature to sustain homogenous gas phase combustion. At this stage filter samples collect particles that (mostly) retain the morphology as at moment of impact (see Section 4.6 for discussion of the morphology of condensed matter collected during phase I and phase II pyrolysis).

As stage II proceeds, fuel bed temperatures increases rapidly as the volatile matter is combusted (Figure 31) until there is insufficient volatile matter evolving from the coal macromolecules to sustain this homogenous gas-phase combustion. This point marks the onset of the coking phase, which results in a good combustion efficiency (Figure 31d). During this phase, heterogeneous gas/solid combustion takes place, with the rate limited by diffusion of oxygen to the char surface. The product of the surface reactions is CO-rich, which undergoes further combustion in the gas phase to CO$_2$ [Makonese, 2011]. CO and particulate emissions remain uniformly low.

However, towards the end of the coking phase and nearing fuel burnout (~100 min), CO emissions begin to increase, ascribed to the gradually reducing depth of the fuel bed and lowering temperature. Some of the evolved CO-rich gas is below the CO ignition temperature, and escapes unburned. These four combustion phases identified by the emission characteristics of CO agree well with the results obtained by Smith et al. [1981] for pulverized coal and Wang et al. [2012] who investigated the combustion in residential coal combustion.
Temperature profile for the TLUD method

For the *Basa njengo Magogo* (TLUD) ignition method, T4 (indicated by the green line) (Figure 33) is the hot zone where kindling wood and a few lumps of coal are thermally decomposed. The decomposition results in the formation of volatile matter as discussed in the preceding sub-section. The ignition of a batch of fuel from the top creates a downward migrating pyrolytic zone [Makonese, 2011]. We see that for each thermocouple, the temperature remains near ambient until the pyrolysis front approaches, whereupon the temperature rises rapidly to a plateau (Figure 33). If we define a particular temperature, say 750°C, as marking the arrival of the pyrolysis front, we can estimate the rate of advance of the pyrolysis front. It took 35 min for the pyrolytic front to reach thermocouple T3 and another 35 min to reach T2 from T3. The thermocouples were placed 100 mm from each other inside the fuel stack (See Figure 16). This equates to a pyrolytic rate of 3 mm per min and hence the rate of the pyrolytic zone is almost constant at 10 mm per 3.5 min.

![Figure 33: Temperature and CO profiles for the TLUD method in a high ventilation brazier with D-grade coal: a) ignition phase; b) pyrolysis stage I; c) pyrolysis stage II; d) coking phase; and e) when whole fuel bed is fully ignited, with uniform temperatures. (Refer to Figure 16 for placement of thermocouples within the brazier)](image)

The thermocouple T2 (indicated by the red line and blue line, respectively), show a colder zone filled with the bulk of the coal, which produces volatile matter and tars upon heating. This volatile matter rises through the hot flame zone (at T4) with a sufficient supply of oxygen to allow for complete homogeneous gas-phase combustion. This results in a significant reduction in visible smoke and particulates. The flame that can be seen jumping out of the stove (T5 as indicated by the brown line) is because of an increase in the homogeneous gas phase combustion rate.
The good combustion condition is indicated by lower PM10 emissions for over 110 minutes of combustion (Figure 34). The stove produces sufficient heat for cooking and is safe to take indoors, from PM point of view, ~25 minutes after ignition. After ~30 minutes from ignition, the final stage of char combustion is similar to the situation for the BLUD ignition method, with reduced PM emission factors (Figure 31, from 60 minutes onwards). At this stage, the initial ignition method has no influence on this last phase of combustion.

In the final stage of the fire, referred to as the smouldering phase, the available heat and fragmentation of the residual char are insufficient to sustain complete CO combustion, and the CO emissions begin to rise. The char surface oxidation rates are primarily a function of how the rate-oxygenated molecules can diffuse to the fuel surface [Grabke, 1999; Matsui & Tsuji, 1987]. According to L’Orange et al. [2012] as solid carbon is pulled from the charcoal an ash layer, composed primarily of silicon dioxide and calcium oxide [Tillman et al., 1981], is left on the surface. The ash layer acts like insulation reducing heat transfer from the charcoal and slowing the overall reaction. As the surface temperature of the charcoal rises reactions forming CO exceed those forming CO$_2$ resulting in reduced combustion efficiencies and emissions of high concentrations of CO gas [L’Orange et al., 2012].

4.5 Effect of Additional Parameters on the Performance of Braziers

The objective of this section is to investigate the influence of factors including fuel moisture content, ventilation rate, and fuel quality on the pollutant emissions from residential coal combustion. Although a wide range of chemical species were monitored, CO and PM2.5 are selected for detailed discussion as the pollutants of major concern in terms of health effects.
4.5.1 Effect of ventilation rates

**Results**

The effect of ventilation rates on the emissions of CO, and CO$_2$ are investigated. Three stoves with different ventilation rates were used for each ignition method, with moisture content and other parameters held constant. The results of these experiments for the lab-designed braziers are presented in Table 15.

When comparing the high and medium ventilation rates, results show that there is a significant difference (p<0.05) in CO emissions, but not for CO$_2$ emissions. When comparing medium and low ventilation rates, there are no significant differences (p>0.05) between the respective emissions of CO and CO$_2$. When comparing the high and low ventilation rates, there are significant differences (p<0.05) in CO emissions, but not for CO$_2$ emissions. This shows that ventilation rates of the tested devices influence CO emissions, but may not affect the combustion characteristics of CO$_2$.

Table 15: Emission factors of CO and CO$_2$ as a function of ventilation rates

<table>
<thead>
<tr>
<th>Ignition Method</th>
<th>Ventilation Rate</th>
<th>CO Emission Factors [g MJ$^{-1}$]</th>
<th>CO$_2$ Emission Factors [g MJ$^{-1}$]</th>
<th>T-start</th>
<th>P-value</th>
<th>Sig @ 95%</th>
<th>T-start</th>
<th>P-value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>4.5 ± 0.1</td>
<td>98 ± 6</td>
<td>-6.6</td>
<td>0.0</td>
<td>Yes</td>
<td>0.2</td>
<td>0.9</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>6.2 ± 0.3</td>
<td>98 ± 6</td>
<td>0.1</td>
<td>0.9</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BLUD</td>
<td>Medium</td>
<td>6.2 ± 0.3</td>
<td>98 ± 6</td>
<td>-0.5</td>
<td>0.7</td>
<td>No</td>
<td>0.4</td>
<td>0.7</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>6.4 ± 0.5</td>
<td>97 ± 5</td>
<td>0.5</td>
<td>0.3</td>
<td>Yes</td>
<td></td>
<td>0.5</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>4.5 ± 0.1</td>
<td>98 ± 6</td>
<td>-5.5</td>
<td>0.0</td>
<td>Yes</td>
<td>0.4</td>
<td>0.7</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>5.0 ± 0.4</td>
<td>99 ± 2</td>
<td>-1.1</td>
<td>0.4</td>
<td>No</td>
<td>1.0</td>
<td>0.4</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>5.7 ± 0.2</td>
<td>102 ± 3</td>
<td></td>
<td>0.2</td>
<td>No</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TLUD</td>
<td>Medium</td>
<td>5.0 ± 0.4</td>
<td>96 ± 2</td>
<td>-2.3</td>
<td>0.2</td>
<td>No</td>
<td>-2.1</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>5.7 ± 0.2</td>
<td>102 ± 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 16 shows emission factors of NOx as a function of ventilation rates. Results show that there are statistically significant differences (p<0.05) in NOx EF between high and low ventilation rates for the BLUD fires; and for the TLUD fires between medium and low ventilation rates, as well as between high and low ventilation rates.
Table 16: Emission factors of NOx [mg MJ$^{-1}$] as a function of ventilation rates

<table>
<thead>
<tr>
<th>Ignition Method</th>
<th>Ventilation Rate</th>
<th>NOx Emission Factors [g MJ$^{-1}$]</th>
<th>T-start</th>
<th>P-value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLUD</td>
<td>High</td>
<td>149 ± 16</td>
<td>2.25</td>
<td>0.15</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>118 ± 11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>87 ± 5</td>
<td>3.63</td>
<td>0.068</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>149 ± 16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>87 ± 5</td>
<td>-8.28</td>
<td>0.014</td>
<td>Yes</td>
</tr>
<tr>
<td>TLUD</td>
<td>High</td>
<td>126 ± 4</td>
<td>2.50</td>
<td>0.13</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>99 ± 6</td>
<td>4.38</td>
<td>0.048</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>75 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The effect of ventilation rates on PM10 emissions were investigated, using three stoves with different ventilation rates, each tested with BLUD and TLUD ignition methods, with moisture content and other parameters held constant. The results of these experiments for the lab-designed braziers are presented in Table 17.

Table 17: PM10 mission factors from D-grade coal in lab-designed braziers at different ventilation rates (Mean and Stdev)

<table>
<thead>
<tr>
<th>Ignition Method</th>
<th>Ventilation Rate</th>
<th>PM10 Emission Factors [g MJ$^{-1}$]</th>
<th>T-start</th>
<th>P-value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLUD</td>
<td>High</td>
<td>1.3 ± 0.1</td>
<td>-5</td>
<td>0.03</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>1.9 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>1.9 ± 0.1</td>
<td>-4</td>
<td>0.06</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.5 ± 0.2</td>
<td>5</td>
<td>0.03</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>1.3 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>2.5 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TLUD</td>
<td>High</td>
<td>0.3 ± 0.02</td>
<td>-6</td>
<td>0.02</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.4 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.4 ± 0.03</td>
<td>-4</td>
<td>0.07</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.6 ± 0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.3 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.6 ± 0.06</td>
<td>-8</td>
<td>0.02</td>
<td>Yes</td>
</tr>
</tbody>
</table>

When comparing the high and medium ventilation rates, results show that there are significant differences (p<0.05) in PM10 emissions for both ignition methods. However, there are no statistically significant differences (p>0.05) in PM10 EF between medium and low ventilation rates for either ignition method. For the high and low ventilation rates, results show that there is a significant difference (p<0.05) in PM10 emissions for both ignition methods. A similar trend can be seen when
using A-grade coal in the lab-designed braziers (Table 18). This implies that the ventilation rates affect the combustion characteristics of PM10 in all the experimental braziers. For a given device, PM2.5 and PM10 emission factors reduce by 50% from low to high ventilation rates. This advantage is generally offset by fire-power too high for convenient cooking and by increased fuel consumption.

Table 18: Comparison of PM10 emissions between ventilation rates for the BLUD and the TLUD methods, using A-grade coal (Mean and Stdev)

<table>
<thead>
<tr>
<th>Ignition Method</th>
<th>Ventilation Rate</th>
<th>PM10 Emission Factors [g MJ⁻¹]</th>
<th>T-stat</th>
<th>P-value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>2.5 ± 0.3</td>
<td>-3.21</td>
<td>0.03</td>
<td>Yes</td>
</tr>
<tr>
<td>BLUD</td>
<td>Medium</td>
<td>3.3 ± 0.2</td>
<td>-1.59</td>
<td>0.19</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.6 ± 0.2</td>
<td>4.40</td>
<td>0.01</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>0.4 ± 0.02</td>
<td>-8.13</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td>TLUD</td>
<td>Medium</td>
<td>0.7 ± 0.07</td>
<td>-2.13</td>
<td>0.10</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.8 ± 0.05</td>
<td>-14.55</td>
<td>0.00</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Discussion

In this study, we have varied the ventilation rates by changing the number of holes, of fixed diameter, in a uniform array around the side of the drum. Reported low, medium and high ventilation rates were based on the empirical observations of stoves in use. Future improvements could explore additional factors, which are not explored in our experiments, and have the potential to influence ventilation rates. These factors include varying the size of ventilation holes and the median size and size distribution of the fuel. We kept the fuel median size and size distribution constant at 20 mm throughout the course of this study. There is a need to further investigate the effect of hole density pattern on ventilation rates by clustering primary air holes below the fuel grate and a limited number of secondary air holes above the level of the packed fuel bed.

Results presented herein show that the performance of braziers could be improved by optimising the air supply through the packed fuel bed, and to the space above the fuel bed (secondary air). An increase in the ventilation rates allows for more stable combustion and higher combustion temperatures, which in turn could lead to improved heat transfer. This could be achieved by using forced draft/ventilation as in some wood pellet and biomass burning gasifiers. However, this option is not viable on brazier stoves as this may require design alterations to existing braziers and a potential increase in the cost of the final product. The target market for these stoves remains the low-income (energy poor) households situated on the Highveld region of South Africa.
In principle, to have the most efficient combustion in any combustion process, there is a need for a perfect fuel and air ratio without any unused fuel or air remaining. This type of theoretical perfect combustion is referred to as ‘stoichiometric combustion’. In practice, however, additional air beyond the stoichiometric ratio is needed to increase the combustion efficiency of the combustion device—this is referred to as “excess air”. In most combustion systems, if some excess air is not added to the combustion process, unburned fuel, soot, smoke, and carbon monoxide exhaust will be emitted and surface fouling may occur. When reducing the amount of airflow going into the combustion chamber, the available amount of oxygen needed for combustion is lowered thereby limiting the combustion reaction. Even though excess air is needed from a practical standpoint, relatively high excess air can lower the combustion efficiency. As such, a balance should be found between providing the optimal amount of excess air.

Low ventilation rates or airflow movements through the brazier may limit the chemical reactions between $O_2$ and gaseous fuel leading to high levels of CO and PM emissions. An increase in oxygen content in the combustion, results in a decrease in the combustion products (including noxious gases) released into the atmosphere. On the other hand, excessive airflow rates/ high ventilation rates may increase the convective cooling of the fire thereby affecting the mixing and local concentration of fuel/oxidant in the gas stream. In addition, air velocity rates may directly affect the reaction rate of the condensed phase. According to ISO 19706, combustion conditions may be considered as incomplete and the atmosphere may be assumed as “vitiated” when the CO/CO$_2$ ratio is higher than 0.05. An important issue in combustion researches is the improvement of combustion efficiency to minimize the emission of harmful pollutants.

In conclusion, the emission of gaseous and particulate matter from incomplete combustion can be minimized by optimising the design of the braziers in terms of size hole distribution and the position of the grate in the brazier. Ideally, the emissions of condensed matter particles (which form the bulk of emitted particles in residential coal fires) can be reduced by allowing for good mixing between the volatile gasses from the fuel bed and the air supply and by ensuring a long residence time in the high temperature, oxygen-rich post combustor zone to allow for complete oxidation. Thus, a brazier with high ventilation rates has a potential to reduce emissions of CO and PM. Future studies on the effect of ventilation rates on fixed-bed coal combustion systems should explore parameters such as size of ventilation holes, distribution pattern of the holes, and fuel size on particulate and trace gas emissions.

### 4.5.2 Effect of moisture content of coal

#### Results – emissions

In this study, the effect of coal moisture content (MC) on efficiency and emission of the braziers was investigated. Each batch of fuel was determined for moisture content prior to each test. The moisture content was determined from the batches of fuel as received from the field. Two distinct moisture content values for two batches of coal fuel were used in this study (2.4% MC and 8.6% MC). The emission factors of PM10, CO, CO$_2$ and the combustion efficiency, at different fuel moisture content
are presented in Table 19. Results show that for both fire ignition methods, measured EF of PM2.5 and CO increased with high coal moisture. The differences in EF between the moisture content levels were small but significant (p<0.05). The correlations were statistically significant, with the correlation coefficients of 0.97–0.99 (p < 0.05).

Table 19: Emission factors of stoves for different levels of moisture content of fuel

<table>
<thead>
<tr>
<th>Ignition Method</th>
<th>MC [%]</th>
<th>Ventilation Rates</th>
<th>PM2.5 [g MJ⁻¹]</th>
<th>CO [g MJ⁻¹]</th>
<th>CO₂ [g MJ⁻¹]</th>
<th>Combustion Efficiency [%]</th>
<th>CO/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Stdev</td>
<td>Mean</td>
<td>Stdev</td>
<td>Mean</td>
<td>Stdev</td>
</tr>
<tr>
<td>BLUD</td>
<td>High</td>
<td>2.4</td>
<td>0.6</td>
<td>0.05</td>
<td>4.5</td>
<td>0.3</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>1.1</td>
<td>0.31</td>
<td>0.03</td>
<td>5.6</td>
<td>0.4</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.7</td>
<td>0.20</td>
<td>0.02</td>
<td>6.2</td>
<td>0.6</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>8.6</td>
<td>2.2</td>
<td>0.32</td>
<td>4.3</td>
<td>0.6</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.2</td>
<td>0.40</td>
<td>0.04</td>
<td>5.4</td>
<td>0.3</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.0</td>
<td>0.40</td>
<td>0.02</td>
<td>6.2</td>
<td>0.3</td>
<td>101</td>
</tr>
<tr>
<td>TLUD</td>
<td>High</td>
<td>2.4</td>
<td>0.6</td>
<td>0.04</td>
<td>4.1</td>
<td>0.3</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.2</td>
<td>0.32</td>
<td>0.03</td>
<td>4.4</td>
<td>0.3</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>1.7</td>
<td>0.20</td>
<td>0.02</td>
<td>5.5</td>
<td>0.3</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>8.6</td>
<td>0.7</td>
<td>0.04</td>
<td>6.5</td>
<td>0.25</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.6</td>
<td>0.05</td>
<td>0.05</td>
<td>7.6</td>
<td>1.1</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.7</td>
<td>0.04</td>
<td>0.03</td>
<td>7.6</td>
<td>1.2</td>
<td>101</td>
</tr>
</tbody>
</table>

Figure 35 shows the trend of PM2.5 emission factors [g MJ⁻¹] as a function of different fuel moisture content levels across three ventilation rates. Results indicate, when employing the BLUD ignition technique, there is a marked increase (~two fold ) in PM2.5 emission factors with increased moisture content levels for all ventilation rates. In contrast, when employing the TLUD ignition technique, there is a slight increase in PM2.5 emission factors with increased moisture content, with the differences not significant at low ventilation rates.
Results - cooking efficiency and fire-power

The effect of moisture content was investigated on cooking efficiency and fire-power of the stoves with ventilation rates, ignition methods, and fuel size held constant. Results are presented in Table 20. Results show that as the level of MC increased from 2.4% to 8.6%, the cooking efficiency increased as the fire-power decreased (Table 20). Fire-power [kW] decreased by 18% from 8 kW at 2.4% MC to 6.5 kW at 8.6% MC, and the cooking efficiency increased by 24% from 7.8% at 2.4% MC to 10.2% at 8.6% MC, when employing the TLUD method in a high ventilation brazier. Generally, there is an average 18% decrease in fire-power from 2.4% MC to 8.6% MC when using the TLUD method for all the ventilations. For the BLUD ignition, there is a 30% decrease in fire-power from 2.4% MC to 8.6% MC across the three ventilation rates (high, medium, low); and the cooking efficiency increases by an average of 25% across the three ventilations as the moisture content increases from 2.4% to 8.6%.

Figure 35: The trend of PM2.5 emission factors [g MJ\(^{-1}\)] with different fuel MC across a range of ventilation rates
Table 20: Comparison between TLUD and BLUD fire ignition method with varying moisture content levels (Mean ± Stdev) N=3

<table>
<thead>
<tr>
<th>Ventilation rate</th>
<th>Moisture Content [%]</th>
<th>TLUD method</th>
<th>BLUD method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fire Power [kW]</td>
<td>Cooking Efficiency [%]</td>
<td>Fire Power [kW]</td>
</tr>
<tr>
<td>High</td>
<td>2.4</td>
<td>7.9 ± 0.8</td>
<td>5.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>6.5 ± 0.5</td>
<td>10.2 ± 1.4</td>
</tr>
<tr>
<td>Medium</td>
<td>2.4</td>
<td>7.4 ± 0.5</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>6.1 ± 0.6</td>
<td>9.6 ± 0.7</td>
</tr>
<tr>
<td>Low</td>
<td>2.4</td>
<td>6.9 ± 0.4</td>
<td>4.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>5.7 ± 0.2</td>
<td>3.1 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 36 shows that when the moisture content increases fire-power decreases and cooking efficiency increases. This is because, stove efficiency tends to decrease as more energy is lost to the surroundings rather than transferred to the pot. The fuel in the combustion chamber was burnt gradually from the top–down (in the case of the TLUD method) and from the bottom–up (in the case of the BLUD method), and the existence of water in the fuel slowed the combustion and reduced the temperature achieved in the combustion zone. This led to less fuel gasified at any given moment resulting in reduced combustion intensity. This result is similar to findings by [McKendry, 2002].

Figure 36: The trend of fire-power [kW] and cooking efficiency [%] at different moisture contents across a range of ventilation rates
Discussion

Results on the effect of moisture content on gaseous emissions are similar to findings by Erdöl et al. [1999]. The increase in CO emission factor appears to be due to lowering of gas phase reaction (oxidation) rates at reduced temperatures caused by higher moisture content [Kumar et al., 2013]. In our study, a positive correlation between MC in fuel and CO emission factor was obtained, which was in contrast to some previous investigations. Shen et al. [2013] and Huangfu et al. [2014] found that CO emission decreased with an increase in MC in the experiments with a top-lit updraft wood stove at four moisture levels. The top-lit updraft (TLUD) stove used in their experiment had secondary air supplied from the top channel ensuring mixing of burned gas with hot secondary air, thereby reducing the amount of CO emitted [El May et al., 2013].

In situations where the fuel is wet, the performance of the fuel/stove combination is overly compromised. Generally, wet fuel is hard to ignite and often more starting fuel is needed to get the fire going. In the burning of high moisture fuel, extra energy is required to vaporise water, resulting in reduced fuel combustion efficiency and increased emissions of incomplete combustion pollutants [Shen et al., 2013; Simoneit, 2002; Rogge et al., 1998]. High fuel moisture content tends to lower the combustion and flame temperatures leading to increased condensation of volatile matter in the post flame region of the stove, resulting in elevated levels of PM emissions. When considering the entire combustion cycle, the concentration of smoke particles tend to decrease rapidly during the pyrolysis phase of combustion. This is because the water in the coal eventually evaporates and the degree of incomplete combustion is reduced.

Another impact on performance is due to condensation that normally occurs at the bottom of the pot. When the flame and combustion temperatures are low, the water evaporating from the fuel tend to condense on the bottom of the pot, which could drop into the combustion chamber or fuel bed, affecting the performance. This is usually typical for small combustion devices. In our experiments, this phenomenon was not observed for any of the stoves tested.

According to Erdöl et al. [1999], the surface-adsorbed superficial free water is removed most readily from the fuel, while capillary condensed water surface moisture and “sorbed” moisture is more difficult to remove and the process is much slower. It is known that moisture plays an important role in shrinkage and swelling of coals leading to the formation of pores, which play an important role in diffusion control. It is possible to understand the emission behaviour of particulates with changing moisture content by viewing present experimental results in light of a typical schematic coal structure (Figure 37), pore-formation mechanism and, heat and mass transfer.

The experimental results may be explained starting with the highest moisture coal (i.e. 8.6%, as used in this study). There is superficial free moisture in high moisture coals compared to coals with low moisture content. In low moisture content coals (<3%), capillary condensed moisture is the main target for evaporation. In this case, the porosity of coal structure is more developed compared to the 8% case. The high porosity in low moisture content coals, and the role of lower rates of evaporation of the remaining “sorbed” water causes less damage to the coal structure. Therefore, particulate
emissions in low (2.4%) moisture content coals are lower compared to high (8.6%) moisture coal. In situations where there is high moisture content in the coal, the relatively high amounts of evaporated water may not be transferred by the available pores resulting in a pressure build up in the coal fuel. This pressure results in “cracking” of particles causing an increase in particulate emissions [Erdöl et al., 1999].

Figure 37: Schematic showing the drying of lignite with thermal upgrading
[Figure source: Erdöl et al., 1999]

The stove type and ignition method are the key reason why the relationships between MC and emission factors were in contrast to the results in the study conducted by Huangfu et al. [2014]. The presence of secondary air holes in the stove plays an important role in minimising emissions of PM and CO. Our results are in agreement with Bhattacharya et al. [2002] and Wei et al. [2012] who both used rocket type stoves [Jetter & Kariher, 2009] without secondary air holes. The braziers used in this study do not have the ability to inject hot secondary airs to the top of the combustion chamber to aid combustion of products of incomplete combustion. For example, when wood logs or firewood chips with higher moisture content are burning in the rocket-type stove or in a typical brazier, the presence of water in the fuel tends to lower combustion temperatures in the fire hopper, causing white thick smoke to escape out of the stove without being burned. Huangfu et al. [2014] used a semi-gasifier cookstove, which was the same type of stove used in the Shen et al. [2010] study. In this type of stove, fuel is batch loaded and lit from the top. The secondary air-feeding system is responsible for burning the gasification products including CO and PM2.5. Although the presence of water in the fuel affects the combustion and flame temperatures, once the wood is lit and charcoal produced on the top, the charcoal would keep the temperatures high enough to gasify the fuel below, producing combustible products, which burn in the presence of the hot air provided by the secondary air-feeding system [Huangfu et al., 2014].
In conclusion, the significant impact of fuel MC on the emission factors observed in this study ascertains the importance of MC in the performance evaluation of fuel/stove combinations. This has implications for future testing protocols that they should specify or restrict the MC of the fuel to be used in the performance evaluation, to avoid any bias resulting from different MC levels [Huangfu et al., 2014]. It can be argued from the present results that in future studies, especially those aimed at estimating total pollutant amounts based on emission factors, there is need to include the MC of the fuel in the different testing regimen and prediction models to minimize the error caused by fuel MC levels.

4.5.3 Effect of fuel quality

**Effect of fuel quality on the gaseous emissions**

Effect of fuel type on gaseous emissions was investigated and the results are presented in Table 21. Emissions from a grade D-type coal were compared with emissions from a grade A-type coal, each with specifications highlighted in Section 3.2. Table 21 presents a comparative analysis of gas emission factors between D-grade and A-grade coal when employing the BLUD method.

Results show that there is no statistically significant difference (p>0.05) in CO EF produced between coal grades at the medium and high ventilation rates. The use of the A-grade coal results in an 11% reduction in CO EF at the medium ventilation rate, while at low ventilation rates CO EF increase by 12%. There was found to be a statistically significant difference (p<0.05) in CO EF between coal grades at low ventilation rates when employing the BLUD method. This difference in CO emissions at different ventilation rates could be a result of the higher volatility of the A-grade coal, which would require more oxygen to combust the volatile components released from the burning coals. Zhang et al. [2008] contends that coals with low maturity usually have relative high volatile contents, which is the precursor material for particulate matter during combustion. Therefore, emission factors are expected to increase as the volatile content of the coal increases.

When comparing the two grades of fuels across ventilation rates, results show that there is no statistically significant difference (p>0.05) in CO₂ emissions. However, the use of A-grade type coal results in an average 4% decrease in CO₂ EF across ventilation rates (Table 21). For NOx emissions, results show that there is a statistically significant difference (p < 0.05) in the emissions between high and low ventilation rates, with no significant differences between high and medium ventilation rate.
Table 21: Comparative analysis of gas emission factors between D-grade and A-grade coals, for the BLUD method

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>Emission Factors [g MJ⁻¹]</th>
<th>Stdev [g MJ⁻¹]</th>
<th>Emission Factors [g MJ⁻¹]</th>
<th>Stdev [g MJ⁻¹]</th>
<th>% diff. between D &amp; A-grade coal</th>
<th>T-Stat</th>
<th>P-Value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>High</td>
<td>4.1</td>
<td>0.3</td>
<td>4.0</td>
<td>0.2</td>
<td>-1%</td>
<td>0.20</td>
<td>0.85</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>4.2</td>
<td>0.4</td>
<td>3.8</td>
<td>0.3</td>
<td>-11%</td>
<td>1.68</td>
<td>0.17</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>4.6</td>
<td>0.3</td>
<td>5.2</td>
<td>0.2</td>
<td>12%</td>
<td>-2.82</td>
<td>0.05</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>High</td>
<td>102</td>
<td>4</td>
<td>98</td>
<td>6</td>
<td>-5%</td>
<td>1.07</td>
<td>0.34</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>102</td>
<td>5</td>
<td>99</td>
<td>7</td>
<td>-3%</td>
<td>0.54</td>
<td>0.62</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>98</td>
<td>6</td>
<td>94</td>
<td>4</td>
<td>-4%</td>
<td>0.87</td>
<td>0.43</td>
<td>No</td>
</tr>
<tr>
<td>NOx</td>
<td>High</td>
<td>195</td>
<td>8</td>
<td>142</td>
<td>9</td>
<td>-37%</td>
<td>7.65</td>
<td>0.002</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>188</td>
<td>10</td>
<td>168</td>
<td>15</td>
<td>-12%</td>
<td>2.00</td>
<td>0.116</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>187</td>
<td>11</td>
<td>147</td>
<td>12</td>
<td>-28%</td>
<td>4.28</td>
<td>0.013</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 22: Comparative analysis of gas emission factors between D-grade and A-grade coals, for the TLUD method

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rate</th>
<th>Emission Factors [g MJ⁻¹]</th>
<th>Stdev [g MJ⁻¹]</th>
<th>Emission Factors [g MJ⁻¹]</th>
<th>Stdev [g MJ⁻¹]</th>
<th>% diff. between D &amp; A-grade coal</th>
<th>T-Stat</th>
<th>P-Value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>High</td>
<td>4.0</td>
<td>0.2</td>
<td>4.5</td>
<td>0.2</td>
<td>11%</td>
<td>-3.10</td>
<td>0.036</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>4.1</td>
<td>0.4</td>
<td>4.0</td>
<td>0.1</td>
<td>-1%</td>
<td>0.19</td>
<td>0.862</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>5.5</td>
<td>0.2</td>
<td>6.1</td>
<td>0.3</td>
<td>10%</td>
<td>-2.95</td>
<td>0.042</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>High</td>
<td>100</td>
<td>6</td>
<td>97</td>
<td>6</td>
<td>-3%</td>
<td>0.58</td>
<td>0.595</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>99</td>
<td>3</td>
<td>97</td>
<td>4</td>
<td>-2%</td>
<td>0.58</td>
<td>0.595</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>101</td>
<td>5</td>
<td>95</td>
<td>4</td>
<td>-5%</td>
<td>1.34</td>
<td>0.251</td>
<td>No</td>
</tr>
<tr>
<td>NOx</td>
<td>High</td>
<td>168</td>
<td>10</td>
<td>130</td>
<td>9</td>
<td>-30%</td>
<td>4.88</td>
<td>0.008</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>163</td>
<td>4</td>
<td>157</td>
<td>10</td>
<td>-4%</td>
<td>1.00</td>
<td>0.374</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>161</td>
<td>9</td>
<td>136</td>
<td>8</td>
<td>-19%</td>
<td>3.51</td>
<td>0.025</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 22 compares gas emission factors between D-grade and A-grade coal when employing the TLUD method. Results show that gaseous pollutant emissions (CO and CO₂) show a similar trend to BLUD fires (Table 21). CO EFs were significantly different (p<0.05) at high and low ventilation rates but not for the medium ventilation rate. Generally, there is a reduction in CO₂ EF and NOx EF when using A-grade coals compared to D-grade coals.
Effect of fuel quality on the particulate matter emissions

We analysed the effect of fuel quality (i.e. A-grade and D-grade coal fuels) on PM emissions, when using the BLUD method (Table 23) and when employing the TLUD ignition method (Table 24). Results show that for BLUD method there is a statistically significant difference ($p<0.05$) in PM EF between fuel grades at high ventilation rates. However, there is no statistically significant difference ($p>0.05$) in PM EF produced between the D-grade and A-grade coal at low and medium ventilation rates. The use of the A-grade coal resulted in a 49% increase in PM relative to D-grade coal at high ventilation rates (Table 23).

Table 23: Comparative analysis of particle emission factors between D-grade and A-grade coals, for the BLUD method

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>BLUD Method D-grade coal</th>
<th>BLUD Method A-grade coal</th>
<th>% diff. between D &amp; A-grade coal</th>
<th>T-Stat</th>
<th>P-Value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM2.5</td>
<td>High</td>
<td>1.3</td>
<td>2.5</td>
<td>49%</td>
<td>-7.55</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.9</td>
<td>3.3</td>
<td>12%</td>
<td>-2.28</td>
<td>0.08</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.3</td>
<td>3.6</td>
<td>8%</td>
<td>-1.75</td>
<td>0.15</td>
<td>No</td>
</tr>
<tr>
<td>PM10</td>
<td>High</td>
<td>1.3</td>
<td>2.5</td>
<td>49%</td>
<td>-7.54</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2.9</td>
<td>3.3</td>
<td>12%</td>
<td>-2.27</td>
<td>0.09</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>3.3</td>
<td>3.6</td>
<td>8%</td>
<td>-1.73</td>
<td>0.16</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 24: Comparative analysis of particle emission factors between D-grade and A-grade coals, for the TLUD method

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ventilation rates</th>
<th>TLUD Method D-grade coal</th>
<th>TLUD Method A-grade coal</th>
<th>% diff. between D &amp; A-grade coal</th>
<th>T-Stat</th>
<th>P-Value</th>
<th>Sig @ 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM2.5</td>
<td>High</td>
<td>0.24</td>
<td>0.36</td>
<td>33%</td>
<td>-7.10</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.64</td>
<td>0.69</td>
<td>8%</td>
<td>-1.10</td>
<td>0.33</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.65</td>
<td>0.78</td>
<td>16%</td>
<td>-2.89</td>
<td>0.04</td>
<td>Yes</td>
</tr>
<tr>
<td>PM10</td>
<td>High</td>
<td>0.24</td>
<td>0.36</td>
<td>33%</td>
<td>-7.13</td>
<td>0.00</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.64</td>
<td>0.69</td>
<td>7%</td>
<td>-1.09</td>
<td>0.34</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.65</td>
<td>0.78</td>
<td>16%</td>
<td>-2.89</td>
<td>0.04</td>
<td>Yes</td>
</tr>
</tbody>
</table>

For the TLUD method, the use of A-grade coal results in significant increases ($p<0.05$) in PM, 33% at high ventilation rates; 16% at low ventilation rates (Table 24). At medium ventilation results, the fuel grade change did not give a significant change in PM ($p>0.05$).
Discussion

Results of the influence of fuel grade on PM emissions are ambiguous, not giving a consistent
difference across fire ignition methods or ventilation rates. This aspect requires further investigation.

In general, PM emissions are dependent on the volatility of the fuels. Fuels with high volatile matter
are likely to produce high PM emission levels especially if the combustion device is poorly designed. During coal pyrolysis, the coal fuel separates into char and volatile matter. Once the volatiles have been released, they travel up through the stove mixing and combusting with primary and secondary air. High volatile fuels have the potential to release large amounts of volatile organic matter upon pyrolysis. If the combustion device is poorly designed or the fire-ignition method not optimised, the volatile matter condenses and is released to the atmosphere as a dense plume of smoke. A-grade type coal fuels used in our experiments were a high-volatile bituminous coal compared to the D-grade coal (See Table 3). This may explain why an increase in PM was noticed with the use of A-grade fuels. However, PM formation is a complex process involving many elemental steps, which can be affected by many factors such as the organic content of a fuel, combustion temperature, oxygen supplying rate during combustion, and the structures of stoves [Ge et al., 2004].

4.6 SEM Analysis of Coal Smoke Aerosols

The study of particle morphology is important because it provides knowledge of the size and shape, and possible composition of primary particles emitted from combustion processes. Information on course and fine particle morphology in fixed-bed domestic coal combustion devices is scarce. In this section, detailed information on fine particle morphology during different combustion conditions from a suite of coal-burning braziers is presented. Semi-quantitative energy dispersive X-ray spectrometry results are presented to demonstrate elemental compositions associated with the different morphologies.

4.6.1 Particle morphologies from field samples

Figure 38 shows micrographs of a quartz aerosol filter with conglomerate particles sampled from coal combustion in typical braziers during pyrolysis stage II. Particles sampled during pyrolysis stage I are discussed in the next section. Figure 38a, for a filter taken during the pyrolysis stage II, shows a conglomerate with a “sponge-like” structure similar to the one observed by Wentzel et al. [1999]. The dendritic form gives rise to a material with a high pore volume and high specific surface area. The presence of the giant carbonaceous conglomerates was observed on the filters from both the traditional (BLUD) and the Basa njengo Magogo (TLUD) ignition technique only when flames were visible above the fuel bed. Major differences include lower particle loading on the filter from TLUD fires, as expected from the lower visible smoke emissions observed during pyrolysis. Typically, conglomerates from TLUD fires have a smaller mode diameter compared to conglomerates from the BLUD method.
On the filter sample from a high ventilation TLUD brazier (Figure 38b), one notes the presence of a heavy loading of fuzzy-textured conglomerates with gross diameters of 5 µm or more. Similar to Wentzel et al. [1999], these giant particles are interspersed with a scattering of smaller particles, either spherical or irregular in shape. Generally, the conglomerate particles are chain-like aggregates of spherical primary particles.

The light scattering properties of these ‘giant’ aerosol particles remain to be investigated. However, this falls outside the scope of this work.

Identification of spherules and “melted toffee” webs

Figure 39 shows a carbon-dominated material forming an uneven carbonaceous film on the filter material. The resultant morphologies are spherules, which are typically spherical organic particles, and ‘melted toffee’ webs. Such samples are not useful in characterizing single particles but they illustrate that the aerosols upon impaction with the filter were in a liquid form. The material then condensed and solidified around the quartz fibre material resulting in the formation of web-like agglomerates (Figure 39a). At low aerosol concentrations and at high temperature (i.e. during the particle decay phase), complete or partially solidified spheres can be found on the filters (Figure 39b). The solidified spheres indicate that the liquid aerosol droplets do not arise on impaction with the filter, but that they already exist in the exhaust/flue or in the atmosphere before condensation occurs.

The BLUD fire-ignition method results in lower flame temperatures during the ignition phase compared to the TLUD method leading to high levels of smoke particles especially during the ignition phase. The lower temperatures coupled with limited oxygen, which is needed for the complete combustion of condensed matter, leads to high smoke emissions and other particles of incomplete combustion. This temperature difference results in differences in particle sizes and morphology emitted to the atmosphere from the fire ignition methods. During low temperature ignition, the volatile components from the fuel are not burned. Rather, they condense on the smaller particles to
form larger droplets, which solidify upon cooling. Figure 39 indicate that at higher combustion temperatures the mass of condensed matter emissions is considerably reduced.

Figure 39: Showing condensation of particles and formation of spherical particles during pyrolysis stage I from: a) BLUD method; and b) TLUD method

Figure 40 shows that the liquid aerosol droplets from the coal fire form spherical and bead-like accretion chains along the length of the fibre material. It is seen that these super-micron particles primarily consist of individual spherical particles. The nearly perfect spherical appearance of the particles implies that the minerals in coal are almost completely melted during combustion [Wu et al., 2011]. Although small bead-like aggregates exist, the surfaces of the spherical particles are quite smooth suggesting that the aggregation and condensation of vaporised species is not the important factor in super-micron particle formation.

Figure 40: SEM micrograph showing the presence of bead-like particle aggregates from a traditional fire ignition method during pyrolysis stage I. The spherical particles are likely to be present in the exhaust or atmosphere as liquid aerosol droplets

Figure 41 shows the morphology of particles collected on a quartz filter, which include the sub-micron and ultra-fine particles. It is seen that the particles on this stage are dominated by individual spherical particles. The morphology of the particles shown in Figure 41 indicates that for particles in between super-micron and ultra-fine particles, condensation of vapour phase species or aggregation of nucleates could be an important formation mechanism. For spherical particles, the specific surface
area increases with decreasing particle diameter. Therefore, this mechanism would be more pronounced for smaller particles (i.e. the contribution of vaporised species/nucleates would be more significant for the formation of smaller particles) [Wu et al., 2011].

Figure 41: Morphology of the particles collected from combustion of coal in a brazier using the TLUD fire ignition method during pyrolysis stage 1.

**Conclusion**

We have shown in this section that the origins of these ‘giant’ conglomerate particles are also emitted from domestic coal combustion in informal braziers. This assertion cements arguments put forward in Wentzel et al. [1999] that these conglomerates are likely to originate from coal combustion processes in the residential sector. China et al. [2014] and Chakrabarty et al. [2014] found that these giant particles are emitted from biomass burning smoke. We argue that particles from the first stages of pyrolysis should be sampled and analysed as this could assist in describing the dynamics of smoke formation and transformation during combustion. We have refined the stage of the fire during which these particles can be sampled. Samples taken during pyrolysis stage I result in filters being clogged with a carbonaceous viscous layer that sometimes covers the whole filter membrane. There has been a tendency to discard these samples as ‘overloaded’ samples due to artefacts. From this study, it has been argued that these particles occur when the exit gases from the fuel bed are below combustion point (Figure 31) and that the filter traps condensates that are liquid at or near room temperature. Discrete particles (if they are present) are engulfed by this liquid layer. Discrete particles may be sampled once the exit temperature is above the combustion point where more volatiles are combusted in homogeneous gas phase reactions.

**4.6.2 Laboratory analyses of particle morphologies from coal combustion**

Particle morphologies (sampled at < 1 m from the braziers) were investigated for the BLUD and the TLUD ignition method in both the high ventilation rate brazier and the low ventilation rate brazier. Results of these findings are presented in this section.

Figure 42 shows micrographs from the pyrolyzation phase of BLUD fires indicating the presence of liquid condensed matter that has coalesced to form a layer that covers filter pores. EDS showed that
this thin film is dominated by C and O with traces of Mo, Zn and Fe. The micrographs show that the ventilation rate has an effect on the amount of condensed matter collected on the filters. The high ventilation BLUD method produced lower emissions of condensed matter compared to the low ventilation BLUD (Figure 42). In the BLUD, low ventilation the filter material rapidly clogged and a continuous layer of liquid/ tarry substance coalesced and covered the entire filter membrane, with some pores completely closed (Figure 42b).

These results could be best explained by referring to the coal used in this study; the coal had relatively high fractions of volatile matter. When employing the BLUD method, an oxygen-depleted atmosphere is created in the brazier above the pyrolytic zone and the gradual heating of the coal allows the semi-volatile organic compounds to be released from the solid fuel and during cooling and condensation. Especially during the pyrolization phase and immediately after refuelling, conditions would favour evaporation and re-condensation, rather than combustion, of volatile and semi-volatile fractions. This suggests that the aerosols are in a liquid form upon impaction with the filter substrate.

**Figure 42:** SEM images from BLUD fires at pyrolyization stage I: a) showing particle decay from the high ventilation; b) showing a layer of liquid tarry substance covering the entire filter, typical of the low ventilation. Scale bars = 5 µm (a); and 2 µm (b)

Figure 43 shows electron micrographs of giant conglomerate particles collected from BLUD fires during the later phases of coal pyrolization (pyrolysis stage II) in a low and high ventilation brazier. Results show that BLUD fires are dominated by ‘giant’ conglomerate particles during pyrolysis stage II (where visible flames are seen from the burning coals), and the mode diameter of the conglomerates is dependent on ventilation rates of the combustion device. Notice the presence of a larger conglomerate particle in the low ventilation BLUD method (Figure 43a) compared to the relatively small conglomerate particle emitted from the high ventilation BLUD method (Figure 43b).
Figure 43: Micrographs from BLUD fire showing giant conglomerate particles during pyrolysis stage II:
a) from the low ventilation; b) from the high ventilation. Scale bars = 10 µm

Figure 44 shows electron micrograph images of particles emitted from the coking phase of BLUD fires. Note the nucleopore filter with a fairly heavy loading of fuzzy-textured conglomerates with diameters less than 2 µm collected from BLUD fires during the early phases of coking in the high ventilation TLUD, and fuzzy-textured conglomerates with diameters greater than 5 µm, with the largest ranging up to 30 µm for the low ventilation TLUD. Results show that BLUD fires are dominated by fine to coarse conglomerate particles during the coking phase compared to the pyrolysis phase (Figure 43) where ‘giant’ conglomerates are significant. Again, the mode diameter of the conglomerates is dependent on ventilation rates of the combustion device. Notice the presence of a lawn of fine mode carbonaceous conglomerate particles in the high ventilation BLUD method (Figure 44a) compared to coarse mode carbonaceous particles in the low ventilation BLUD method (Figure 44b).

Figure 44: Micrographs showing conglomerate particles from BLUD fires during the early stages of 
coking: a) for the high ventilation; b) for the low ventilation. Scale bar = 2 µm (a); scale bar = 5 µm (b). Notice the presence of spherical fly ash particles in both samples.

Figure 45 shows electron micrographs of conglomerate particles collected from TLUD fires during coal pyrolysis phase in low and high ventilation rate braziers. Results show that TLUD fires are dominated by fine to coarse mode conglomerate particles during the pyrolysis phase, and size of
the conglomerates is dependent on ventilation rates of the combustion device. Notice the presence of ‘giant conglomerates’ in the low ventilation TLUD method compared to the coarse mode carbonaceous particles emitted from the high ventilation TLUD method (Figure 45).

This result can be explained by referring to the general observations made during the TLUD fires. During the pyrolysis stage II, less visible smoke could be seen and visible flames could were observed above the fuel bed. This suggest that at lower particle concentration and a higher degree of drying of liquid aerosols (i.e. the decay phase), partially or completely solidified primary spherules can be formed, and as they aggregate they form conglomerates. The growth into ‘giant’ conglomerates is likely to occur in the high concentration zones of the stove, as once released into the atmosphere further growth through joining of conglomerates would be inhibited on account of their size and low diffusion velocities [Wentzel et al., 1999]. The decrease in the yield of the conglomerates with increasing temperature (i.e. high temperatures at pyrolysis in the TLUD compared to the BLUD method) can be explained by the stability of tar molecules at high temperatures and the reactions of tar by gaseous species existing in the post-flame region of the stove. Increases in temperature favour the ‘cracking’ reaction, which leads to a lower soot yield. Another reason for the decrease of soot with temperature may be due to reactions of the oxygen-containing species, especially OH and O radicals, with tar molecules and intermediate PAH. The concentration of oxygen-containing radicals such as OH and O increased drastically with an increase in temperature [Fletcher et al., 1997].

Figure 45: SEM images of soot particles from TLUD fires during the pyrolysis stage II: (a) from low ventilation brazier (b) from high ventilation brazier. Scale bars = 5 µm (a); scale bar = 10 µm (b)

Figure 46 shows electron micrographs of conglomerate particles collected from TLUD fires during the coking phase of the fire in low and high ventilation braziers. Results show that during the coking phase TLUD fires are dominated by fine mode carbonaceous particles compared to the pyrolization phase (Figure 46). During this phase, the mode diameter of the particles is not dependent on the ventilation rate of the combustion device as less condensed matter particles are released during the coking phase of the fire. These results can be supported by explanation given above, where combustion temperatures play a significant role in the reduction of giant and coarse mode conglomerates from the fire.
When all the coals in the brazier have been fully *coked* and are red-hot, in the BLUD and TLUD ignition methods, there is no noticeable difference in the particle sizes and morphologies of particles emitted between the ignition methods and across ventilation rates. Results show that during the later stages of the coking phase in both the BLUD and TLUD ignition methods, fine conglomerate particles are formed.

**Identification of spherical organic particles**

Figure 47 shows a micrograph of spherical organic particles sampled and fractal aggregates (collected < 1 m from the brazier) from a BLUD fire during pyrolysis stage II. The size and shape of the spherules were dependent on the ventilation rates. In the high ventilation brazier, fewer spherical particles were observed compared to samples collected from the low ventilation brazier. Carbon and oxygen comprised the bulk of the elemental composition of these spherules. [Pósfai et al., 2003] argues that particles of this type are carbonaceous in nature and are formed in smouldering fires, and their abundance increases in the atmosphere with the age of the plume. The observed particles are similar to spherical C-rich particles collected from coal combustion processes in previous studies [Shi et al., 2003]. As a result, we have termed these particles spherical organic particles (SOP). However, since EDS analyses only gave elemental compositions, we had no direct evidence that the C element in these particles occurred in organic compounds.

Spherical organic particles have similar morphologies to fly ash, though they are smaller, usually below 2 µm in diameter, while fly ash could be more than 5 µm in diameter. Without chemical information from each particle, it is impossible in this study to identify distinctively these particles apart due to the overlap in size and similarity in morphology. Unlike organic coated particles and sulphate spherules, the observed spherical organic particles (SOP) were not beam sensitive and did not evaporate under prolonged exposure to the electron beam at an HV of 20. This is similar to findings of ‘tar-balls’ reported from biomass combustion [China et al., 2014; Hand et al., 2005; Pósfai et al., 2004]. Fu et al. [2012] argues that such insusceptibility against the electron beam may be because of the presence of high-molecule organic compounds, such as HULIS (i.e. humic-like substances that are typically polycyclic aromatic hydrocarbons).
Figure 47: SEM image showing particles emitted from BLUD low ventilation fire with the advent of visible flames (pyrolysis stage II). The yellow arrows show spherical organic particles, the red arrows show fine mode soot particles and the blue arrows show dark halos indicating the presence of moisture in the sample.

Similar to Tóth et al. [2014] and based on the most characteristic features of the relatively fresh spherical organic particles (SOP) (i.e. spherical shape, large size, homogeneous composition, and high C/O ratios); we suggest a direct emission mechanism for the spherules. The spherical particles indicate that the droplets do not only occur on the filter, but are already present in the exhaust or atmosphere where they are formed by a condensation process. These spherical particles are likely to be produced by the direct emission of liquid droplets followed by heat transformation upon coal burning. Our hypothesis is that the spherules are ejected from the pores of coal particles as liquid organic carbon droplets then undergo chemical transformations that increase their viscosity, form aggregates, and solidify into highly refractory particles, as is generally observed in the atmosphere.

### 4.6.3 Ageing of condensed matter particles

To investigate the effect of ageing (on the scale of a few seconds) on condensed matter emissions, and to note how commonly these conglomerates and spherical organic particles occur in different fires and ventilation rates, aerosols contained in coal smoke-laden exhaust we collected ~5 m above the brim of the burning brazier through a 4 m long exhaust duct. Results are presented for the BLUD and TLUD ignition methods in both the high and low ventilation braziers, during the pyrolysis (stage I and or stage II) and the coking phase of the fire.

**During the pyrolysis phases**

Results show that when sampling particles ~5 m above the combustion devices, spherical organic particles (SOPs) are dominant for both fire-ignition methods. TLUD fires emitted spherical organic particles with smaller mode diameter compared to BLUD fires. The spherical particles form diffusion accretion chains in TLUD fires, whereas BLUD fires show numerous condensation spherules (Figure 48). This suggests that the particle mass concentration and particle mean diameters are influenced by the ignition method employed, and the subsequent evolution of particles and gases though and above the fuel bed.
Figure 48(a & b) shows micrographs of condensed matter particles sampled during the pyrolysis phase (stage I) from BLUD fires in low and high ventilation braziers, respectively. For the low ventilation rates, the spherical organic particles observed are two to three times larger compared to those observed for the high ventilation rate. Also, note the presence of a thick film of carbonaceous material on samples collected from the low ventilation brazier (Figure 48a).

Figure 48: Spherical particles sampled during pyrolysis stage I from BLUD fires in: a) a low ventilation brazier, and b) a high ventilation brazier. Scale bars = 2 µm

Figure 49 shows an electron micrograph of a typical ‘giant’ spherical organic particle collected from the low ventilation BLUD during the coal pyrolysis stage I. These particles are three-fold larger compared to particles from the corresponding high ventilation BLUD brazier. This suggests that ventilation rates may have an influence on the particle mode diameter of the spherical particles in BLUD fires. However, it should be noted that this is a qualitative observation based on visual inspection of the micrographs—automated particle recognition and counting facilities were not available on the SEM instrument used. There is a need in future studies to use commercial particle sizers (e.g. differential mobility particle sizers–DMPS, and scanning mobility particle sizer–SMPS) to analyse the specific mode diameter of particles obtained from such studies. In the absence of these expensive tools, one suggestion would be to use the ImageJ software package (free-online graphics software) for image processing and analysis. However, this requires high-level expert knowledge on how to threshold the SEM images before analysing the particles.

Figure 49: Giant spherical organic particles from the ignition phase of a BLUD fire
For the TLUD method, diffusion accretion chains were observed during the pyrolyzation phase (with the fire not completely established above the coal bed) in both the low ventilation and the high ventilation braziers. The size and length of the diffusion accretion chains were dependent on the ventilation rates. Low ventilation TLUD produced lengthy diffusion accretion chains compared to the high ventilation emissions (Figure 50).

**Figure 50: Diffusion accretion chains from TLUD fires during pyrolysis stage I when the fire is establishing above the coal bed: a) a high ventilation brazier; and b) a low ventilation brazier**

**Scale bars = 5 µm**

**During the pyrolysis phase in a high ventilation brazier**

Figure 51 shows micrographs of the particles formed during the flaming phase of BLUD and TLUD fires, when using a high ventilation brazier. Results show that during the initial pyrolysis stage (phase I) of the fire, spherical particles are formed in BLUD fires (Figure 51a), whereas conglomerate chained particles are evident in TLUD fires (Figure 51b). During pyrolysis (stage II), ‘giant’ conglomerates are formed from BLUD fires (Figure 51c); whereas in the TLUD fires fine mode conglomerate particles are formed.

**Identification of diffusion accretion chains**

Figure 52 shows an electron micrograph with numerous diffusion accretion chains. These agglomerates have not been reported in previous studies on coal combustion, although there have been observed in experiments involving biomass burning smoke [China et al., 2014; Chakrabarty et al., 2009; Chakrabarty et al., 2006, Pósfai et al., 2004; Pósfai et al., 2003]. These diffusion accretion chains are formed from bimolecular homogeneous nucleation with water vapour and they grow by coagulation and condensation. Low volatile organic compound (LVOC) released from the burning coal undergoes polymerization reactions with OH radicals in droplets, yielding larger molecular weight and less water-soluble species. Due to the Raoult effect\(^2\), the equilibrium size of the droplet is reduced. As the size of the droplet decreases, the solution becomes concentrated and the rate of polymerization increases, which results in turning the organic polymer largely insoluble in water. Spherical organic particles observed in this study are believed to remain as dry, low-vapour pressure solid particles.

\(^2\)Raoult law states that the partial vapour pressure of each component of an ideal mixture of liquids is equal to the vapour pressure of the pure component multiplied by its mole fraction in the mixture. The effect of the law is that the saturated vapour pressure of a solution will be lower than that of the pure solvent at any particular temperature.
Figure 51: Ageing particles sampled from BLUD and TLUD fires; a) Spherical organic particles from BLUD fires (pyrolysis stage I); b) numerous condensation spherules and diffusion accretion chains from TLUD fires (pyrolysis stage I); c) dendritic particles for BLUD during pyrolysis stage II; and d) fine soot particles for TLUD during the coking phase. Scale bars = 2 µm (a & d); 5 µm (b & c)

Figure 52: Numerous spherical organic particles and diffusion accretion chains.

Thujadeen et al. [2015] contends that particle–particle collisions are the dominant particle growth mechanism [Thajudeen et al., 2012], especially in the final stages of the flame synthesis process. The particles may restructure/rearrange following collision but they do not fully coalesce. This is because the diffusion-driven sintering time scales for viscous flow and grain boundary are slow relative to the
time-scale for collisions, even in high temperature combustion conditions [Thajudeen et al., 2015; Eggersdorfer et al., 2012]. Consequently, flame synthesis generally leads to the production of aggregates/agglomerates (i.e. ensembles of point-contacting or overlapping near-spherical primary particles) [Thajudeen et al., 2015; Eggersdorfer & Pratsinis, 2014; Grass et al., 2006].

**Morphology of spherical organic particles**

The morphologies of the sampled spherical organic particles from residential coal smouldering ignition conditions (typical of the BLUD method) are similar to atmospheric tar-ball particles [China et al., 2014; Pósfai, 2003; 2004] and polymeric organic compounds [Fu et al., 2012] reported in biomass smoke. These particles are presented as aggregates and individual particles.

From this study, it is evident that spherical organic particles occur in plumes of smouldering rather than of flaming fires. Martins et al. [1998] noted that smouldering combustion produced more spherical particles than flaming combustion. Pósfai et al. [2004] argued that ‘tar-balls’ occur exclusively in biomass and biofuel combustion smoke, since fossil fuel burning releases mostly apolar compounds that do not tend to polymerize under atmospheric conditions. They further argued that tar balls do not possess a semi-ordered microstructure or form aggregates. The authors then claimed that to their knowledge, individual particle studies of coal and oil burning emissions and of urban aerosols do not show the presence of tar balls. However, in this study, we have shown the presence of tar-ball-like spherical organic particles from coal combustion smoke particles, and we have identified ‘bead-like’ aggregates/diffusion accretion chains from spherical organic particles as they interact with each other (Figure 52).

**Mixing states in spherical organic particles**

The spherical organic particles are found in three distinct states: (i) Bare – spherical organic particles without any inclusions (Figure 49); (ii) Agglomerated – resulting in the formation of chains or aggregates (Figure 52); (iii) Spherical organic particles with inclusions – the surface of the spherical organic particle will have inclusions of fine mode particles. For example, Figure 53b shows a micrograph of observed spherical organic particles, with smaller spherical aggregates on the surface. These small aggregates may either originate from direct condensation of vapour phase species or aggregation of nucleates formed from organic vapours [Wu et al., 2011]; and (iv) Deformed particles – with structural defects, not uniformly smooth and spherical (Figure 54).
In this study, for the TLUD method, 50% of the spherical particles analysed were bare particles without any inclusions, 35% were constituted of diffusion accretion chains, 10% had inclusions and 5% were structurally deformed. For the BLUD method, we noticed that bare spherical particles constituted 65% of the spherical particles analysed, with chain aggregates constituting about 25% and 7% for particles with inclusions, and structurally deformed spherical organic particles constituting 3%. We should caution that the count of bare spherical particles might be under-estimated because some spherical particles had smaller diameters making it difficult to determine whether they had inclusions. As such, ultra-fine particles in the nanometre range diameters (i.e. below 500 nm) were not included in this estimate— if the particle could not be easily distinguished then the particle would not be classified in any of the groups.

Structural defects were observed in some of the near-spherical organic particles, as shown in Figure 54. Prolonged atmospheric processing of the spherical organic particles or ageing of the particles while fire emissions are drawn through the SEM filter (~10 min) may explain the observed structural defects in some of the spherical organic particles. Similar results have been reported in Chakrabarty et al. [2006], Pósfai et al. [2004; 2003].

Figure 53: SEM micrographs showing mixed states of spherical organic particles: a) coalescing spherical organic particles; b) spherical organic particles with surface inclusions

Figure 54: Spherical organic particle from the flaming phase of the BLUD fire showing structural defect
**Chemical composition of the spherical particles**

Figure 55 shows an EDS spectrum of a spherical organic particle produced from smouldering combustion conditions in the BLUD method of igniting a coal fire in a brazier. The majority of the identified spherical particles contained only C and O, and other particles contained C and O plus other elements such as Si, S, Mo, K, Al in trace amounts (Figure 56), which is consistent with previous observations of atmospheric tar-ball particles [Adachi & Buseck, 2011; Niemi et al., 2006; Pósfai et al., 2004; 2003].

**Figure 55:** Typical EDS spectrum from a spherical organic particle containing only C and O

(The gold peaks are artefacts that originate from the gold-coated membrane filters)

**Figure 56:** Typical EDS spectrum from a spherical organic particle containing C, O and traces of Mo

(The gold peaks are artefacts that originate from the gold-coated membrane filters)

The average carbon-to-oxygen ratio of the spherical organic particles was calculated and determined to be ~9. The carbon background signal from the polycarbonate SEM filter substrate makes it difficult to determine the exact carbon to oxygen ratio of particles. It is not possible to apply any correction factor for the background as it varies from particle to particle [Chakrabarty et al., 2006]. Our semi-quantitative EDS data show a higher average molar C/O ratio (ranges from 8 to 10) in spherical
organic particles from residential coal burning smoke, a difference that could result from the loss of O-rich functional groups (decarboxylation) in the vacuum of the electron microscope [Pósfai et al., 2004].

‘Electronically’ dark and bright spherical particles

By way of using secondary electron (SE) imaging of individual particles at low accelerating voltage (1 kV), we identified two forms of spherical organic particles defined by China et al. [2014] as ‘electronically’ dark and bright. We classified the spherical organic particles into ‘electronically’ dark and bright based on their grayscale intensity on the SE low accelerating voltages images. Semi-quantitative energy dispersive X-ray analysis was conducted on 30 dark and 30 bright spherical organic particles of comparable size. Results show that out of the 30 dark spherical organic particles, 24 showed higher average minor oxygen and carbon content (Figure 56) than in bright spherical organic particles (Figure 55). The remaining six dark spherical organic particles showed similar oxygen content to the bright spherical organic particles, possibly due to the presence of an insulating layer or due to a ‘somewhat’ subjective segregation of each spherical organic particle group [China et al., 2014]. It should be noted that these two forms of spherical organic particles could not be distinguished from each other at high accelerating voltages (20 kV). We contend that the enhanced contrast at low accelerating voltages is due to various degrees of oxidation states on the surface of the spherical particles. The darker spherical particles may be more oxidised and possibly have less volatile coating compared to bright spherical organic particles. China et al. [2014] found these two forms of tar balls from smouldering conditions of biomass fires. Tivanski et al. [2007] observed that tar balls from biomass combustion typically consist of 55% atomic carbon and 45% atomic oxygen, suggesting the presence of an oxygenated layer on the surface of the tar balls. Ivey [2010] observed a similar SE contrast effect on zinc and zinc oxide samples.

We further investigated to see if the backscattered electrons (BSE) could be used distinguish between the two forms of spherical organic particles. There were no contrast differences between the two types. This result is similar to findings by China et al. [2014] who argued that SEs are sensitive to the surface, whereas BSEs are sensitive to the bulk of the particle. Different contrasts in the SE images and similar contrasts in the BSE images highlight the fact that there could be an existence of a layer of different composition at the surface of the spherical organic particles. This phenomenon needs to be investigated further.

4.6.4 Conglomerate particles from domestic coal combustion

Mixing of soot particles

The compactness of soot aggregates varied from closely packed particles to chained and open branched aggregates. Figure 57 shows micrographs of soot particles from residential coal combustion fires, classified into six categories, based on morphology and visual estimation of coating, according to China et al., [2014:3]:

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**Type I** – embedded soot, where the particle is heavily coated [China et al., 2014] (potentially corresponding to a large optical absorption enhancement), but where some monomers are still evidently visible;

**Type II** – dendritic soot particle, where soot voids are filled by coating material, but the soot is not completely engulfed;

**Type III** – bare soot, where monomers are easily distinguished and no considerable coating is evident from the SEM image, although very thin coating might be present on the monomers (corresponding to no or little optical absorption enhancement);

**Type IV** – sponge-like soot particles;

**Type V** – melted soot particle with inclusions of diffusion accretion chains;

**Type VI** – melted ‘toffee’ soot particle, where the soot particles are melted to an amorphous mass. Primary spherical particles and diffusion accretion chains are not visible in this structure.

Figure 57 shows micrographs of the mixing states and classification of soot particles collected and analysed during the study.

The compactness of soot aggregates varied from closely packed particles (Figure 57a – Type I) to chained and branched aggregates (Figure 57c – Type III). Similar to findings by Gwaze [2007], we found that some aggregates were agglomerated with large spherical particles with diameters greater than 100 nm, and are likely to be tar balls or spherical organic particles that were embedded in soot particles during the coagulation process in the cooling smoke. High magnification images (Figure 57c & f) of soot particles revealed minimal coating of condensed organic matter on the monomers.

Figure 57b shows a conglomerate with a highly dendritic structure (Type II), giving rise to an object with high pore structure and high specific surface [Wentzel et al., 1999]. EDS analysis revealed that the conglomerate is composed on C and O, indicating that it is organic or carbonaceous material.
Figure 57c shows the presence of large numbers of spherical organic particles. Present in this group are numerous clusters of spherules, containing a few to hundred or more spherical particles. These clusters resemble the thread-like basic structure of the dendritic soot particles. EDS analysis shows that these clusters are carbonaceous, with C and O being the dominant elements. Such clusters are a result of fine particle growth and are likely to be formed through nucleation of nanometre size particles and diffusion aggregation [Wentzel et al., 1999]. Figure 57d shows an image of carbonaceous sponge-like soot particle (Type IV) collected from BLUD fires. Note the Nucleopore filter with fuzzy-textured, rounded conglomerates with average diameters greater than 10 µm, with the largest observed up to 50 µm in diameter.

Figure 57e shows a conglomerate with an external mixing of clusters made from minute spherical particles (Type V). This conglomerate suggests the possibility that the object underwent some form of post-formation heating/or longer residence time in a higher temperature zone, causing partial melting, and collapse of the structure under surface tension [Wentzel et al., 1999]. We propose that similar effects may be produced if the conglomerates were acting as condensation nuclei for lower boiling point organic solvents, sometime after primary formation. The condensing liquids could then partially dissolve the matter comprising the primary spherules, forming an amorphous mass or viscous glue-like substance. Under surface tension, the viscous glue could lead to the partial or complete collapse of the conglomerate, before the process is stopped under ambient conditions due to cooling [Wentzel et al., 1999].

The morphology shown in Figure 57f suggests that the super-micron particles are primarily generated from the minerals in coal that are (partially) melted during combustion in the brazier (Type VI). The formation mechanisms may involve coalescence of inherent minerals, fragmentation of chars, and the melting of excluded minerals [Wu et al., 2011; Linak et al., 2007]. However, the contribution of different mechanisms to the formation of super-micron particles is difficult to distinguish from the present results.

Carbonaceous particles with mineral inclusions were observed from our experiments (Figure 58). The micrograph shows a carbonaceous amorphous mass with a calcium rich mineral inclusion.

Figure 58: SEM micrograph showing a carbonaceous particle with mineral inclusions
Some of the compact soot particles had surface diameters larger than 10 µm (Figure 59). Semi-quantitative EDS spectra of these particles revealed C and O, with traces of Si, Al and Fe indicating that they are carbonaceous materials from coal combustion. These large soot particles have the potential to contribute significantly to mass of carbonaceous particulate matter.

Figure 59: Large and compact soot aggregate greater than 10 µm with EDS spectra showing the presence of C, O and traces of Si, Al and Fe.

In conclusion, the sequence of particle formation in a coal brazier, as a function of the phase of combustion is presented in Figure 60. It is evident from the micrographs that particle morphology and size is a consequence of exit gas temperatures and the phase of combustion. During the ignition phase (stage I), particles are collected as liquid droplets or a carbon-dominated viscous liquid that forms an uneven carbonaceous film on the filter material. During stage II of ignition, when exit gas temperatures increase (but not to a point of combusting the emitted volatiles), an amorphous mass of particles is collected on the filters. These samples have in the past been discarded as “overloaded samples”, especially when the goal is to analyse single particles. Although such samples are not useful in characterizing single particles, they illustrate that the aerosols generated during the ignition phase, were in liquid form upon impaction with the filter. During pyrolization phase, combustion temperatures increase and the volatiles are burned. At low aerosol concentrations and at high temperature (i.e. during the particle decay phase) (pyrolization stage I), complete or partially solidified spheres can be found on the filters. The solidified spheres may form diffusion accretion chains. These indicate that the liquid aerosol droplets do not arise on impaction with the filter, but that they already exist in the exhaust/flue or in the atmosphere before condensation occurs. Conglomerate with a “sponge-like” structure are formed during pyrolization stage II. The dendritic form gives rise to a material with a high pore volume and high specific surface area. During the coking phase, fine mode
soot particles are formed. This is because most of the volatile matter has been driven off, leaving behind a solid residue of impure carbon.

![Sequence of particle formation during different combustion phases in a coal brazier](image)

**Figure 60:** Sequence of particle formation during different combustion phases in a coal brazier: particles collected during a) initial ignition phase; b) ignition stage II; c) pyrolysis phase – stage I; d) particles pyrolysis phase – stage II; and e) coking phase

4.6.5 An overview of ‘Other’ particles from domestic coal combustion

*Fly ash particles*

All individual spherical particles were identified as either spherical organic particles or fly ash particles. Fly ash particles, with composition mainly of heavier elements (Z > 10) were found only in samples collected from the TLUD fires in high ventilation braziers, during the intense flaming periods characterized by high combustion temperatures and rapid airflow through the fuel bed. The SEM images of spherical fly ash particles are shown in Figure 61 (a) & (b).
Energy dispersive spectrometry (EDS) spectra showed that these spherical fly ash particles contained mainly Al and Si, with minor or trace components of K, Ca, Ti, Mn and Fe (Figure 62). The fly ash particles were stable under the electron beam, and therefore could be distinguished from sulphates, for example. These particles were collected during the high-temperature pyrolysis stage II, when temperatures in the combustion chamber exceeded 800°C (See section 4.4.4). The morphology of a fly ash particle is controlled by combustion temperature and cooling rate [Kutchko & Kim, 2006]. Spherical fly ash particles are formed by vaporisation and condensation of mineral compounds in the fuel matrix during combustion, especially in coal and peat combustion [Baumbach, 1996]. High-resolution TEM imaging shows that fly ash particles are amorphous in structure [Li et al., 2003]. The main sources of fly ash particles are boiler and power plants, but may be produced from small high power combustion devices. For example, Li et al. [2012] contends that direct emissions from low temperature household heating stoves (with no emission control) and coal fired power plants and factories (with limited emission control) contributes large quantities of coarse fly ash particles into the atmosphere.

Figure 62: EDS spectra of fly ash particles shown in Figure 61(a) & (b), respectively.
The chemical and physical properties of fly ash particles are dependent on the mineral matter in the coal, the combustion conditions, and post-combustion cooling [Kutchko & Kim, 2006]. During the combustion process, the heated inorganic mineral grains in the fuel are exposed to a reducing environment (hydrogen ions and absence of free oxygen). Under these conditions, oxides are reduced to metals, which generally have a lower melting and vaporisation temperatures than the parent oxides. During cooling, the melted or vaporised metals condense and solidify to form amorphous spherical particles, or may condense and mix externally with other particles. In this study, we discovered from the morphology and elemental data of the fly ash particles that the particles were composed of over 50% amorphous aluminosilicate spheres and a lesser amount of iron-rich spheres. The relative amount of aluminium and silicon varied from sphere to sphere and, similarly, the particle size diameters varied. The relatively weak signal intensities for Ca, K, Na, Ti and Fe indicate much lower concentrations of these elements in the particles, in accord with the average crustal composition of the Earth.

In addition to the spherical fly ash particles, non-spherical, crystalline mineral particles were observed for what braziers/ignition methods as examples, comprising elements Mg, Al, Si, S, K, Ca, Ti and Fe. Figure 63 presents a selection of such particles. The silicate particle is composed of Si, Al and O with traces of Fe, Ca, Mn and Ti (Figure 63a). The calcite particle is composed of Ca, Mg and O, with traces of Al, Si, S, Cl, Na (Figure 63b), while Figure 63c shows a carbonaceous particle rich in C and O with traces of Ca, Mg, Si, Na, N, K and Cl. The particles are rich in the indicated elements throughout the entire particle despite their large size of approximately 20 µm.

**Figure 63:** Micrograph showing non-spherical mineral particles (BLUD fires during coking phase): a) particles rich in Si, O and Al; b) rich in Ca, O, and Mg; c) carbonaceous particle rich in mineral elements such as Ca, Mg and Si

**Coal particles**

Figure 64 shows electron micrographs of coal particles collected during the brazier fires. Coal particles are distinct from the other particle types because of their size (typically larger than 30 µm, and up to 100 µm on the filters), morphology (broken edges and cracks, which are not typical in dust particles), and mainly carbon composition. EDS analyses showed that heavier elements within these
large particles occurred in localised inclusions–mineral grains. Unburned coal particles arise from ‘cracking’ of the coal pieces during initial heating and swelling (pyrolization stage I). The smaller resultant fragments could be carried up into the airstream.

**Figure 64:** SEM images of unburned coal particles. EDS analysis shows presence of traces of Na, Al, Si, K, Ca, Ti and Fe. Scale bars = 10 µm

**Beam sensitive particles**

Figure 65 shows a particle, which changed appearance and then disintegrated upon exposure to the electron beam at 20 kV. Physical damage distorts the original particle shape because of particle charging by the electron beam [Chakrabarty et al., 2006]. This suggests that the particle may be composed of organic material and sulphates, which disintegrates upon exposure to high electron beams in SEM. EDS of the particles showed the presence of S in the particles (Figure 66).

**Figure 65:** Evidence of particle disintegration due to high electron beams (e.g. 20 kV): a) particle morphology before high beam exposure and; b) particle morphology after high beam exposure. Scale bars = 10 µm
Fu et al. [2012] contended in their study that when doing EDS analyses beam exposure should be limited to 30 s to minimize radiation and potential beam damage. Decomposition of the particles in the vacuum or under the electron beam complicates EDS analyses. However, some particles such as tar balls/ spherical organic particles and soot particles, do not show any changes when exposed to the electron beam. In contrast, particles with organic coatings and/ internally mixed particles containing sulphates tend to change under the electron beam [Fu et al., 2012]. As a result, the morphologies of some aerosol particles, as observed in the SEM, may differ from their shapes prior to collection [Li et al., 2003]. Despite possible changes in morphology after beam exposure, the compositions of the particles measured herein should reflect their original compositions before collection. In this study, we used a relatively moderate accelerating voltage of 20 kV for most images. Compared to lower accelerating voltages, the use of 20 kV improves imaging of the surface structure of the particles. At this operating voltage, shape distortion due to charging was observed in ~2% of the particles analysed.

This concludes presentation and direct discussion of the experimental results. A summary and discussion of the broader implications of the research findings and the significance of the research will be given in the concluding chapter.
CHAPTER FIVE

This chapter presents a summary of the study and a discussion of the significance of the findings. The hypothesis is unpacked and checked against the findings, for each of the mentioned conditions of how poor combustion conditions influence particle formation. Recommendations are made for continuation of research into remaining open questions related to combustion tests in domestic braziers.

5. Conclusions and Recommendations

5.1 Summary of Findings

In this section, findings are summarised under headings related to each of the five key objectives. In this summary, the term “emissions” is used as a synonym for emission factors related to the energy content of the fuel, reported in units \( \text{[g MJ}^{-1} \text{]} \). The term “significant” is related to statistical inferences presented in the results chapter, and in all cases refer to 95% confidence levels.

Objective (a): To review scientific literature concerning adverse health effects from ambient air pollution in relation to domestic coal combustion

The literature established that emissions from residential coal combustion have adverse health effects. Studies carried out in China and other developing countries suggest that there is a link between continued coal use and increased morbidity and premature mortality. Household and ambient exposures to combustion emissions have been associated with diseases such as emphysema, cardiopulmonary failure and cancer. Over the past decade, there have been dedicated epidemiological studies to ascertain the effects of solid fuel combustion emissions on human health. However, the importance particulate properties other than mass concentration (i.e. morphology, chemical composition, surface reactivity, nanoparticles) remain to be elucidated. In terms of interventions to mitigate the adverse effects of domestic emissions, there has been a surge of interest among international agencies and NGOs, governments, regulatory bodies and donor agencies to implement clean stove programmes.

In South Africa, the wide use of coal braziers in the residential sector leads to copious emissions of products of incomplete combustion, contributing to elevated smoke pollution concentrations in the near-surface atmosphere. Studies on the emissions from small fixed-bed domestic coal-fired appliances, especially vis-à-vis fine particle emissions and their composition during different combustion conditions have been scarce. Moreover, there have been limited comprehensive, systematic studies of coal stoves in terms of emissions and thermal performance in the South African context. For example, previous studies carried out in South Africa on coal braziers were limited to single devices, without specifications of the ventilation rates, fuel properties (fuel quality and fuel moisture content) or the design of the braziers. In each of the tests, it was reported that fire-ignition method reduces PM emissions but no systematic experiments were carried out to ascertain the
influence of fuel and stove properties on the emissions of particulate matter and trace gases from these
devices. There was therefore a need for further systematic studies to determine the effects of
parameters such as fire-ignition method, coal quality, coal moisture content, and primary and
secondary ventilation rates on the performance of the braziers. This information is needed to lay the
groundwork for improvement of existing coal braziers; to derive appropriate emission factors for
dispersion modelling; to develop novel low-emission combustion technologies; to understand
relationships between health and climate effects; and to select appropriate strategies and technologies
to mitigate health and climate problems.

Objective (b): To design a dilution sampling system for emission measurements in residential coal-
fired appliances

In one of the practical tasks of this thesis, we have made a methodological innovation by designing,
constructing and testing a portable smoke dilution system for use in the investigation of condensed
matter emissions from residential coal combustion. This was motivated by the fact that off the shelf
dilution systems are cumbersome, are not variable and so cannot cope with the dense smoke emitted
from braziers during the initial phases of combustion. This dense smoke saturated the analytical
instruments, which results in under reporting of emission factors due to overshooting the tolerance
range of the instruments, or causing the machines to clog from condensed organic deposits, resulting
erroneous readings. An apparatus for exhaust gases flow dilution, designed by C. Pemberton-Pigott
(pers comm.) and termed the SeTAR dilutor, was constructed and evaluated. This dilutor proved a
suitable device to characterize, under controlled laboratory conditions, the very dense particulate
emissions from coal combustion and their rapid morphological evolution in the first seconds after
emission. The SeTAR dilutor was designed to have a variable dilution factor, which allows the
experimenter to change the dilution ratio during an experiment as the fire evolves and emission
density changes by large factors (>100). The SeTAR dilutor is smaller than some commercial
laboratory-based systems—the units weighing less than 7 kg each, convenient for portability. The
current design was used in all the emission factor tests reported in this thesis.

Objectives (c) and (d): To systematically determine the characteristics and quantities of selected
gaseous and particulate emissions from informal domestic coal-burning braziers as functions of (i)
fire-ignition method; (ii) ventilation rate; (iii) coal grade; and (iv) coal moisture; and to report
related emission factors as [g MJ⁻¹] and emission rates as [g s⁻¹].

Emission factors

A systematic investigation has been carried out of emissions and thermal performance of coal-fired
braziers under controlled laboratory conditions in which the following parameters were varied: (a) the
fire-ignition method; (b) ventilation rates; (c) coal grade; and (d) coal moisture content. The
experimental work included combustion studies with a number of field-collected and lab-designed
braziers. Elemental composition and heating value of the fuels were performed by an external
laboratory. From these multiple inputs, an overall understanding of the significance of different
factors influencing condensed matter (smoke) emissions and trace gases from domestic coal-burning
appliances was obtained.
By switching fire-ignition methods from conventional bottom-lit updraft (BLUD) to top-lit updraft (TLUD), we found considerable reductions in the emissions of products of incomplete combustion. For a specific coal grade and moisture content, PM2.5 emissions for either BLUD or TLUD ignition were higher for low ventilation braziers than for high ventilation braziers. For D-grade coal, PM2.5 emission factors (EF) were determined in the range of 1.3–3.3 g MJ⁻¹ for the BLUD method, and 0.2–0.7 g MJ⁻¹ for the TLUD method, for both field and lab-designed stoves. When using an A-grade coal, PM2.5 emission factors were in the range 2.5–3.6 g MJ⁻¹ for BLUD fires and 0.4–0.8 g MJ⁻¹ for TLUD fires. On average, all stoves tested showed an 80% PM2.5 and PM10 emissions reductions when using the TLUD in contrast to the business-as-usual BLUD method.

The influence of ventilation rates on the stove emissions was investigated. Three laboratory-designed stoves with different ventilation rates (different number and total area of ventilation holes punched in side of brazier drum) were used for each ignition method. The set of tests were repeated, for two grades of coal, and for two moisture contents of D-grade coal. Results showed that PM emissions are significantly increased with reduced ventilation rate—for a given ignition method, PM2.5 and PM10 emission factors reduce by 50% from low to high ventilation rates (an advantage offset by firepower too high for convenient cooking and increased fuel consumption). CO emissions are significantly increased with reduced ventilation. NOx emissions increase significantly with increased ventilation. The emissions of CO₂ are similar between ventilation rates.

Effects of fuel quality on gaseous and particulate emissions were investigated. Emissions from A-grade and D-grade coal were compared. Results showed that for the BLUD ignition method, PM emissions are similar between fuel grades, for low and medium ventilation, but significantly different at high ventilation rates. For the TLUD method, PM emissions increase (~2-fold) with a switch from D-grade to A-grade coal, except at medium ventilation. Results for the BLUD show that there are no significant differences in CO and CO₂ emissions between the two fuel qualities. NOx emissions increase with a switch from D-grade to A-grade coal. For the TLUD method, emissions of CO and NOx increase with switch from D-grade to A-grade coal. CO₂ emissions are similar between fuel grades.

The influence of coal moisture content on emissions and efficiencies of the braziers was investigated. Emissions of PM10, CO, CO₂ and the combustion efficiency were determined for two distinct moisture content levels (2.4% and 8.6%). Results show that for both ignition methods, emission factors of PM2.5 and CO increased with increasing coal moisture, while CO₂ emission factors were not influenced. Higher moisture content reduced the combustion efficiency and fire-power, while increasing the cooking efficiency.

Included in the products of incomplete combustion are polycyclic aromatic hydrocarbons (PAH). Polycyclic aromatic hydrocarbon emission characteristics were determined for a range of residential coal combustion appliances during different ventilations rates and fire ignition methods. Changes in the relative composition of PAHs with TLUD and BLUD ignition methods were not measured quantitatively in terms of flue gas flow rates—only peaks and relative proportions of PAHs are...
reported. Beside naphthalene, which was the dominant PAH in all the coal fires, phenanthrene and fluorene were abundant. Changes in combustion conditions appeared to have a marked effect in the ratios of various PAH emissions—relative concentrations of phenanthrene and fluorene, normalised to naphthalene, are higher in BLUD than in the TLUD ignition method. The overall reductions in PAHs may be inferred from the reductions in PM2.5.

**Emission rates**

The emission rates of CO, CO$_2$ and PM10 for selected braziers with three different ventilation rates, using D-grade coal, were calculated from measurements using the TLUD and BLUD ignition methods. The emission rates are expressed in units [g s$^{-1}$], as required by dispersion model input specifications. Emission rates are reported per hour of the burn cycle (nominally three hours long) and for the average over the three hours, allowing dispersion modellers to use these factors to construct emission scenarios adapted to the lifestyle patterns of the modelled communities. Highest emission rates occur in the first hour of combustion (ignition and pyrolysis phases) compared to the second and third hours, associated with volatiles that are driven off from the kindling and during initial heating of the coal. When all the volatiles are driven off (generally within the first hour), the emission rates decrease considerably, reaching lowest levels during last hour of the three-hour combustion cycle. The combined average the combined average PM10 emission rates are determined in the range 0.0028–0.0120 g s$^{-1}$, whilst the combined average CO emission rates are in the range 0.20–0.26 g s$^{-1}$.

**Objective (e): To carry out an investigation of the morphology of condensed matter particles formed during different phases of combustion, and compare the morphologies between bottom-lit updraft (BLUD) and top-lit updraft (TLUD) fires.**

Using scanning electron microscopy of smoke particles collected onto filters, a characterization of the physical morphological properties of particulate matter generated from coal-fired residential combustion devices under varying combustion conditions was undertaken, from which possible formation mechanisms were inferred. Based on an interpretation of the time variations of emission concentrations and temperatures in the fuel bed, we classify the pyrolysis phase of a coal brazier fire into two stages: stage I and stage II. The separation between these stages is defined by the temperature of the exit gases reaching ignition point for the emitted organic gases. We hypothesize that particle formation during pyrolysis differs between the two phases. Attempts to collect filter samples from undiluted exhaust gases during pyrolysis stage I results in filters becoming blocked rapidly as the droplets merge into a continuous viscous layer. Electron micrographs reveal continuous layers of merged tar-like deposits with no discrete particles visible. During pyrolysis stage II, filters collect particles that (mostly) retain their morphology on impact, showing appearance on the electron micrographs of discrete particles with a range of morphologies.

Images of filters sampled during pyrolysis stage II and during coking phase show that that the fire ignition method and ventilation rates influence aerosol formation, and morphology of the of emitted particles. Giant carbonaceous conglomerates (up to 100 µm) were observed during pyrolysis stage II of a low ventilation bottom-lit updraft (BLUD) fire. These conglomerates had a range of internal
morphological forms, which have been described as ‘dendritic’, ‘sponge-like’ and ‘melted toffee’. However, no conclusive explanation is given as to why the conglomerates reach such a large size. The quantification in terms of the microphysics of nanoparticle collision in high number density assemblages has been attempted by Wentzel [2000] and needs further work.

To monitor ageing of the emitted particles, samples were collected close to the fire (<1 m) and at the exit of a 5 m chimney—estimated transit time 2 s. When sampling close to the fires (at ignition and pyrolysis stage I), the filter material rapidly clogged and a continuous layer of liquid/tarry substance coalesced and covered the entire filter membrane, with some pores completely closed. At the 5 m exit point, micrographs showed distinct particles morphologies, including giant spherical organic particles that had condensed as the exhaust stream cooled. Perfectly spherical giant organic particles, very similar to atmospheric tar balls, were observed in ageing smoke from smouldering combustion conditions typical of poorly ventilated BLUD fires. The spherical organic particles were found as individual spherical particles and as aggregates forming diffusion accretion chains. Two distinct forms of spherical organic particles were identified, one less oxidised than the other. The mixing states of these spherical particles we found to be as follows: 50% are bare single particles; 35% particles are aggregated and form diffusion accretion chains; 10% have inclusions; and 5% are deformed due to impaction on filter material during sampling. It is hypothesized that spherical organic particles may have been formed by the ejection of liquid tar droplets (pyrolysis stage I products of coal burning) from the pores of the burning coal, followed by rapid thermal transformation upon passing through the flame or glow zone of the fire. The flame chemistry in the fire zone or multiphase chemical reactions in the smoke plume may contribute to the ageing of the ejected tar droplets forming accretion chains or aggregates. During pyrolysis stage II, dendritic particles comprised of much smaller primary condensation spherules were collected on the filters regardless of the ignition method.

5.2 Synthesis and Logical Analysis of Hypothesis - Objective (f)

This study hypothesized that the formation modes of condensed matter emissions from domestic packed-bed coal combustion are a consequence of poor combustion conditions relating to method of ignition, properties of the fuel, and supply of primary and secondary air. To determine whether the hypothesis is true or false, we first review conditions necessary for good combustion namely: fuel, availability of oxygen, sufficient heat, good fuel/air mixing, and adequate time in the combustion zone to allow all primary and secondary components to be fully oxidised. Conversely, poor combustion conditions imply the absence or limiting of one or more of these conditions. With respect to particle emissions, we have investigated four factors that may influence particle formation under poor combustion conditions (ignition method, ventilation rates, moisture content, and fuel quality). In testing the hypothesis for this synthesis chapter, we summarised the evidence of particle formation for each of these components, with explicit reference to which of the necessary combustion conditions are limiting.
**Ignition method**

Particulate matter emissions are influenced by the ignition method. For the bottom-lit updraft (BLUD) method, during pyrolysis stage I, the temperature of exit gases was below the ignition point for homogenous phase combustion. The temperature at the top of the coal bed is insufficient to ignite the emitted hydrocarbons. This poor combustion condition persisted for 30 minutes, resulting in the release of liquid droplet condensates. During pyrolysis stage II, the temperature at the top of the coal bed is sufficient to sustain a flame. However, turbulent mixing above the fuel bed cools the gas mixture before all the condensed hydrocarbons have combusted. Some of the more volatile components combust, but less volatile components persist, resulting in dendritic particles being emitted.

For the top-lit updraft (TLUD) method, the combustion conditions allow for gases released during pyrolysis to pass through a high temperature zone (descending combustion front). The temperature at the top of the coal bed is sufficient to combust the emitted hydrocarbons, resulting in much reduced duration of pyrolysis stage I compared to BLUD ignition. During pyrolysis stage II, high temperatures above the burning coal bed are sufficient to burn the low vapour pressure hydrocarbons (main components of dense white coal smoke) and less prolific (~20%) dendritic particles are formed. For both ignition methods, the coking phase shows good combustion with low CO and PM emissions, except towards the end of the combustion cycle when CO emissions increase due to reduced bed temperatures.

The hypothesis is conditionally confirmed for ignition method as a major factor influencing particle formation modes. The ignition method reduces particle emissions by up to 80% but not more, at any ventilation rate. Other factors would have to be identified that could reduce formation of the residual pyrolysis stage II emissions.

**Ventilation rates**

Condensed matter emissions are influenced by ventilation rates of the braziers. For both ignition methods, high ventilation rates reduced PM emissions by 50%. An increase in the ventilation rates allows for more stable combustion and higher combustion temperatures, which in turn could lead to improved heat transfer and combustion efficiencies. Low ventilation rates or restricted airflow movements through the fuel bed may limit the chemical reactions between O\(_2\) and evolved gaseous fuel components, leading to high levels of CO and PM emissions. High ventilation rates may be achieved by using forced draft ventilation, as in some wood pellet and biomass gasifiers. However, excessive airflow may increase the convective cooling of the fire thereby affecting the mixing and local concentration of fuel/oxidant in the gas stream, leading to increased emissions of condensed matter, and mechanically entraining ash components.

The hypothesis is conditionally confirmed for ventilation rates as a factor influencing particle formation modes. High ventilation rates reduce particle emissions by up to 50% but not more, for either ignition methods. The combination of high ventilation rate and the top-lit down updraft ignition
gives the lowest overall emissions. However, this does not necessarily give an appropriate cooking power or optimum fuel burn rate.

**Moisture content**

Fuel moisture content has an influence on condensed matter emissions. Higher moisture content reduces fuel bed and flame temperatures, resulting in an increase in condensed matter emissions in the post flame region of the stove. When considering the entire combustion cycle, the concentration of smoke particles tend to decrease rapidly during the pyrolysis phase of combustion. This is because the water in the coal eventually evaporates and the degree of incomplete combustion is reduced.

The hypothesis is conditionally confirmed for moisture as a factor influencing particle formation modes. Low fuel moisture content reduces particle emissions by up to 50% but not more, for the BLUD ignition method, moist coal produces higher pollution in conventionally ignited imbaulas. For the TLUD ignition, particle emissions are similar for the two moisture levels for medium and high ventilation rates; for low ventilation, the TLUD emissions for the low moisture fuel are significant but small.

**Coal quality**

Coal quality influences the combustion conditions and the formation of condensed matter emissions. The two fuel batches used in this study had an ash contents 14%–A-grade and 24%–D-grade. Changing from A-grade to D-grade reduces particulate emissions in the top-lit braziers. For the BLUD method, particle emissions are similar with a switch from A-grade to D-grade, except at low ventilation.

The hypothesis is conditionally confirmed for coal quality as a factor influencing particle formation modes. For the TLUD method, low ash A-grade coal increases particle emissions by up to 100% at any given ventilation rate.

### 5.3 Conclusions and Significance

By using a disparate set of techniques to study small-scale packed bed combustion over a range of ignition methods, ventilation rates, fuel quality, and moisture content, we have gained new insights into the dynamics of combustion particle formation and gaseous emissions. The formation of condensed matter emissions from domestic packed-bed coal combustion are a consequence of poor combustion conditions relating to method of ignition, properties of the fuel, supply of primary and secondary air, and fuel moisture content. We have shown that different phases of combustion have an influence on the nature and characteristics of condensed matter (smoke) emissions. An original contribution in this regard is identification of *stage I and stage II of pyrolysis* as separate physical stages of combustion, and labelling these stages.

Prior studies have reported particulate emission factors varying by a factor of ten. This study is the most comprehensive systematic study to date of emission factors from domestic coal braziers. The insights gained on the controlling variables go a long way to understanding the divergent results from
prior studies that did not take into account or control for all these variables. This study reports emission factors in terms of emissions per net MJ of energy in the fuel, for use in rating and comparison of stoves. The experimentally determined emission rates, in units [g/s], directly applicable in standard dispersion models, represent a considerable improvement in previously reported emission factors for coal stoves.

This thesis provided detailed information about gaseous and particle emissions from small fixed-bed residential coal-burning braziers, which can be used in the development of combustion technologies that are more efficient and less polluting, and as the scientific base for further studies. We have a better understanding of how to make further modifications to the ventilation rates and inlet patterns, to improve the combustion efficiency and reduce pollutant emissions from the braziers. It is expected that the scientific insights gained from this thesis will contribute to improved intervention programmes of safe, clean and affordable uses of coal based domestic technologies. Investment in public campaigns could be more effective if they took into account, not only the reduced smoke emissions, but by ensuring that the devices match user needs in terms of power output, safety and convenience.

5.4 Recommendations

5.4.1 Recommendations emanating directly from this work

Ventilation rates in braziers
Our experiments took a simple approach to secondary air by placing the holes in a uniform pattern around the fuel bed. If the secondary air holes are placed above the coal bed and a limited amount of hot secondary air is introduced above the fuel bed, this would contribute to further emissions reduction.

Fuel size
In this study, we used sieved coal nuggets with a mean size diameter of 20 – 40 mm. Fuel size has been shown to have an influence on combustion conditions. Flow resistance of the fuel bed is dependent on the size of the coal nuggets used and how they are packed in the bed. Exploration of using smaller size coal pieces warrants further investigation.

Particle losses in the SeTAR dilution system
In this study, we did not evaluate particle losses in our system. Wall losses in our design were assumed to be similar to, or smaller than, those determined for larger samplers such as the Hildemann et al. [1989] dilution sampler; the SeTAR (straight) sampling section is 900 mm long compared with the curved, longer sampling section in the larger samplers. In the future, there is a need to determine particle losses in the system using laboratory-generated polystyrene latex spheres (PSL) with 0.5 to 10 μm diameters. These tests should be able to show the transmission efficiencies of the system at different dilution ratios. The evaluation should include losses in the sample transfer line from the particle source to the inlet of the dilution system. This can be estimated from theoretical calculation of
diffusion, gravimetric settling, and thermophoretic deposition based on the flow rate, length, temperatures, and inclination angle of the transfer line for a specific experimental setup [Wang et al., 2012; Kulkarni et al., 2011].

**Evaluation of the SeTAR dilutor against reference standards**

There is need to validate the SeTAR dilutor using a reference dilution system such as the Caltech design and other existing models. This will allow for results obtained from different dilution systems to be comparable.

**Analysis of particle morphology from real-world uses**

It is recommended that additional experiments be performed to determine the cause of the large soot agglomerate formation in residential coal combustion processes in a brazier and to understand further the different phases of combustion (ignition, pyrolysis stages I and II, coking and smouldering). The presence of large agglomerates in combustion smoke has the potential to affect particle detection monitors that use laser light scattering to estimate the concentration of pollutants. Taking into account both the abundance of giant soot aggregates in the atmosphere from the combustion of residential coal, and their microphysical properties, our findings bring to the forefront the significant impacts of these pollutants on human health, air pollution monitoring, and mitigation strategies. Because of this, there is a need for instrument development for real-time detection and measurement of giant soot aggregate using different size conventions, such as mobility, aerodynamic, and volume-equivalent diameters. The widely used particle-size monitoring instrument, for example laser light scattering particle monitors (DustTrak aerosol monitors) is incapable of detecting these particles [Chakrabarty et al., 2014].

**Laboratory analysis of PAH emissions**

In future studies, it is recommended that the multi-channel silicon rubber traps be integrated into the SeTAR dilutor to monitor PAH emissions from laboratory combustion of coal in braziers. Currently, the denuders are designed to take in low sample volumes and are susceptible to overloading if they are exposed to direct exhaust fumes for even short periods. A successful integration of the two systems would allow direct comparison between field and laboratory tests, and possibly determination of quantitative emission factors.

**Multi-disciplinary approach to household air pollution**

An attempt to address household air pollution issues in communities still using coal as a source of energy is a prerequisite, given documented evidence on the effect of household air pollution on morbidity. To address these issues there is a need to do crosscutting research involving different disciplines of physical and social sciences. According to Boman [2005], the closely linked research fields of combustion related energy production, air pollution and environmental health calls for:

- A solid basic understanding of the processes and mechanisms that control the behaviour of different pollution by-products during combustion, dispersion and exposure (as presented in this study).
• Multi-disciplinary collaborations within fields of e.g. combustion engineering, process chemistry, aerosol science, atmospheric science and respiratory and cardiovascular medicine.

For the multi-disciplinary project financing from government departments involved in energy, environmental affairs, and science and technology (e.g. Department of Energy, Department of Environmental Affairs, Department of Science and Technology, academic and research institutions) is required. Such a project will involve dedicated human exposure studies with different residential coal combustion or biomass related pollutants and mixtures. Additionally, the project would need to focus on the following key areas: (i) detailed characterization of coal combustion aerosols generated under different conditions (such as the experimental work and results presented in this thesis), (ii) controlled generation of synthetically produced (combustion) aerosols, (iii) determination of biological responses during controlled chamber exposures, and (iv) determination of respiratory particle deposition [Boman, 2005].

**Development of alternative combustion devices**

It is recommended that studies that centres at improving the combustion process in such braziers be undertaken. Further evaluation and validation of the possibilities for emission minimization for commercial residential coal combustion, especially at varying combustion and operation conditions is needed. Priority should be given to the design and development of efficient and less polluting coal braziers or alternative coal-burning stoves. The follow on study of this thesis would be to optimise the design of ventilation holes, starting with the medium case, which has a moderate fuel consumption rate and lower fire-power compared to the high case. A further approach would be to optimise designs by computational fluid dynamic (CFD) modelling. Since the commercial CFD FLUENT software does not have an interface for a fixed-bed model, there exists a need to develop a sub-model for fixed-bed combustion, which could then be implemented into the CFD FLUENT code to simulate a residential brazier unit. As such, the fixed-bed sub-model would have to be validated against measurement of temperature and gas compositions as presented in this thesis.

**5.4.2 Recommendations for policy formulations and strategies**

**Establishment of robust energy policies and strategies**

Residential coal combustion contributes to diseases already affecting large portions of the South African population, including asthma, tuberculosis, heart disease and stroke. The emissions interfere with lung development; increase the risk of heart attacks; and compromises intellectual capacity [Lockwood *et al.*, 2009]. Coal pollutants have a potential to affect most of the major body organ systems. Deaths due to of CO poisoning from residential coal combustion is rife in the winter seasons in many low-income urban households. However, it is difficult to ascertain the proportion of this disease burden that is specifically attributable to coal combustion. This does not mean that translating concerns for human health into policy recommendation should be neglected.

An integrated approach to reduce potential exposure to coal fuel emissions should be explored. The first of these recommendations is to cut down on CO emissions from residential coal burning
appliances. To achieve satisfactory health outcomes, reduction of CO emissions should be pursued through three simultaneous strategies: (i) Provision of cost effective, efficient and less polluting improved residential coal-burning devices and innovative fire ignition techniques; (ii) energy efficient housing, which would cut down on the need for space heating in during cold winter periods; (iii) and appropriate community education campaigns. Improved economic conditions could help to alleviate these problems by allowing coal users to purchase commercial coal briquettes.

**Education and awareness campaigns**

Ideally, people need to be educated on the dangers and shortcomings of using coal in poorly ventilated and inefficient cooking and heating devices. This could be through organised seminars, workshops, and media amongst others. On the other hand, the government through its various arms (e.g. Department of Energy, Department of Environmental Affairs, Department of Trade and Industry) need to harmonise their strategies and efforts to curb pollution from residential coal combustion. On the other hand, the cost burden of air pollution on the fiscal due to business as usual approach needs to be refined. When new and efficient technologies including improved braziers are introduced in affected communities follow up monitoring and evaluation campaigns should be undertaken to assess the effects of this strategy on local air pollution. Again, the cost burden of air pollution on the fiscal needs to be evaluated to determine if there are any significant cost savings due to the introduction of such technologies.

**Adoption of the GAINS model and adapting it for South Africa**

There is a great need for adopting integrated assessment models for human health and ecosystem health, to improve the evidence base for policy action in South Africa. Such a framework can be used to inform key negotiations on air pollution control agreements. During the course of this study, the author of this thesis was part of the Greenhouse gas–Air pollution Interactions and Synergies (GAINS) model formative workshop and a member of the liaison team for the framework to be adopted and adapted for South Africa. The GAINS model was developed as a tool to identify emission control strategies that achieve targets on air quality and greenhouse gas emissions at least cost. The model considers measures for the full range of precursor emissions that cause negative effects on human health via the exposure of fine particles and how specific mitigation measures simultaneously influence different pollutants. This allows for a comprehensive and combined analysis of air pollution and climate change mitigation strategies, which reveals important synergies and trade-offs between these policy areas [Amann, 2012].

Availability of emissions data from a variety of economic activities (e.g. domestic, agricultural, transport, industry etc.) and related emissions abatement options are a critical requirement for the framework to work optimally. The role of technology (improved braziers and the TLUD ignition method) and abatement option penetration on future emissions is an area of particular importance that needs to be considered in exploring policy options for South Africa. Therefore, there is a greater need to understand, from country specific activities, a portfolio of available technologies (including improved braziers and coal stoves) to reduce greenhouse gas emissions and ambient air pollution.
Information on how quick the technology penetration can happen, taking into account factors such as resistance to change and barriers to implementation, should be made available.

**Advocating for improved kitchen management**

There is a greater need to create a healthy living environment, with adequate ventilation on the houses, and chimneys on stoves to duct smoke to the outside environment. The cooking area must be detached from the sleeping or living space especially if the room or house is poorly ventilated. Campaigns advocating for behavioural change should be encouraged and funded. The success of the *Basa njengo Magogo* was dependent on changing user behaviour without any costs incurred by the user. The users of residential coal combustion devices should be encouraged to reduce smoke generation by:

- Changing cooking practices;
- Reducing the time spent in the kitchen/cooking area;
- Always employing the TLUD method when igniting a coal fire in a brazier;
- Not using the brazier indoors for cooking or space heating (i.e. even when the coals are burning red, CO emissions are high);
- Children must always be kept away from smoke to reduce the risk of accidents occurring.
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Appendix A – Instrument Calibration Certificates

**CERTIFICATE OF CALIBRATION AND TESTING**

T4 Instruments Ltd, Stirling Road,ccross Business Park
High Wycombe, Bucks HP12 3T1 England
Tel: (01296) 699-457 Fax: (01296) 699-45700 http://www.titan.co.uk

**Environments Condition**
- Temperature: 22.2 °C
- Relative Humidity: 30.0 %RE
- Barometric Pressure: 993.0 kPa

**Model** 8533
**Serial Number** 8533094403

**Concentration Linearity Plot**

**Flow and Pressure Verification**

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<th>Standard</th>
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<th>Allowable Range</th>
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<td>3.0</td>
<td>2.50 – 2.75</td>
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**System D7102-01**

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<th>Parameter</th>
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<th>Allowable Range</th>
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<tbody>
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<td>99.4</td>
<td>99.4</td>
<td>91.46 – 104.0</td>
</tr>
</tbody>
</table>

T4 Incorporated does hereby certify that all materials, components, and workmanship used in the manufacture of this equipment are in strict accordance with the applicable specifications agreed upon by T4 and the customer and with all published specifications. The performance and acceptance tests required under this contract were successfully conducted according to required specifications. There is no NIST standard for optical mass measurements. Calibration of this instrument performed by T4 has been done using empty oil and has been manually adjusted to resemble mass of standard ISO 1210-1. All test data (Arizona data). The calibration ratio is greater than 1.21.

**Measurement Variable**

- Temperature
- Humidity
- Mass Balance
- Pressure
- 2.5 um PSL
- DC Voltage

**System ID**

- Latest Cal: 17-03-15
- Cal Date: 17-03-15

**Measurement Variable**

- Temperature
- Humidity
- Mass Balance
- Pressure
- 2.5 um PSL
- DC Voltage

**System ID**

- Latest Cal: 17-03-15
- Cal Date: 17-03-15

**Date of Calibration**

30 April, 2014
Calibration Certificate

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>ANALYZER</th>
<th>Control Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Testo</td>
<td>Testo</td>
</tr>
<tr>
<td>Type</td>
<td>350-XL</td>
<td>350-XL 454</td>
</tr>
<tr>
<td>Part No.</td>
<td>0563 0388</td>
<td>0563 0380</td>
</tr>
<tr>
<td>Serial No.</td>
<td>01549737</td>
<td>01539809</td>
</tr>
</tbody>
</table>

Location
Laboratory – Unitemp cc.
7 Vuurslag Street
Spartan Ext 7
Kempton Park
Johannesburg

Customer
University of Johannesburg
37 Nind Street
Doornfontein
JHB

Internal Order No.
315441

Date of calibration
27/01/2015

Date of issue
27/01/2015

Recommended re-calibration date
Jan 2016

Was adjustment of the instrument done?

- [X] Yes
- [ ] No

The accuracy of all measurements is traceable to the National Measuring Standards.

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2 providing a level of confidence of approximately 95%. The uncertainty of measurement has been estimated in accordance with the principles defined in the GUM, guide to uncertainty of measurement, ISO, Geneva, 1993.

The calibration certificate may not be reproduced other than in full and with the permission of Unitemp Laboratory.

Calibrated by C.B. Noelle

JR Taylor
Signatory
## Calibration certificate

**Certificate number**: CAL-UG-N-FG-150127102

### Reference Standards

<table>
<thead>
<tr>
<th>Reference Gas Description</th>
<th>Cylinder Number</th>
<th>Certificate Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ – Sulfur Dioxide</td>
<td>D19 4856</td>
<td>PRGM0004888</td>
</tr>
<tr>
<td>CO – Carbon Monoxide</td>
<td>MS8 8384</td>
<td>PRGM0008384</td>
</tr>
<tr>
<td>O₂ – Oxygen</td>
<td>D35 8400</td>
<td>PRGM20008400</td>
</tr>
<tr>
<td>NO – Nitrogen Monoxide</td>
<td>D54 3905</td>
<td>PRGM200054905</td>
</tr>
<tr>
<td>NO₂ – Nitrogen Dioxide</td>
<td>M63 906</td>
<td>PRGM0003906</td>
</tr>
<tr>
<td>CO₂ – Carbon Monoxide</td>
<td>D63 8328</td>
<td>PRGM20008329</td>
</tr>
</tbody>
</table>

Note: The H₂S and NO(tlow) cells were not calibrated as test gas is not available.

### Ambient Conditions

**Temperature**: 23°C ± 5°C

### Measuring procedure

The standard gas values were applied to the instrument at a controlled flow rate and the results are as follows. The errors were calculated against the standard gas values.

### As Found Measurement results

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ – Sulfur Dioxide</td>
<td>1001 ppm</td>
<td>966 ppm</td>
<td>-3.5%</td>
<td>±5%</td>
<td>±2%</td>
</tr>
<tr>
<td>CO – Carbon Monoxide</td>
<td>998.5 ppm</td>
<td>*708ppm</td>
<td>-29.1%</td>
<td>±5%</td>
<td>±1%</td>
</tr>
<tr>
<td>O₂ – Oxygen</td>
<td>3.001%</td>
<td>2.89%</td>
<td>-0.1%</td>
<td>±0.2%</td>
<td>±0.05%</td>
</tr>
<tr>
<td>NO – Nitrogen Monoxide</td>
<td>1000.3 ppm</td>
<td>987ppm</td>
<td>-1.3%</td>
<td>±5%</td>
<td>±2%</td>
</tr>
<tr>
<td>CO₂ – Carbon Dioxide</td>
<td>5.002%</td>
<td>*5.59%</td>
<td>+0.0%</td>
<td>±0.35%</td>
<td>±0.05%</td>
</tr>
</tbody>
</table>
Calibration certificate

Certificate number: CAL-UG-N-FC-160127702

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ – Sulfur Dioxide</td>
<td>1001 ppm</td>
<td>1000 ppm</td>
<td>-0.1%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO – Carbon Monoxide</td>
<td>996.5 ppm</td>
<td>994 ppm</td>
<td>-0.5%</td>
<td>±5%</td>
<td>1%</td>
</tr>
<tr>
<td>O₂ – Oxygen</td>
<td>3.001%</td>
<td>2.85%</td>
<td>-0.1%</td>
<td>±0.2%</td>
<td>0.05%</td>
</tr>
<tr>
<td>NO – Nitrogen Monoxide</td>
<td>1000.3 ppm</td>
<td>987 ppm</td>
<td>-1.3%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO₂ – Carbon Dioxide</td>
<td>5.002%</td>
<td>5.00%</td>
<td>-0.6%</td>
<td>±0.35%</td>
<td>0.05%</td>
</tr>
</tbody>
</table>

Validity of certificate

The measurement results recorded in this certificate were correct at the time of calibration. * indicates this result falls outside the manufacturers specifications. The subsequent accuracy will depend on factors such as care, handling and frequency of use. It is recommended that recalibration be undertaken at an interval that will ensure that the instrument remains within the desired limits.

End of certificate
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Analyzer</th>
<th>Control Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Testo</td>
<td>Testo</td>
</tr>
<tr>
<td>Type</td>
<td>350-XL</td>
<td>350-XL 454</td>
</tr>
<tr>
<td>Part No.</td>
<td>0563 0366</td>
<td>0563 0353</td>
</tr>
<tr>
<td>Serial No.</td>
<td>01549731</td>
<td>01539810</td>
</tr>
</tbody>
</table>

Location
Laboratory – Unitemp cc.
7 Vuurslag Street
Spartan Ext 7
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37 Nind Street
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Internal Order No
315441

Date of calibration
27/01/2015

Date of Issue
27/01/2015

Recommended re-calibration date
Jan 2016

Was adjustment of the instrument done?
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Calibrated by: C.B. Ngole

JR Taylor
Signature
Calibration certificate

Reference Standards

<table>
<thead>
<tr>
<th>Reference Gas Description</th>
<th>Cylinder Number</th>
<th>Certificate Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ – Sulfur Dioxide</td>
<td>D19 4860</td>
<td>PRGM30004686</td>
</tr>
<tr>
<td>CO – Carbon Monoxide</td>
<td>MS5 8934</td>
<td>PRGM50008384</td>
</tr>
<tr>
<td>O₂ – Oxygen</td>
<td>D95 8400</td>
<td>PRGM20008400</td>
</tr>
<tr>
<td>NO – Nitrogen Monoxide</td>
<td>DS4 3905</td>
<td>PRGM200043905</td>
</tr>
<tr>
<td>NO₂ – Nitrogen Dioxide</td>
<td>M65 905</td>
<td>PRGM60003908</td>
</tr>
<tr>
<td>CO₂ – Carbon Monoxide</td>
<td>D05 8328</td>
<td>PRGM20008328</td>
</tr>
</tbody>
</table>

Note: The H₂S and NO(low) cells were not calibrated as test gas is not available.

 Ambient Conditions

Temperature 23°C ± 5°C

Measuring procedure

The standard gas values were applied to the instrument at a controlled flow rate and the results are as follows. The errors were calculated against the standard gas values.

As Found Measurement results

<table>
<thead>
<tr>
<th>Applied Reference Gas</th>
<th>Reference Gas Concentration</th>
<th>Instrument Displayed Concentration</th>
<th>Error</th>
<th>Manufacturers Tolerance</th>
<th>Uncertainty %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ – Sulfur Dioxide</td>
<td>1001 ppm</td>
<td>975ppm</td>
<td>-2.6%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO – Carbon Monoxide</td>
<td>998.5 ppm</td>
<td>839ppm</td>
<td>-16.0</td>
<td>±5%</td>
<td>1%</td>
</tr>
<tr>
<td>O₂ – Oxygen</td>
<td>3.001%</td>
<td>2.97%</td>
<td>-0.03%</td>
<td>±0.2%</td>
<td>0.05%</td>
</tr>
<tr>
<td>NO – Nitrogen Monoxide</td>
<td>1000.3ppm</td>
<td>688ppm</td>
<td>-1.4%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO₂ – Carbon Dioxide</td>
<td>5.002%</td>
<td>5.16%</td>
<td>+0.2%</td>
<td>±0.35%</td>
<td>0.05%</td>
</tr>
</tbody>
</table>
### Calibration certificate

**CAL-UG-N-6150127L01**

**Certificate number**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ - Sulfur Dioxide</td>
<td>1001ppm</td>
<td>997ppm</td>
<td>-0.4%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO - Carbon Monoxide</td>
<td>998.5ppm</td>
<td>994ppm</td>
<td>-0.5%</td>
<td>±5%</td>
<td>1%</td>
</tr>
<tr>
<td>O₂ - Oxygen</td>
<td>3.001%</td>
<td>2.97%</td>
<td>-0.03%</td>
<td>±0.2%</td>
<td>0.05%</td>
</tr>
<tr>
<td>NO - Nitrogen Monoxide</td>
<td>1000.3ppm</td>
<td>986ppm</td>
<td>-1.4%</td>
<td>±5%</td>
<td>2%</td>
</tr>
<tr>
<td>CO₂ - Carbon Dioxide</td>
<td>5.002%</td>
<td>5.16%</td>
<td>+0.2%</td>
<td>±0.35%</td>
<td>0.05%</td>
</tr>
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</table>

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---

End of certificate

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UNIVERSITY OF JOHANNESBURG