Effect of coal and microalgae biomass co-firing on CO₂, SO₂ and NOx emissions: An experimental evaluation

PhD Thesis

N.E. MAGIDA

2021
EFFECT OF COAL AND MICROALGAE BIOMASS CO-FIRING ON CO$_2$, SO$_2$ AND NO$_x$ EMISSIONS: AN EXPERIMENTAL EVALUATION

By

Nokuthula Ethel Magida

Honours of Biochemistry, University of Fort Hare, 2011
Masters of Science in Engineering Sciences in Chemical Engineering, North West University, 2013

Submitted in fulfilment of the requirements for the degree of
DOCTOR OF PHILOSOPHY IN CHEMISTRY
To be awarded at the Nelson Mandela University, Port Elizabeth, South Africa

December 2021

Supervisor: Prof. Ben Zeelie (late)
Supervisor: Dr. Gary Dugmore
Co-Supervisor: Dr. Adeniyi Ogunlaja
DECLARATION

I, Nokuthula Ethel Magida (213511460), hereby declare that the thesis entitled “Effect of coal and microalgae biomass co-firing on CO₂, SO₂ and NOx emissions: An experimental evaluation” for Doctor of Philosophy in Chemistry to be awarded is my own work and it has not been submitted assessment or completion of any postgraduate qualification to another for University or for another qualification.

Signature................................
Nokuthula Ethel Magida
December 2021

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ABSTRACT

There is increasingly stringent legislation on the environmental impact of energy production from coal combustion, and this has led to growing pressure to reduce the emission of greenhouse gases (GHGs). Thus, there is a significant need to develop and implement clean coal combustion technologies that would reduce the environmental gas pollutants. For power generation, the co-firing of biomass fuels at conventional coal-fired power stations is recognised as one of the low-cost, low-risk options to achieve significant reductions in GHG emissions. When coal is co-utilized with biomass there is added attractiveness because the biomass is CO₂ neutral, and there is interest in using waste biomass and microalgae. Thus, the co-combustion of coal and biomass for energy production results in pollutant reduction, especially in the emissions of NOx, SOx, volatile organic compounds and polyaromatic hydrocarbons. The synergistic activity observed for toxic organic emissions is not well understood and is thought to involve chemical interaction between the volatiles from each fuel coupled with possible catalytic activity from the inorganic constituents of the fuels. The characterization of co-firing products and gases emitted from coal and microalgae (particularly the Scenedesmus strain) co-combustion has received limited attention.

Therefore, this study seeks to understand possible interactions occurring during co-combustion of coal and Scenedesmus microalgae (Coalgae®). Additionally, the study aims to determine the effect of co-firing coal and Scenedesmus microalgae on CO₂, SO₂ and NOx emissions. The term “Coalgae®” refers to the mixture of coal and microalgae biomass. The study looks at physico-thermal characteristics as well as CO₂, SO₂ and NOx emissions of various coal-microalgae blending ratios by mass; 100:0 (coal), 95:5 (Coalgae® 5%), 90:10 (Coalgae® 10%), 85:15 (Coalgae® 15%) and 80:20 (Coalgae® 20%). Characterization techniques carried out included proximate and ultimate analyses, Fourier-transform infrared (FT-IR) and Scanning electron microscopy and X-ray energy dispersive spectroscopy (SEM/EDS). For combustion studies two techniques were applied. Low heating rate was obtained through a Thermogravimetric-Mass spectrometer analysis (TG-MS). Other combustion experiments were performed on the five lumpy fuels (coal and Coalgae® 5% - 20%) exposed to the flame in a fixed-bed combustion
reactor. The emission concentrations of CO$_2$ (%) and NOx (ppm) of coal and Coalgae® blends were measured during the combustion of the five materials using a Lancom 4 portable flue gas analyser. The mass reduction (g) and temperature (°C) at the reactor exit were recorded during the combustion tests to compare the combustion behaviour of the four mixtures to that of raw coal.

TG-DTG curves of coal and microalgae confirmed that the combustion behaviour of these materials was different. Coal showed one reaction during the combustion process, while microalgae and the Coalgae® blends showed three reactions. A significant reduction in activation energies of 160.4 kJ/mol, 159.6 kJ/mol, 151.3 kJ/mol, and 134.2 kJ/mol for Coalgae® 5% - Coalgae® 20%, respectively, compared to coal (161.3 kJ/mol) was achieved. The lowering of activation energy could be attributed to the relative fixed carbon content. SEM morphology images of ash obtained from the combustion of coal and Coalgae® 5% - 20% confirmed changes in devolatilization and combustion behaviour of solid raw fuel. The ash of Coalgae® blends had higher fluxing elements (Fe, Ca, K and Mg) than coal and this shows possibility of slagging and fouling in combustion systems. The Coalgae® blends showed a synergistic effect due to different combustion characteristics of coal and *Scenedesmus* microalgae.

The combustion results obtained from the fixed-bed reactor showed significant reductions in concentrations of CO$_2$, SO$_2$ and NOx emissions for Coalgae® blends compared to baseline coal. Microalgae reduced CO$_2$ emissions from baseline coal by 14.9%, 19.5%, 23.5% and 31.4% for Coalgae® 5%, 10%, 15% and 20%, respectively. SO$_2$ reductions of 1.9%, 10.6%, 15.8% and 18.2%, and NOx reductions of 22.4%, 26.1%, 24.4% and 16.9% were achieved with Coalgae® 5%, 10%, 15% and 20%, respectively. Moreover, the combustion efficiency of Coalgae® blends increased significantly by up to 14.5% from baseline coal (86.4%) to Coalgae® 20% (98.9%). Based on the above findings, the co-firing of coal and *Scenedesmus* microalgae biomass was necessary for the reduction of CO$_2$, SO$_2$, and NOx emissions. As such, Coalgae® blends can be considered as alternative fuels in any coal driven process for energy generation.

*Key words: Coal, Coalgae®, Scenedesmus microalgae, Co-firing, Greenhouse gases*
ACKNOWLEDGEMENTS

“I CAN DO ALL THROUGH CHRIST WHO STRENGTHENS ME”, Philippians 4:13

First and foremost, I would like to thank God for His unconditional love and merciful grace upon my life. I wish to express my deep gratitude to the following individuals and institutions that I hereby acknowledge as having been instrumental in bringing this project to success:

❖ To my late supervisor Prof. Ben Zeelie for his supervision, invaluable guidance and support. May his soul rest in peace!!!

❖ To Dr. Gary Dugmore and Dr Adeniyi Ogunlaja for their supervision, support and picking up all the pieces to make this work successful.

❖ To the Nelson Mandela University for allowing me to conduct this study.

❖ To the Department of Science and Innovation (DSI), Technology Innovation Agency (TIA) and National Research Foundation (NRF) for financial research support.

❖ To my late son Khwezi Magida for his love, patience and understanding. May his precious soul rest in peace!!!

❖ To my husband Melikhaya Matomela for his support, encouragement and patience.

❖ To my parents Mr Lunga H. Magida and Mrs Nothozamile E. Magida, and my whole family for their love, support and encouragement.

❖ Lastly, to my colleagues and the InnoVenton team for their support and advice.
RESEARCH OUTPUT

Conference Proceedings and publications


   Oral presentation: Evaluation of greenhouse gas emissions during co-firing of coal and microalgae biomass.

5. Renewable Energy for Postgraduates Symposium, University of Fort Hare, Alice, South Africa, 05 – 06 September 2016.
   Poster presentation: An evaluation of the greenhouse gas reduction potential through the co-firing of coal and microalgae biomass.

6. Postgraduate Chemistry Department Seminar, Nelson Mandela University, South Campus, Port Elizabeth, 28 August 2015.
   Oral presentation: Greenhouse gas emissions reduction through the co-firing of coal and microalgae biomass: An experimental evaluation.

   Poster presentation: Reduction of greenhouse gas emissions through co-firing of coal and microalgae biomass.
DEDICATION

To my late son Khwezi Magida who waited until he couldn’t anymore during this long journey.

“I dedicate this Doctorate to you boy even if you are not here to celebrate it with me. However, I do know that your soul will be there when I walk up to receive our degree. You will always be in my heart”
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NOMENCLATURE

Coalgae® - A composite of coal and microalgae

GHG - Greenhouse gas

NOx - Oxides of nitrogen

PM - Particulate matter

VM - Volatile matter

FC - Fixed carbon

M - Moisture

A - Ash

ad - Air dry basis

db - Dry basis

daf - Dry ash free basis

VOC - Volatile organic carbon

HHV - High heating value

A/F - Air to fuel ratio

AFR - Air flow rate

Mt - Million tonnes

ppm - Parts per million

ppb - Parts per billion

µg - Micro gram

µm - Micro metre
mm - Millimetre

m³ - Cubic meter

v - Volume

g - Gram

kg - Kilogram

°C - Degrees Celsius

% - Percentage

wt. % - Weight percentage

MJ/kg - Mega Joules per kilogram

kJ/mol - Kilo Joules per mole

Min - Minutes

s - Second

hr - Hour

l - Litre

rpm - Revolutions per minute

V - Volt

Min. - Minimum

Max. - Maximum

XRF - X-ray fluorescence

NMR - Nuclear magnetic resonance spectroscopy

SEM – Scanning electron microscope
EDS - Energy dispersive spectroscopy
TGA - Thermogravimetric analysis
DTG – Derivative thermography
FTIR – Fourier-transform infrared
SANS - South African national standard
ISO - International Organisation for Standardisation
ASTM - American Society for Testing and Materials
CCT - Clean coal technology
Chapter 1

1 INTRODUCTION

The background review of coal was conducted to have a broader understanding current happening in the coal industry worldwide with focus on South Africa. There are, a variety of problems associated with the use of coal, particularly the combustion process. Co-firing technology offers advantages with respect to the use of biomass (such as microalgae) offers higher efficiency, lower pollutant emissions and lower costs.

1.1 BACKGROUND

Coal is primarily used as fuel for the generation of energy for domestic and for industrial applications (Helle et al., 2003). Coal is responsible for at least 27.2% of the world’s primary energy needs (BP Statistical Review of World Energy, 2019), and has generated over 38% of the world’s electricity (International Energy Agency, 2019). In 2018, about 70.8% of the primary energy needs in South Africa was generated from coal with the remainder of sources contributing a combined 29.2% (Figure 1.1) (BP Statistical Review of World Energy, 2019).

In South Africa, coal is a very important natural source of energy because it is the most accessible and abundant fuel resource (Helle et al., 2003). South Africa is amongst the prominent coal producing and exporting countries in the world with a reported production capacity of 257 Mt and exporting capacity of 71 Mt in 2018 (Table 1.1) (International Energy Agency, 2019).
Table 1.1: Global coal production and exports in Million tonnes (Mt) in 2018

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<td>700</td>
<td>Others</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 1.1: Energy consumption in South Africa (BP Statistical Review of World Energy, 2019).
According to Eskom SA (2018) about 90% of the electricity generated in South Africa is from coal. As it can be seen in Figure 1.2, most of the coal is used by Eskom (53%) (Eskom Fact Sheet, 2016). This further proves reliance on coal as an energy source, which is unlikely to change for the next decade. The combustion of coal poses several environmental challenges which contribute directly to climate change which in turn is responsible for receding of glaciers, rise in sea levels and putting human health at risk (Gullison et al., 2007).

The combustion of coal produces emissions such as carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen oxides (NOx), nitrous oxide (N₂O) and particulate matter (PM). Coal combustion was responsible for about 44.1% of the world’s carbon dioxide emissions in 2017 (International Energy Agency, 2019). To address the issues emanating from the use of coal, alternative energy sources with lower greenhouse gas (GHG) emissions and energy output comparable or better than coal are required. Alternatively, a clean coal technology (CCT) approach can be employed as a means of
mitigating GHG emissions. The challenge has been identifying such alternatives. This is largely due to the accessibility, affordability and availability of high-quality coal, particularly in South Africa and other leading coal producing countries. This is also encouraged by lack of policy regulations around the use of coal at a world platform (Eberhard, 2011). As a result, transition from coal to other alternative energy sources will stagnate until stringent measures are put into place for all countries to abide.

Although South Africa has not yet been obligated by international treaty to reduce GHG emissions, action to reduce the CO₂ footprint has been taken. Act No.39 of 2004 for air quality was passed in 2004. Coal powered plants/sectors are the most affected by such regulatory and legislative acts due to their large consumption of coal to produce some form of energy (Government Gazette, 2009; SANS 1929, 2011). There exists also a Carbon Tax Policy Paper (2013) which proposes a carbon tax of R120 per tonne of CO₂-eq above the tax-free threshold that will apply to all coal users in South Africa. This to some extent encourages industries to consider alternative energy sources that are environmentally friendly, sustainable and accessible. Penalties are to be imposed for failure to comply with these acts. In 2018, the consumption of coal in South Africa dropped by 7.8% from 2008 due to considerations of other energy sources as depicted in Figure 1.1 (BP Statistical Review of World Energy, 2019). The decline can be directly linked to sectors slowly adopting the new approach.

1.2 PROBLEM STATEMENT

The combustion of raw coal especially high-quality coal emits high amounts of GHG emissions into the atmosphere. Continual emission of such GHG’s has a significant negative impact on the environment. The impact of GHG emissions can be directly linked to global warming and climate change (Sahu et al., 2014) which in the long run will have a severe effect on human existence and every living thing on the planet. To address such concerns, the co-firing of coal with biomass or waste is a potential technology to achieve
a reduction in CO₂, SO₂ and NOₓ emissions relative to coal-based power plants (Baxter, 2005; Eskom, 2016). Furthermore, the co-firing of coal with biomass increases energy security and improves green energy production. Biomass refers to renewable energy resources which are derived from plant materials such as wood, switch grass and crop residues, as well as animal waste such as manure. Microalgae is a potential energy source due to its high growth rate and productivity, simple nutrient requirements, use of non-productive lands and less competition with food compared to other biomass – it is a third-generation fuel source (Kucukvar and Tatari, 2011). Microalgae can be added to coal or any carbonaceous material before thermochemical processing such as combustion, gasification, liquefaction, distillation, pyrolysis and coking (Zeelie, 2016). When microalgae slurry is adsorbed onto coal fines, a new material “Coalgae®” with different properties, is formed (Zeelie, 2016). The newly formed material has a potential of reducing GHG emissions during the co-combustion process.

1.3 NOVELTY OF THE STUDY

Despite considerable discussions on the co-firing of coal with biomass, the *Scenedesmus* microalgae strain used in this study has a low ash yield (7.3 wt.%), higher volatile matter content (77.5 wt.%) and calorific value (21.4 wt.%) (Baloyi and Dugmore, 2019) compared to most microalgae strains reported in the literature (Agrawal and Chakraborty, 2013; Tahmasebi et al., 2013; Sanchez-Silva, 2013; Kucukvar and Tatari 2011). The high volatile matter content (>77 wt.%) is advantageous to provide a stable flame during combustion, and the low ash yield (<10 wt.%) reduces the unburned minerals after combustion. Several studies on coal and microalgae co-firing have been reported, however, *Scenedesmus* microalgae strain co-firing has not been studied, hence, the need to address this gap. The characteristics of this strain of microalgae (*Scenedesmus*) make it a good biomass with excellent combustion performance and unique thermochemical properties, hence, the study of coal and *Scenedesmus* microalgae co-combustion characteristics and emissions is significant.
1.4 HYPOTHESIS

Blends of freshly harvested *Scenedesmus* microalgae slurry and fine coal (250 µm) will have improved physico-thermal properties, leading to enhanced combustion behaviour and different emission level of greenhouse gases when compared to the parent coal. This study provides a better understanding of the coal-microalgae interaction chemistry, combustion process and the information required for the design and operation of firing systems for these blends.

1.5 RESEARCH QUESTIONS

- What is the effect of *Scenedesmus* microalgae on the physico-thermal properties and combustion behaviour of the coal?

- Is there a synergistic effect in the blends of coal and *Scenedesmus* microalgae?

- What is the effect of *Scenedesmus* microalgae on the levels of CO₂, SO₂ and NOₓ emissions during the combustion process of coal?

- Is the ash formed after the combustion process affected by blending coal with *Scenedesmus* microalgae?

- How does the co-firing of coal and *Scenedesmus* microalgae affect the combustion efficiency?
1.6 AIM AND OBJECTIVES

1.6.1 Aim

The aim of the study was to evaluate the effect of partial substituting coal with *Scenedesmus* microalgae biomass on combustion performance and combustion efficiency. The main aim of the study was to determine if co-firing *Scenedesmus* microalgae and coal will have any advantage on the emission levels of CO$_2$, SO$_2$ and NO$_x$.

1.6.2 Objectives

The following objectives were set in order to accept or reject the hypothesis:

- Characterization of coal and *Scenedesmus* microalgae to determine their chemical and thermal properties. This was performed to measure the effect of microalgae blending on coal properties.

- Evaluation of the effect of *Scenedesmus* microalgae and coal co-firing on the combustion behaviour and the level of GHG emissions through TG-MS and a lab-scale fixed-bed reactor.

- Analysis of the ash residue of Coalgae® blends compared to that of coal. This was to give a partial view of the effect of microalgae co-firing on ash deposition.

- Determination of the combustion efficiency of Coalgae® blends compared to that of raw coal.
1.7 THESIS OUTLINE

The scope of the study is outlined below.

**Chapter 1** provides the background of coal, problem statement, as well as research questions. This chapter includes the hypothesis, aim and objectives.

**Chapter 2** is a literature review on the formation, classification and properties of coal and biomass as well as the combustion process and its emissions, combustion mechanism and emission control technologies. Research that has been done on coal and biomass co-firing and particularly microalgae has been summarised in the literature review section.

**Chapter 3** describes the materials used in the study, methods used to prepare samples as well as the analytical techniques used to analyse samples and products from combustion tests. The combustion procedure and description of the fixed-bed combustion reactor are included in this chapter.

In **Chapter 4**, the characterization results of materials used in the study are provided and discussed, including proximate and ultimate analyses, SEM/EDX, FT-IR, TGA and MS analyses.

**Chapter 5** provides the combustion results and discussion which include mass reduction measured during combustion, combustion temperature and emissions. This chapter also presents ash analysis, combustion efficiency and mass balance of elements burned.

**Chapter 6** presents the conclusions drawn from the findings of the study and recommendations for future work.
Chapter 2

2 LITERATURE REVIEW

To fully understand the impact and implications of coal combustion, a thorough literature study was conducted to identify and describe the morphology of coal as well as to understand its combustion mechanism to devise a means of using coal in a cleaner and environmentally friendly way. Some research on coal and biomass co-firing, particularly microalgae, has been done and is reviewed at the end of this section.

2.1 FORMATION OF COAL

Coal is a complex material formed millions of years ago from plant remains that have been compacted, hardened, chemically altered and metamorphosed by combined effect of microbial action, high temperature and pressure (Western Climate Initiative, 2007). This formation process is known as coalification (Williams et al., 2000). A carbon-rich material called peat formed due to the availability of water on plant material which limited the supply of oxygen and allowed the thermal and bacterial decomposition to take place (Speight, 2005). In the geochemical stage following the biochemical stage (peat-forming stage), coals with different properties were formed (Speight, 2005). The coal formation diagram is shown in Figure 2.1.
Coal can be defined as an organic sedimentary, combustible black or brownish-black rock, mainly composing of combustible organic matter, mineral matter and moisture content (Williams et al., 2000; Alpern et al., 2002). The various levels which coal reach during coalification process are called its rank. The classification or ranking of coal is significant because it is used in predicting the combustion behaviour of different coals from all over the world (Speight, 2005).

### 2.2 CLASSIFICATION OF COAL

Coal can be classified into four major types: lignite, sub-bituminous, bituminous, and anthracite. These are differentiated from each other by their level of maturity which can be determined by proximate and ultimate analyses. Ranks of coal, formed after peat, are described below (Speight, 2005; Bowel and Irwin, 2008).

- **Lignite**, often referred to as brown coal, is a lowest ranked coal, often distinguished by its high inherent moisture content, usually up to 45% by weight (Falcon and Ham, 1988). It is a brownish-black coal with high volatiles, low fixed...
carbon content and a heat content that ranges between 19.8 – 24.4 MJ/kg on moisture and mineral matter free basis (Speight, 2005; Bowel and Irwin, 2008).

- Sub-bituminous coal is a dark brown to black coal with properties which range between those of lignite and bituminous coal (Speight, 2005; Bowel and Irwin, 2008). It has an inherent moisture content that ranges between 10 – 25% by weight and a calorific value around 24.6 MJ/kg (Speight, 2005; Idris et al., 2012).

- Bituminous coal is a black or sometimes dark brown middle ranked coal, with inherent moisture content usually less than 25% by weight and heat content that ranges between 24.4 – 34.9 MJ/kg on moisture and mineral matter free basis (Speight, 2005; Bowel and Irwin, 2008).

- Anthracite coal is the highest ranked or older coal, often referred to as hard coal, due to its high fixed carbon content and low moisture content. The inherent moisture content of anthracite is usually less than 15% by weight and its heat content ranges between 25.6 – 32.6 MJ/kg. It produces less smoke compared to other coals and is used for heating and electricity generation (Speight, 2005; Bowel and Irwin, 2008).

### 2.3 PROPERTIES OF COAL

Each rank of coal has a specific set of properties. Such properties can be ascertained through proximate and ultimate analysis as well as caloric value. Calorific value can be determined by a bomb calorimeter or calculated from proximate or CHNS data (Speight, 2005). A typical content of the proximate and ultimate analyses of different coal ranks is presented in Table 2.1.
Table 2.1: Typical chemical composition of different coals (Speight, 2005).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lignite</th>
<th>Sub-bituminous</th>
<th>Bituminous</th>
<th>Anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>24 – 32</td>
<td>28 – 45</td>
<td>15 – 45</td>
<td>2 – 12</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>25 – 30</td>
<td>30 – 57</td>
<td>50 – 70</td>
<td>75 – 85</td>
</tr>
<tr>
<td>Ultimate analysis (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>35 – 45</td>
<td>55 – 70</td>
<td>65 – 80</td>
<td>75 – 85</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6 – 7.5</td>
<td>5.5 – 6.5</td>
<td>4.5 – 6</td>
<td>1.5 – 3.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>38 – 48</td>
<td>15 – 30</td>
<td>4.5 – 10</td>
<td>5.5 – 9</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.6 – 1</td>
<td>0.8 – 1.5</td>
<td>0.5 – 2.5</td>
<td>0.5 – 1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.3 – 2.5</td>
<td>0.3 – 1.5</td>
<td>0.5 – 6</td>
<td>0.5 – 2.5</td>
</tr>
</tbody>
</table>

Proximate analysis is a technique to assay moisture content, volatile matter content, ash yield and fixed carbon content in weight %. Proximate analysis of coal is determined using a series of standard test methods: ASTM D-3172; ASTM D-3173; ASTM D-3174; ASTM D-3175; ASTM D-5142; ISO 1171. Ultimate analysis is a technique used to determine the weight % contents of carbon, hydrogen, nitrogen, sulphur and oxygen (calculated by difference). Ultimate analysis of coal is determined by the standard test method ASTM D-3176.

The chemical composition of coal significantly influences its combustion behaviour; hence it is important to know the fuel composition to obtain an optimum and efficient combustion process. High carbon content and low ash yield coal has high energy value and longer combustion time. High volatile matter content coals ignite easily and are highly reactive in combustion application (Munir et al., 2011).
2.4 COAL COMBUSTION

Coal is processed through several conversion methods which include combustion, gasification and liquefaction. Gasification is a thermo-chemical process used to convert coal or other solid fuels into syngas by reacting the fuel with steam and/or air or pure oxygen at high temperatures (Williams et al., 2000). Liquefaction is a thermo-chemical process in which coal or other solid fuels are converted into liquid fuels and petrochemicals (Williams and Larson, 2003). Combustion, also known as burning, is an exothermic chemical reaction that occurs between a fuel (solid, liquid or gas) and an oxidant (oxygen) giving off heat and combustion products (Williams et al., 2000). A general example of a combustion reaction is given in Equation 2.1, in which methane gas reacts with oxygen producing carbon dioxide (CO₂) and water (H₂O) releasing heat energy.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{Heat} \quad (2.1)
\]

Coal is generally used for electricity generation, heating and cooking especially in rural and semi-urban areas. The different coal structures differ from each other depending on the way the coal was formed. The average coal structure determined by $^{13}$C NMR (Perry, 1999) shows a very complex substance with many functional groups attached to the aromatic rings. The complexity of coal structure makes it difficult to ignite due to less accessibility for oxygen to react with available elements. A typical sub-bituminous coal structure is shown in Figure 2.2.
2.4.1 Coal combustion mechanism

Coal combustion involves three stages, (1) the drying up step which occurs between 100 and 200°C, (2) devolatilization step which occurs between 200°C and 650°C (Shen, 2009), and the third stage is the combustion of the remaining solid, known as char, which is a mixture of carbon and minerals (Yu et al., 2007). Figure 2.3 illustrates the combustion steps of a single coal particle which are discussed in subsection 2.4.1.1, 2.4.1.2 and 2.4.1.3.
2.4.1.1 Heating and drying

Coal particles contain water which is adhered to their surface and pores inside. The coal particles are loaded into a combustion reactor at low temperature and are heated rapidly, increasing the surface temperature (Dooley, 2017). As coal particles are heated up in a combustion system at temperatures above 100°C, the inherent water within the pores start evaporating (Spliethoff, 2010). The heating of high moisture fuels increases the duration of the heating and drying step, resulting in increased overall combustion time (Dooley, 2017).

Heat within the reactor environment is transferred by radiation and convection to the particle surface and then to the particle centre by conduction (Dooley, 2017). When the centre of the particle reaches a temperature of approximately 120°C and has been heated sufficiently; water is released as a vapour. The vapour travels to the particle surface through the porous structure and through the boundary layer to the reactor environment (Wu, 2005). The loss of moisture results in overall weight reduction of the particle. High temperature may cause the particle to fracture due to increased internal pressure (Tillman, 1991).
Devolatilization (also known as pyrolysis) refers to the decomposition of organic material and formation of gaseous products which occurs when coal is heated up at moderate temperatures between 200°C and 600°C (Shen, 2009; Spliethoff, 2010). The efficiency of devolatilization is highly dependent on coal type, particle size, heating rate and final heating temperature. The higher the volatile content is, the faster the devolatilization step. Table 2.2 shows the ignition and devolatilization temperature ranges for various types of coal.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Ignition temperature (°C)</th>
<th>Initial volatile release temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>250 – 450</td>
<td>130 – 170</td>
</tr>
<tr>
<td>Bituminous</td>
<td>400 – 500</td>
<td>200 – 300</td>
</tr>
<tr>
<td>Anthracite</td>
<td>700 – 800</td>
<td>380 – 400</td>
</tr>
</tbody>
</table>

Devolatilization alters the chemical structure of coal, making it easier for O₂ to penetrate the char and react with carbon, hydrogen, nitrogen and sulphur. During the devolatilization of coal aliphatic and functional groups break first, producing and separating molecular fragments (also known as metaplast or liquid coal components) from the macromolecular structure (Dooley, 2017). When the devolatilization stage occurs with a high heating rate, the metaplast fragments are released as tar if the fragments are small enough to vaporise (Solomon et al., 1988). Otherwise, the fragments crosslink back to the macromolecular structure and stabilise the evolving char matrix (Solomon and Fletcher, 1994). In the work conducted by Hardesty (1990), the ¹³C NMR analysis showed considerable amounts of aliphatic material liberated during coal devolatilization with little alteration in aromatic cluster size.
Char, gases and tar are the main products the coal devolatilization process; and gases include CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, NH₃, HCN and SO₂ (Dooley, 2017). When these volatile gases are released, they may ignite causing flaming combustion and this part is called volatile combustion. There are two ignition scenarios (homogeneous and heterogeneous ignition) in which the ignition of a particle can happen, depending on the particle size, composition and temperature. Homogeneous ignition is the ignition of volatiles which occurs when volatiles are oxidised by the furnace atmosphere and this process is gas-gas combustion (Dooley, 2017). Heterogeneous ignition refers to the direct attachment of the oxidiser on the char matrix (Dooley, 2017). The coal particle remains unchanged at temperatures up to 400°C and starts softening at temperatures above 400°C (Spleighthoff, 2010). At temperatures slightly above 550°C, the tar and gases which are formed within coal particle can swell the particle which further solidifies into a semi-char. At temperatures above 600°C, semi-char is converted to char and soot as well as light gases such as H₂ and CO which are formed from the tar (Spleighthoff, 2010).

### 2.4.1.3 Char combustion

The char particle resulting from coal devolatilization is often porous with a lot of cracks caused by the escape of volatile gases (Shen, 2009). Char contains a high amount of carbon, most of the mineral matter and some nitrogen and sulphur (Sadhukhan et al., 2009; Shen, 2009). The char, at a sufficiently high surface temperature, is oxidised by O₂, CO, CO₂ and H₂O in a slow solid-gas reaction (Shen, 2009). Char combustion reaction is much slower than the volatile combustion reaction, can last for several minutes to hours. Complete char combustion produces bottom ash and fly ash (particulates) in addition to GHG emissions (CO₂, SO₂, NOx (NO and NO₂) and N₂O). Char combustion reaction determines the overall combustion time (Spleighthoff, 2010).
The char combustion reactions take place at temperatures above 700°C. The reactions which show the heterogeneous oxidation of carbon by O₂, CO₂, and H₂O at the surface of coal (Spleighthoff, 2010; Rafal, 2011) are shown Equations 2.2 to 2.4.

\[ \text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} \quad (2.2) \]

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad (2.3) \]

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad (2.4) \]

Initially, only carbon monoxide forms during char oxidation taking place directly at the particle surface (Zelkowski, 2004). The formation of a gaseous atmosphere consisting of combustion products CO and H₂ and oxidants O₂ (combustion), CO₂ and H₂O (gasification) takes place around the coal particle (Spleighthoff, 2010). Homogeneous reactions which take place at the boundary layer are shown in Equation 2.5 and 2.6.

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (2.5) \]

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad (2.6) \]

The oxidant (oxygen) diffuses from the combustion atmosphere to the particle surface through the laminar boundary layer and penetrates the porous particle and, vice versa, the combustion products from the particle surface to the combustion atmosphere. The oxidation of carbon by oxygen on the particle surface and at the pore walls forms CO which can further oxidise in the gas phase around the particle producing CO₂ (Dooley, 2010). When the char gets depleted, a porous structure evolves affecting the entire surface area, active site concentration and gas diffusion within the porous structure hindering the combustion process (Spleighthoff, 2010; Dooley, 2017).

The pathway of the combustion reaction of char depends not on chemical composition but on physical structure of char such as particle size, pore structure, surface area, ash
content and active site availability (Dooley, 2017). According to active site theory, reactions that occur at the favoured sites on the surface of the char particle can be attributed to (1) carbon edges or defects throughout the carbon structure (Jones and Godefroy, 2002), (2) inorganic impurities (Dooley, 2017) and (3) heteroatoms such as hydrogen, oxygen, nitrogen and sulphur (Marsh and Kuo, 1989).

### 2.4.2 Greenhouse gas emissions

Unlike other fuels, solid fuels like coal contain oxygen, sulphur and nitrogen in their aromatic structures which results in sulphur dioxide (SO$_2$) and nitrogen oxide (NOx) emissions during combustion. Insufficient amount of oxygen during combustion leads to emission of carbon monoxide (CO) which further react with supplied excess oxygen to form carbon dioxide (CO$_2$) (Williams et al., 2000). Some of the oxidation reactions which occur during combustion of coal with oxygen are depicted in Equations 2.7 – 2.11.

\[
\begin{align*}
C + \frac{1}{2} O_2 & \rightarrow CO + \text{Heat} \quad (2.7) \\
C + O_2 & \rightarrow CO_2 + \text{Heat} \quad (2.8) \\
2H + \frac{1}{2} O_2 & \rightarrow H_2O + \text{Heat} \quad (2.9) \\
N + O_2 & \rightarrow NO_2 + \text{Heat} \quad (2.10) \\
S + O_2 & \rightarrow SO_2 + \text{Heat} \quad (2.11)
\end{align*}
\]

CO is a product of incomplete combustion and CO$_2$ is produced by complete combustion of coal. Apart from atomic carbon, oxygen, nitrogen and sulphur, ultimate analysis also shows that coal contains some hydrogen atoms in its structure which results in water (H$_2$O) as one of the combustion products (Zhang et al., 2013).

Mining, processing and utilization of coal all contributes significantly to greenhouse gas (GHG) emissions leading to environmental implications. These include emissions of CO$_2$
Greenhouse gas emissions reduction through the co-firing of coal and microalgae biomass: An experimental evaluation
Magida N.E. – PhD Thesis

and their implications for global warming; formation of particulate matter (PM) emissions, SO$_2$, NO$_x$ and toxic trace elements; and pollution of water and land associated with mining activities and ash disposal (Nelson et al., 2010). Climate change is a serious concern which requires both global and national response and/or efforts to reduce GHG emissions. The Annex 1 developing countries have committed to reduce their emissions by signing the United Nations Framework Convention on Climate Change (UNFCCC) associated Kyoto Protocol in agreement to reducing GHG emissions in a period of 2008 – 2012 by 5% below the 1990 levels (Department of National Treasury, 2010). To respond to such Protocol, coal-fired power plants installed flue gas cleaning equipment such as gas scrubbers and dust filters, however they have not met the required target (Department of National Treasury, 2017).

South Africa (non-Annex 1) has not been obliged to reduce GHG emissions; however, it is amongst the 20 most carbon-intensive countries. Hence it has volunteered to reduce its CO$_2$ emissions by 34% by 2020 and 42% by 2025 at the COP meeting held in Copenhagen in 2009 (Department of National Treasury, 2010). South Africa has thus set national ambient air quality standard limits for SO$_2$, NO$_2$, PM$_{10}$, ozone (O$_3$), benzene (C$_6$H$_6$), lead (Pb) and CO (Government Gazette, 2009; SANS 1929, 2011) which are tabulated in Table 2.3 The Government Gazette (2009) states that each of these pollutants shall be analysed according to the standard methods listed next to each gas in Table 2.3.
Greenhouse gas emissions reduction through the co-firing of coal and microalgae biomass: An experimental evaluation  
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Table 2.3: National ambient air quality standards (Government Gazette, 2009).

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Averaging Period</th>
<th>Concentration</th>
<th>Frequency of Exceedance</th>
<th>Compliance Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ (ISO 6767)</td>
<td>10 min</td>
<td>500 µg/m³ or 191 ppb</td>
<td>526</td>
<td>Immediate</td>
</tr>
<tr>
<td></td>
<td>1 hour</td>
<td>350 µg/m³ or 134 ppb</td>
<td>88</td>
<td>Immediate</td>
</tr>
<tr>
<td></td>
<td>24 hours</td>
<td>125 µg/m³ or 48 ppb</td>
<td>4</td>
<td>Immediate</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>50 µg/m³ or 19 ppb</td>
<td>0</td>
<td>Immediate</td>
</tr>
<tr>
<td>NO₂ (ISO 7996)</td>
<td>1 hour</td>
<td>200 µg/m³ or 106 ppb</td>
<td>88</td>
<td>Immediate</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>40 µg/m³ or 21 ppb</td>
<td>0</td>
<td>Immediate</td>
</tr>
<tr>
<td>PM₁₀ (EN 12341)</td>
<td>24 hours</td>
<td>120 µg/m³</td>
<td>4</td>
<td>Immediate – 31 December 2014</td>
</tr>
<tr>
<td></td>
<td>24 hours</td>
<td>75 µg/m³</td>
<td>4</td>
<td>1 January 2015</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>50 µg/m³</td>
<td>0</td>
<td>Immediate – 31 December 2014</td>
</tr>
<tr>
<td></td>
<td>1 year</td>
<td>40 µg/m³</td>
<td>0</td>
<td>1 January 2015</td>
</tr>
<tr>
<td>O₃ (SANS 13964)</td>
<td>8 hours (running)</td>
<td>120 µg/m³ (61 ppb)</td>
<td>11</td>
<td>Immediate</td>
</tr>
</tbody>
</table>
Coal combustion emissions that are considered as major GHGs are discussed below; N\textsubscript{2}O was not included in this study but is also a major concern.

- Carbon dioxide (CO\textsubscript{2}) is a by-product formed from the complete combustion oxidation reaction of fuel-bound carbon and oxygen. Combustion of coal, especially high-grade coal (with high carbon content), produces high levels of CO\textsubscript{2} which represents 80% of the global GHG emissions (Quadrelli and Peterson, 2007). CO\textsubscript{2} has not been identified as a criteria pollutant and the explanation is that it does not have a direct or strong indirect effect on the environment health risks (Gaffney and Marley, 2009; Patel, 2012). Therefore, CO\textsubscript{2} has not been included in air quality standard regulations; nevertheless, it is important to reduce its emission levels as it contributes significantly to the effect of global warming. Potential technologies to reduce CO\textsubscript{2} include biomass co-firing.

- Carbon monoxide (CO) is a toxic gas formed by incomplete combustion. It indicates low combustion temperature, insufficient air and poor mixing of fuel

<table>
<thead>
<tr>
<th>(\text{C}_6\text{H}_6) (EP Acompendium method TO-14 A or TO-17)</th>
<th>1 year</th>
<th>10 (\mu\text{g/m}^3) (3.2 ppb)</th>
<th>0</th>
<th>Immediate – 31 December 2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pb}) (ISO 9855)</td>
<td>1 year</td>
<td>0.5 (\mu\text{g/m}^3)</td>
<td>0</td>
<td>Immediate</td>
</tr>
<tr>
<td>(\text{CO}) (ISO 4224)</td>
<td>1 hour</td>
<td>30 (\text{mg/m}^3) (26 ppm)</td>
<td>88</td>
<td>Immediate</td>
</tr>
<tr>
<td></td>
<td>8 hour</td>
<td>10 (\text{mg/m}^3) (8.7 ppm)</td>
<td>11</td>
<td>Immediate</td>
</tr>
</tbody>
</table>
and air. This gas is considered a criteria pollutant as it is poisonous and can lead to death when inhaled (Ighodalo et al., 2013).

- Oxides of nitrogen (NOx) is a combination of NO and NO2 which forms through many reactions. It can be formed when the nitrogen contained in the fuel is oxidised at low temperatures (fuel NOx) and when the nitrogen in the air is oxidised at high temperature (Sami et al., 2001). NOx is a poisonous and corrosive gas which contributes to the formation of smog and acid rain (Hu et al., 2000). In Eskom’s report, Patel (2012) acknowledged that Eskom is the major source of NOx on the Highveld and that none of their plants were designed with NOx reduction controls. Eskom however intend to install NOx controls on their new plants.

- Sulphur dioxide (SO2) is a gas formed from the reaction between sulphur contained in the fuel with oxygen; it is the major contributor to acid rain. Emissions of sulphur dioxide can be controlled by wet flue gas desulphurization.

- Particulate matter (PM) is the dust in the flue gas and is a major air quality problem in South Africa. It is also a serious pollutant that causes environmental health risks such as asthma and cardiovascular diseases. PM control equipment includes electrostatic precipitators, fabric filters and flue gas conditioning (Patel, 2012).

2.5 EMISSION CONTROL TECHNOLOGIES

Chemical and physical means are available to control emissions that are regarded as pollutants. These include but are not limited to flue gas desulphurization to control SO2 emissions, selective catalytic reduction to control emissions of NOx, electrostatic precipitators, cyclones and ceramic filters to control PM. Sorbents and oxidising agents
can be used to control mercury (Franco and Diaz, 2009). Carbon dioxide sequestration is one of the emission control technologies which aspire to the future of CO₂-free power plants (Basu et al., 2011). These control technologies have the potential to reduce emissions by up to 99% (Franco and Diaz, 2009). Installing these technologies in power plants is however very expensive and would result in an increase in the cost of electricity (Franco and Diaz, 2009; Patel, 2012), estimated at 60% (Basu et al., 2011). This is a huge economic burden on the industry and as a result implementation of these technologies will take years.

2.6 BIOMASS FUEL

Biomass is a renewable energy source which has been used as a fuel for thermal power generation for decades. In South Africa, biomass is responsible for approximately 0.2% of the country’s energy generation (BP Statistical Review of World Energy, 2016). Biomass refers to organic materials that can be converted to energy such as forest residues, agricultural residues and animal waste. Most biomasses contain less carbon, sulphur and nitrogen compared to hard coal; hence biomass combustion is regarded as low emission technology (Senecca, 2007; Basu et al., 2011; Shao et al., 2012). Biomass does not add additional fossil carbon back into the atmosphere and therefore biomass combustion is considered carbon neutral. Additionally, some of the SO₂ produced from biomass combustion is trapped by alkaline metals in ash (Khan et al., 2009; Fernando, 2012). NOx emissions might increase, decrease or remain the same depending on the type of biomass combusted, firing and operating conditions (Sahu et al., 2014). Additionally, the nitrogen contained in biomass is converted to NH radicals (mainly ammonia (NH₃)) during combustion (Sami et al., 2001; Sahu et al., 2014), leading to further reduction of NOx emissions. Combustion of waste biomass such as sewage sludge has an added advantage of solving waste disposal challenges.
Biomass utilization on large scale however raises concerns of availability, affordability and ash deposition in biomass-fired boilers (Shao et al., 2012). Certain biomass types contain higher quantities of chlorine and alkali/alkaline earth metals (e.g., K, Ca and Na) compared to coal (Sami et al., 2001; Seneca, 2007). These elements, particularly chlorine and potassium, may cause ash related problems such as slagging, fouling and corrosion (Khan et al., 2009; Shao et al., 2012; Sahu et al., 2014). The presence of these elements may cause severe damage to the combustion unit. Other issues associated with firing biomass alone include its low calorific value due to high moisture and volatile content (Zhou et al., 2016). The above limiting factors are hindering the use of biomass in existing combustion units and therefore the priorities have shifted to biomass and coal co-firing.

### 2.6.1 Properties of biomass

It is important to understand the properties of a fuel as these would affect the release of gas emissions and burning performance during combustion. Fuel properties normally form the basis for the technology selected for a combustion process. Biomass fuel can be excluded for a specific combustion option, based on its properties, partially for technical and environmental reasons (Khan et al., 2009). The most important fuel properties for a combustion process are those given by proximate and ultimate analysis, heating value and ash fusion point (Khan et al., 2009).

The properties of biomass fuels differ significantly from those of coal and the variation amongst biomass properties is larger than amongst coals as shown in the Van Krevelen diagram (Seneca, 2007) in Figure 2.4. Biomass fuels generally have lower fixed carbon, higher oxygen content, higher hydrogen content and sometimes lower sulphur as well as higher nitrogen content compared to coal (Annamalai et al., 2003; Seneca, 2007; Munir et al., 2009; Gil et al., 2010; Mitchell et al., 2016; Zhou et al., 2016).
Biomass fuels also tend to have lower heating value than coal due to their relative low carbon content and high oxygen content. Therefore, O/C and H/C ratios (calculated from elemental composition) of biomass fuels are much higher than that of coal. The O/C ratios of biomass fuels are at around 1 while the H/C ratios are above 0.1 compared to coals which have their O/C ratios below 0.2 and H/C ratios at around 0.05. The energy contained in C-O and C-H bonds is less than the energy contained in C-C bonds (Munir et al., 2009). The fuel properties of microalgae have previously been reported (Chen et al., 2011; Sanchez-Silva et al., 2013; Tahmasebi et al., 2013; Gai et al., 2015). The O/C ratio of *Chlorella Vulgaris* microalgae is 0.52 and H/C ratio is 0.13 – these were calculated from elemental composition reported by Chen et al. (2011). The elemental composition reported by Tahmasebi et al. (2013) gives an O/C ratio of 1.45 and an H/C ratio of 0.17 for the *Tetraselmis Suecica* microalgae. The O/C ratio of the *Nannochloropsis gaditana* microalgae is 0.81 and H/C is 0.15 as was calculated from
elemental composition reported by Sanchez-Silva et al. (2013). There is a great variation in microalgae properties as the elemental composition reported differs significantly from species to species.

Typical properties of various biomass fuels are presented in Table 2.4. Biomass fuels have higher moisture content, higher volatile matter, lower fixed carbon and lower ash content compared to coals (Annamalai et al., 2003; Senneca, 2007; Munir et al., 2009; Gil et al., 2010; Mitchell et al., 2016; Zhou et al., 2016). Biomass fuels typically have a volatility (VM/FC) ratio of >4.0, while coals have a volatility of <1.0 (Tillman, 2000). The volatility of *Chlorella Vulgaris* microalgae is 1.61 (far lower than most biomass fuels) and was calculated from proximate analysis reported by Chen et al. (2011).

**Table 2.4: Typical properties of various biomass types.**

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Wood&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Wheat Straw&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Grass&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Sawdust&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Rice husk&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Microalgae&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>-</td>
<td>11.40</td>
<td>7.90</td>
<td>9.05</td>
<td>8.18</td>
<td>-</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>76.33</td>
<td>68.80</td>
<td>71.30</td>
<td>72.30</td>
<td>57.48</td>
<td>55.37</td>
</tr>
<tr>
<td>Ash</td>
<td>2.16</td>
<td>5.07</td>
<td>6.35</td>
<td>1.35</td>
<td>16.13</td>
<td>10.28</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>21.51</td>
<td>26.1</td>
<td>14.55</td>
<td>17.30</td>
<td>18.21</td>
<td>34.35</td>
</tr>
<tr>
<td>Carbon</td>
<td>49.60</td>
<td>43.75</td>
<td>43.73</td>
<td>46.13</td>
<td>48.05</td>
<td>47.84</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.58</td>
<td>5.67</td>
<td>4.27</td>
<td>4.49</td>
<td>7.27</td>
<td>6.41</td>
</tr>
<tr>
<td>Oxygen</td>
<td>37.35</td>
<td>45.17</td>
<td>37.07</td>
<td>35.61</td>
<td>44.50</td>
<td>25.00</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.19</td>
<td>0.2</td>
<td>0.35</td>
<td>3.09</td>
<td>0.18</td>
<td>9.01</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.12</td>
<td>0.14</td>
<td>0.09</td>
<td>0.04</td>
<td>0</td>
<td>1.46</td>
</tr>
</tbody>
</table>

<sup>a</sup> – Kastanaki and Vamvuka, 2006; <sup>b</sup> – Damstedt et al., 2007; <sup>c</sup> – Pokothoane, 2010; <sup>d</sup> – Saikaew et al., 2012; <sup>e</sup> – Chen et al., 2011
The high volatility and oxygen content indicate that biomass fuels have a higher thermal reactivity during combustion compared to coals (Gil et al., 2010). This means the main combustion stage will take place via the gas-phase oxidation of the volatile compounds. Other components of biomass fuels include cellulose, hemicellulose, lignin, lipids and proteins (Khan et al., 2009; Lv et al., 2010; Shen et al., 2013; Zhou et al., 2016). These properties differ from biomass to biomass depending on species, type of plant tissues, growth stages and growing conditions (Khan et al., 2009).

Figure 2.5: Plant cell wall and lignocellulosic components adopted from Tumuluru et al. (2011).
Cellulose (shown in Figure 2.5) is a long chain, linear polymer and high molecular weight \((10^6\) or more) fibrous material which strengthens the biomass cell wall (Tumuluru et al., 2011; Sehume, 2014; Dooley, 2017). The thermal degradation of cellulose occurs at a temperature range of \(240 \text{ – } 350°C\) (Tumuluru et al., 2011). Hemicellulose (shown in Figure 2.5) is a branched and low molecular weight polymer consisting of short sidechains with \(500 \text{ – } 3000\) sugar units compared to cellulose with \(7000 \text{ – } 15000\) glucose molecules per unbranched polymer (Tumuluru et al., 2011). Hemicellulose degrades in a low temperature range of \(130 \text{ – } 300°C\) (Sehume, 2014). Lignin (shown in Figure 2.5) is a complex material with aromatic, highly branched and amorphous cross-linked polyphenolic resin with no exact structure (Brebu and Vasile, 2009; Tumuluru et al., 2011). The decomposition of lignin is longer and occurs in a temperature range of \(280 \text{ – } 500°C\) (Tumuluru et al., 2011) compared to cellulose and hemicellulose when it is thermally treated. Vassilev and Vassileva (2016) reported an average lignocellulosic composition for all algae types and hemicellulose (78.5 wt.%) was the dominant component, followed by cellulose (14.1 wt.%) and small amounts of lignin (7.4 wt.%).

### 2.7 BIOMASS AND COAL CO-FIRING

Biomass and coal co-firing (or co-combustion) is a new developing technology which has a potential to mitigate GHG emissions. Co-firing is the cheapest emission control technology and can be easily implemented as it uses the existing combustors/boilers (Federal Energy Management Program, 2004). In this technology, biomass or waste can partially substitute coal (which is a main fuel) used in a utility boiler. Although high blending ratios of biomass to coal would result to high emission reduction, low blending ratios (20% maximum) are recommended to avoid the technical challenges emanating from firing biomass alone (Annamalai et al., 2003; Pokothoane, 2010; Munir et al., 2011). Co-firing refers to the combustion of two or more materials. Biomass co-firing technologies have been divided into three classes: direct co-firing, indirect co-firing and
parallel/gasification co-firing (Tillman, 2000; Sami et al., 2001; Demirbas, 2003; Basu et al., 2011; Fernando, 2012).

Direct co-firing involves the direct injection/feeding of biomass into an existing utility boiler. In this technique, coal and biomass can be premixed prior to injection into a boiler and be injected as a single fuel in one pipeline, or fuels can be injected into an existing single boiler using separate pipeline as shown in Figure 2.6 (Demirbas, 2003; Basu et al., 2011). This option is suitable for low biomass blending ratios of up to 20% (Tillman, 2000; Fernando, 2012).

![Diagram of direct co-firing](image)

**Figure 2.6: Direct co-firing.**

Advantages of direct co-firing option include least expensive approach, simplest and as a result most widely used (Tillman, 2000; Fernando, 2012; IEA-ETSAP and IRENA, 2013). Additionally, Sami et al. (2001) reported that this option provides proper mixing, high combustion efficiency and low emissions. However, direct co-firing has the highest risk of interfering with the coal firing ability of the boiler due to different characteristics.
of coal and biomass (Basu et al., 2011). Furthermore, this option has a higher risk of causing slagging and fouling in the boiler unit due to alkali species in the biomass. High volatiles in the biomass may also increase the combustion temperature and damage the boiler unit.

Indirect co-firing (also known as gasification co-firing) involves the gasification of biomass in an external gasifier. The syngas produced from the gasification of biomass is then used as a co-firing fuel in a coal firing boiler as shown in Figure 2.7 (Sami et al., 2001; Demirbas, 2003; Fernando, 2012). The separate gasification of coal and biomass offers the best flow rate control of a fuel (Sami et al., 2001). In this option, the risk of coal ash contamination by alkali metals in biomass is avoided and therefore has no risk of slagging or fouling in the main plant (Fernando, 2012). These advantages make this option suitable for high co-firing ratios and allow a range of different biomass types to be used (Fernando, 2012; IEA-ETSAP and IRENA, 2013).

![Diagram of indirect co-firing](image)

**Figure 2.7: In-direct co-firing.**

This technology is less common compared to direct co-firing due to additional equipment required, leading to high capital and maintenance cost (Sami et al., 2001; Basu et al.,
Additionally, independent burning of biomass has a high risk of poor combustion efficiency due to its low calorific value. This however depends on the type of biomass co-fired.

Parallel co-firing involves two separate boilers and biomass is combusted independently as depicted in Figure 2.8. The steam generated from combustion of biomass is routed to the steam cycle of a coal-fired plant turbine (Demirbas, 2003; Basu et al., 2011; Fernando, 2012; IEA-ETSAP and IRENA, 2013). Similar to indirect co-firing, the independent firing of fuels avoids any challenges related to biomass combustion. Despite the high cost, the indirect co-firing and gasification co-firing options offer the highest reliability due to factors such as easy removal of ash, flexibility in the choice of biomass and zero risk of fouling or corrosion in a coal-fired plant (Sami et al., 2001; Basu et al., 2011).

**Figure 2.8: Parallel co-firing.**

All the above-mentioned co-firing options have their advantages and disadvantages. The selection criteria of these options are defined by fuel type, cost, co-firing ratios, technical issues and site factors. The direct co-firing seems to be much more suitable for cooking
and heating, while indirect and parallel co-firing are most suitable for industrial power generation.

2.7.1 Effect of biomass co-firing on emissions

The effect of biomass and coal on emissions have been previously studied and most researchers reported reductions in emissions of CO$_2$, SO$_2$ and NOx (Robinson et al., 1998; Tillman, 2000; Annamalai et al., 2003; Demirbas, 2003; Pokothoane, 2010; Wang et al., 2011; Sebastian et al., 2011; Holtmeyer et al., 2012). This section focuses on the effect of biomass co-firing on individual pollutants, particularly CO$_2$, SO$_2$ and NOx.

2.7.1.1 Effect of biomass co-firing on carbon dioxide (CO$_2$)

Biomass is considered a carbon neutral fuel in that the CO$_2$ it produces when combusted is part of the active carbon cycle, unlike the fossil CO$_2$ which when released in the atmosphere is additive to the total GHG (Gayan et al., 2004; Federal Energy Management Program, 2004). The CO$_2$ produced from coal and biomass co-firing may be higher in the stack than that obtained with coal combusted alone as the boiler is de-rated during co-firing (Fernando, 2012). Nonetheless, this is not a problem if biomass is grown sustainably, since 10% coal replacement by biomass results in approximately 10% net CO$_2$ reductions (Federal Energy Management Program, 2004). Furthermore, the decrease or increase in CO$_2$ emissions depends on the type and proportion of biomass that is co-fired with coal. An increase in CO$_2$ emissions is rare and few studies have reported this (Kazagic et al., 2009; Kucukvar and Tatari, 2011). Most studies have demonstrated relative reductions in CO$_2$ when co-firing coal and various biomass types at lower co-firing ratios (<50%) (Tillman, 2000; Sami et al., 2001; Ross et al., 2002; Demirbas, 2003; Pokothoane, 2010; Wang et al., 2011; Bragato et al., 2012).
2.7.1.2 Effect of co-firing on sulphur dioxide (SO$_2$)

The reduction of SO$_2$ when co-firing coal and biomass is explained by difference in sulphur content, as most biomasses usually contain lower sulphur content compared to coal (Fernando, 2012). Further reductions can be expected as sulphur is retained in ash due to alkali/alkaline earth compounds in most biomasses (Fernando, 2012). Such reductions are however significantly influenced by the biomass type, plant technology and operation conditions (IEA-ETSAP and IRENA, 2013). The effect of co-firing coal and biomass on SO$_2$ emissions have been studied by many researchers (Robinson et al., 1998; Tillman, 2000; Sami et al., 2001; Ross et al., 2002; Demirbas, 2003; Pokothoane 2010; Kucukvar and Tatari, 2011; Munir et al., 2011; Holtmeyer et al., 2012; Yang et al., 2015). They reported SO$_2$ reductions to be a result of lower sulphur content in biomass compared to coal.

2.7.1.3 Effect of co-firing on oxides of nitrogen (NOx)

Several studies have been previously carried out to investigate the effect of co-firing coal and biomass on NOx emissions (Ross et al., 2002; Annamalai et al., 2003; Munir et al., 2011; Wang et al., 2011; Sebastian et al., 2011; Yang et al., 2015). The prediction of NOx emissions is difficult with biomass compared to coal; it may increase, decrease or remain the same depending on the type of biomass co-fired, firing conditions and operation conditions (Fernando, 2012).

Annamalai et al. (2003) reported a 10% NOx reduction with 90:10 blending ratio of coal to cattle manure. Ross et al., (2002) conducted research on the prediction and measurements of the emission pollutants from the combustion of coal and biomass. They reported significant reductions in NO$_2$ emissions (reduced by 59% and 68%, respectively) when co-firing briquettes of coal and pine sawdust at a blending ratio of 63:33 by weight. Munir et al. (2011) reported 21% overall reduction in NO emissions when they co-fired...
coal with five different biomasses at ratios of 95:5, 90:10 and 85:15. Yang et al. (2015) also reported a reduction in NO from co-firing of coal and sewage sludge at 800°C.

Microalgae are amongst biomasses which can be used as an energy source and has received much attention due to numerous benefits (laid out in section 2.8) over other plants.

2.8 BENEFITS OF MICROALGAE BIOMASS

Microalgae are amongst the solid fuels which are promoted for energy generation in the specifications of ISO 17225 norm (2014). Microalgae are a group of single-celled microorganisms that store energy in the form of oil and carbohydrates (Hannon et al., 2010). Additionally, microalgae convert sunlight, CO₂ and other nutrients into long carbon chains that can be converted to energy. Microalgae are promising long-term and sustainable source of biomass fuels due to the following reasons:

- Fast growth rate – microalgae can double their number every few hours and may be harvested every day the sun shines compared to land crops such as food grains which require a full season to produce a single crop (Huesemann et al., 2009).
- Ability to consume CO₂ for their growth which can be supplied by power-plant emissions. Microalgae are responsible for more than 40% of global carbon fixation with the majority from marine species (Hannon et al., 2010).
- Ability to be grown both on land that is unsuitable for traditional agriculture and with water that is unusable for other crops, such as sea-, brackish- and wastewater (Hannon et al., 2010).

A study of the various mass yields of several microalgae strains confirmed variable biomass yields with *Scenedesmus* having 2.73 g/L (Chan et al., 2010). *Scenedesmus* strain has also been identified as a promising microalgae strain due to its high efficiency for CO₂ capture amongst green microalgae (Chan et al., 2010). As shown in Table 2.5,
Scenedesmus microalgae has low ash, high volatile matter and high calorific value (Baloyi and Dugmore, 2019) compared to most microalgae strains studied (Kucukvar and Tatari 2011; Agrawal and Chakraborty, 2013; Tahmasebi et al., 2013; Sanchez-Silva, 2013; Gai et al., 2015).

Table 2.5: Properties of various microalgae strains.

<table>
<thead>
<tr>
<th>Strains</th>
<th>Proximate analysis (wt.%)</th>
<th>Ultimate analysis (wt.%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM</td>
<td>FC</td>
<td>A</td>
</tr>
<tr>
<td>Scenedesmus</td>
<td>77.5</td>
<td>15.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Tetraselmis suecica</td>
<td>58.3</td>
<td>15.8</td>
<td>21.7</td>
</tr>
<tr>
<td>Nannochloropsis gaditana</td>
<td>75.9</td>
<td>8.3</td>
<td>10.7</td>
</tr>
<tr>
<td>Chlorella vulgaris</td>
<td>37.3</td>
<td>5.0</td>
<td>48.6</td>
</tr>
<tr>
<td>Chlorella pyrenoidosa</td>
<td>94.4</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>Spirulina platensis</td>
<td>90.3</td>
<td>-</td>
<td>9.7</td>
</tr>
</tbody>
</table>

2.9 LITERATURE ON COAL AND MICROALGAE CO-FIRING

Microalgae biomass is also considered for co-firing in coal fired power plants as it presents reductions in GHG emissions. There are two ways that microalgae can reduce GHG and these are (1) co-firing microalgae with coal and (2) application of microalgae cultivation systems in coal fired power plants has the potential to reduce CO$_2$ by recycling and using CO$_2$ for microalgae growth (Brune et al., 2009; Kirtania et al., 2011; Ghayal and Pandya, 2013). The application of the two microalgae options could significantly reduce GHG. Microalgae biomass co-firing is one of the clean coal technologies and is considered a potential technology due to advantages such as high growth rate, less competition with food stocks and high carbon content which can be approximately 50
wt.% (Demirbas and Demirbas, 2010; Kucukvar and Tatari, 2011). However, the carbon content varies with different species of microalgae.

Kucukvar and Tatari (2011) blended dry algae biomass with coal at ratio from 0% to 100% and assessed the life cycle emission of CO₂, CO, NOx, SOx, PM and volatile organic carbon (VOC) in a coal power plant. They found that CO, CO₂, NOx and VOC emissions increased with increasing algae co-firing rate while SOx decreased with increasing algae co-firing rate and PM was not affected by the increase of co-firing rate, it remained constant. Similarly, Kadam (2002) reported insignificant increase in CO emissions and 39% reduction in each emission of SOx, NOx and particulate emissions and 30 – 40% reduction in CO₂, N₂O and CH₄. From these reports, it can be concluded that co-firing of coal with microalgae at lower blending ratios reduces the GHG emissions. Furthermore, the increase in CO₂ and NOx reported by Kucukvar and Tatari (2011) can be associated with higher blending ratio of algae up to 100% as high biomass amount is required to make up the high blending ratios. The higher the blending ratio is, the higher the volatility of the fuel which may result in higher temperatures causing thermal NOx formation (Kucukvar and Tatari, 2011).
Chapter 3

3 EXPERIMENTAL

The materials which were used in this study and how they were prepared are described in this chapter. The detailed experimental methods and analytical techniques used are also provided in this chapter.

3.1 MATERIALS

The coal (lumpy) used in this study was supplied by a local coal merchant in Port Elizabeth, South Africa. The coal used was characterized by low ash yield and was ranked/ categorized as bituminous coal. The *Scenedesmus* dominated culture of microalgae was supplied by InnoVenton – Institute for Chemical Technology at the Nelson Mandela University. *Scenedesmus* microalgae were cultivated in the integrated vertical column photo-bioreactors – raceway cultivation system developed at InnoVenton (Figure 3.1).

![Microalgae cultivation system at InnoVenton.](image)

Figure 3.1: Microalgae cultivation system at InnoVenton.
Different mass ratios of South African coal fines and *Scenedesmus* microalgae slurry were mixed to prepare Coalgae® blends of 5 – 20% by mass, as shown in Table 3.1. Coalgae® is a newly formed composite material after mixing coal fines with microalgae slurry. *Scenedesmus* microalgae were harvested from the cultivation system when the solids of microalgae were between 2 – 5 g/l.

**Table 3.1: Fuel materials analysed.**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Coal to microalgae ratio (mass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>100:0</td>
</tr>
<tr>
<td>Coalgae®</td>
<td>95:5</td>
</tr>
<tr>
<td>Coalgae®</td>
<td>90:10</td>
</tr>
<tr>
<td>Coalgae®</td>
<td>85:15</td>
</tr>
<tr>
<td>Coalgae®</td>
<td>80:20</td>
</tr>
<tr>
<td>Microalgae</td>
<td>0:100</td>
</tr>
</tbody>
</table>

**3.2 SAMPLE PREPARATION**

**3.2.1 Coal preparation**

Coal lumps were pulverized to a particle size of < 250 µm. A small portion of the coal fines was stored in an air-tight container to avoid absorption of moisture, for subsequent characterization. Another fraction of coal fines was used to prepare coal lumps and Coalgae® blends. Coal lumps were prepared by mixing coal fines with de-ionised water – forming lumps while air drying the coal slurry. Coal lumps with moisture content of ±5 wt% were used for combustion tests. Figure 3.2 illustrate the different steps involved in the preparation of coal fines and coal lumps.
Greenhouse gas emissions reduction through the co-firing of coal and microalgae biomass: An experimental evaluation
Magida N.E. – PhD Thesis

Figure 3.2: Sample preparation of coal.
3.2.2 Coalgae® preparation

Prior to mixing coal fines and microalgae slurry, the moisture content of the two materials was measured as described in section 3.3.1.1. The moisture content of microalgae was used to calculate the microalgae solids from the slurry using Equation 3.1.

\[
\text{Microalgae solids (\%) = 100 \text{ } \% M}
\]  

(3.1)

Where, M is the total moisture content of microalgae (in \% by weight).

Microalgae slurry of a known concentration or moisture content was used. The correct amount of microalgae slurry required to achieve the desired Coalgae® mass ratios was accurately determined as stipulated in Equation 3.2.

\[
\text{Microalgae slurry required (g) = mass of dry microalgae (g) / \% microalgae solids /100}
\]  

(3.2)

After establishing the required amounts of microalgae slurry to coal, the two materials were mixed under constant stirring at room temperature to form the desired Coalgae® blends as shown in Figure 3.3.
The coal-microalgae mixtures were centrifuged at 4500 rpm for 10 minutes using a HERMLE Z 383 (Lasec SA) centrifuge (Figure 3.4). The supernatant was decanted, and
the solids were washed with de-ionised water to remove any residual nutrients from the growth medium.

Figure 3. 4: HERMLE Z 383 (Lasec SA) centrifuge.

On completion, the Coalgae® mixtures were air-dried and allowed to form lumps – to make them suitable for loading onto a grate in a fixed-bed reactor. The entire process took approximately 2 – 3 days, depending on the amount of sample and weather conditions. The resultant lumpy Coalgae® samples were used for the combustion tests in a fixed-bed reactor. For analytical purposes, the lumpy Coalgae® samples were ground using a hand mortar and sieved to < 150 µm prior to analysis.

3.2.3 Scenedesmus microalgae preparation

*Scenedesmus* microalgae with solids between 2 – 5 g/l were harvested by naturally concentrating microalgae in the growth medium and letting it settle overnight in a settling pond. The top layer of the growth medium was then returned to the cultivation system.
3.3 CHARACTERIZATION

The characterization of coal, *Scenedesmus* microalgae and Coalgae® blends were performed to determine their characteristics prior to performing any tests. Such characterization provides a theoretical insight to the behaviour of the fuel during combustion or any other related processes. The characterization tests employed in this study are categorised into ultimate and proximate analysis. For reproducibility, the analyses were repeated three times and the average values were reported.

3.3.1 Proximate analysis

Proximate analysis is the determination of moisture, volatile matter, fixed carbon contents and ash yield of a solid fuel material. The moisture, volatile matter, fixed carbon contents and ash yield were determined using the international standard methods ASTM E871, D3175, E870 and E1755, respectively.

3.3.1.1 Moisture content

The moisture contents of coal, *Scenedesmus* microalgae and Coalgae® blends were determined in accordance with the ASTM E871, by heating empty glass crucibles (with lids opened) in an oven (shown in Figure 3.5) for 30 minutes at 105°C ± 20°C, then cooled in a desiccator for 15 minutes and weighed. This was done to determine the mass of the glass crucibles before determining the moisture content of the fuel. One gram (1 g) of the fuel was weighed into a crucible and heated in an oven for 1 hour at 105°C ± 20°C with the lid opened. This was followed by cooling in a desiccator for 15 minutes before weighing. Equation 3.3 was used to calculate the moisture content of the material.
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\[ M \text{ (%) } = \left( \frac{\text{CB} - \text{CA}}{\text{CB}} \right) \times 100 \]  

(3.3)

Where;
M = the total fuel moisture content (in % by weight)
CB = the pre-oven fuel sample (g)
CA = the post-oven fuel sample (g)

Figure 3.5: Oven used for moisture content determination.

3.3.1.2 Volatile matter content

The volatile matter contents of coal, *Scenedesmus* microalgae and Coalgae® blends were determined in accordance with the ASTM D3175, by heating empty ceramic crucibles (with lids on) in a muffle furnace (picture shown in Figure 3.6) pre-set at 950°C ± 20°C for 7 minutes. The crucibles were removed from the furnace and placed on a metal block to dissipate heat for 2 minutes, followed by cooling in a desiccator for approximately 15
minutes before weighing. Approximately one gram (1 g) of the fuel was accurately weighed into a crucible and heated in a muffle furnace for 7 minutes at 950°C ± 20°C under N₂ atmosphere with the lid closed. On completion, the sample was allowed to cool to room temperature in a desiccator before weighing. The volatile matter content (weight percentage) was calculated using Equation 3.4.

\[
\text{Volatile matter content (\%) = \% loss of weight - \% of total moisture content (3.4)}
\]

![Muffle furnace used to determine volatiles and ash.](image)

**Figure 3.6: Muffle furnace used to determine volatiles and ash.**

### 3.3.1.3 Fixed carbon content

Fixed carbon is the material which remains after determining moisture, volatile matter and ash, and was determined in accordance with the ASTM E870. The fixed carbon contents of coal, *Scenedesmus* microalgae and Coalgae® blends were calculated using Equation 3.5.
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\[ FC (\%) = 100 - M - VM - A \]  (3.5)

Where;

FC = the fixed carbon content (in weight percentage)
M = the total moisture content (in weight percentage)
VM = the volatile matter content (in weight percentage)
A = the ash yield (in weight percentage)

3.3.1.4 Ash yield

The ash yields of coal, *Scenedesmus* microalgae and Coalgae® blends were determined in accordance with the ASTM E1755, by heating empty ceramic crucibles in a muffle furnace pre-set at 750°C ± 20°C for 2 hours. The crucibles were removed from a furnace and placed on a metal block to dissipate heat for 2 minutes, followed by cooling in a desiccator for approximately 15 minutes before weighing. Approximately one gram (1 g) of the fuel was accurately weighed into a crucible and heated in a muffle furnace for 2 hours at 750°C ± 20°C under air. The sample was then cooled in a desiccator and weighed. The ash yield (in weight percentage) was calculated using Equation 3.6.

\[ \text{Ash yield (\%) = } \left[ \frac{A - B}{C} \right] \times 100 \]  (3.6)

Where;

A = the weight of a crucible and ash residue (g)
B = the weight of an empty crucible (g)
C = the weight of a sample (g)
3.3.2 Ultimate analysis

Ultimate analysis is the determination of the elemental composition of a fuel which is usually reported in moisture and ash free basis. The elemental compositions of coal, *Scenedesmus* microalgae and Coalgae® blends were determined according to the ASTM D3176 standard test method. The elemental analyser (ElementarVario EL cube), shown in Figure 3.7, was used to determine the weight percentages of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S). Oxygen (O) was calculated by difference from ash free % values.

![ElementarVario EL Cube](image)

**Figure 3.7: ElementarVario EL Cube.**

Fuel samples of approximately 5 mg were weighed on a micro balance and encapsulated in tin boats and tin capsules respectively together with tungsten trioxide. The fuel samples were then loaded into a carousel and combusted in an oxygenated atmosphere at 1150°C for 90 seconds. The NOx formed was reduced to N₂ in a combustion tube packed with copper. The eluted H₂O, CO₂ and SO₂ were trapped by three selective absorption columns while the N₂ was passed directly to the thermal conductivity detector. Helium was used as a flushing and carrier gas. The trapped components were then sequentially thermally desorbed and passed to the detector by helium. The concentrations of C, H, N and S were
then calculated from the detector response signal and sample weight. The element concentrations were converted to weight percentages (wt.%). The method parameters in which the elemental analysis was performed are depicted in Table 3.2.

Table 3.2: Method parameters for elemental analysis.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion tube</td>
<td>1150</td>
</tr>
<tr>
<td>Reduction tube</td>
<td>850</td>
</tr>
<tr>
<td>CO₂ col. standby</td>
<td>25</td>
</tr>
<tr>
<td>H₂O col. standby</td>
<td>25</td>
</tr>
<tr>
<td>SO₂ col. standby</td>
<td>140</td>
</tr>
<tr>
<td>Cooling temperature</td>
<td>170</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flush time</td>
<td>10</td>
</tr>
<tr>
<td>O₂ delay</td>
<td>30</td>
</tr>
<tr>
<td>Integrator reset delay peak N</td>
<td>20</td>
</tr>
<tr>
<td>Integrator reset delay peak C</td>
<td>10</td>
</tr>
<tr>
<td>Integrator reset delay peak H</td>
<td>3</td>
</tr>
<tr>
<td>Integrator reset delay peak S</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ball valve</th>
<th>(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. Permitted ball valve current</td>
<td>20</td>
</tr>
<tr>
<td>Max. Permitted ball valve current</td>
<td>100</td>
</tr>
<tr>
<td>Critical ball valve current</td>
<td>250</td>
</tr>
<tr>
<td>Acoustic signal</td>
<td>no</td>
</tr>
</tbody>
</table>
3.3.3 Calorific value

Calorific values of coal and Coalgae® blends represent the combined heats released by the combustion of carbon, hydrogen, nitrogen and sulphur. A bomb calorimeter (Leco AC 600), shown in Figure 3.8, was used to determine calorific value of a fuel. Approximately gram (1 g) of a fuel was accurately weighed and burned in a bomb calorimeter under oxygen at standard conditions. The gross calorific value, often referred to as high heating value (HHV), was computed from temperature observations made before, during and after combustion and were reported in MJ/kg.

![Bomb calorimeter Leco AC 600](image)

**Figure 3.8: Bomb calorimeter Leco AC 600.**

3.3.4 Thermogravimetric-Mass spectrometer analysis (TG-MS)

Thermogravimetric analysis (TGA) is one of the commonly used techniques to study the thermal behaviour of a fuel (Vuthaluru, 2003; Marinov *et al.*, 2009; Gil *et al.*, 2010). TGA provides mass loss of a sample as a function of temperature and time and a derivative...
(DTG) can be calculated from mass loss readings (Chen et al., 2009; Gil et al., 2010; Moon et al., 2013). Thermogravimetric-mass spectrometer (TG-MS) analyses of coal, *Scenedesmus* microalgae and their blends (Coalgae® 5% - Coalgae® 20%) were performed through a TA Instruments TGA Discovery 5500 series attached to a TA-Instruments Discovery mass spectrometer, which is a bench top quadruple mass spectrometer (shown in Figure 3.9). Samples were combusted at a heating rate of 10°C/min under a constant gas stream of air. Each sample was heated from ambient temperature up to 650°C at a flow rate of 50 mL/min and a pressure of 120 kPa. The samples were contained in platinum pans and a sample mass of 5 mg (±0.2 mg) was used for all combustion runs. The synergistic effect was deduced from the comparison of mass loss versus temperature of coal, *Scenedesmus* microalgae and Coalgae® blends.

Figure 3.9: TA Instruments Discovery 5500 thermogravimetric analyser (TGA).

The evolved gas in the combustion process was swept into the MS instrument and tested online over the entire temperature range. To avoid condensation during transportation, the TGA furnace chamber outlet was connected to the MS instrument inlet through a heated quartz capillary at 300°C. The Discovery MS (TA instruments) mass spectrometer
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(mass range 1 to 200 amu) was operated with an electron-impact ion source at 70 eV electron energy. The MS was operated in a peak jump mode by scanning and identifying ions of mass to charge ratios (m/z) in the range 1–200 a.m.u. The masses 44 and 64, which correspond with CO₂ and SO₂, respectively. The intensities of the selected ions should be normalised to the sample mass to compare the test results obtained for different samples at different conditions (Yurum et al., 1985; Raemaekers and Bart, 1997; Reyes et al., 2001).

The derivative of the weight loss curve allows the determination of maximum peak temperature, combustion rates and activation energies (Eₐ) for the thermal decomposition. The distributed activation energy model that assumes that several parallel and irreversible first order reactions occur simultaneously was employed for the determination of activation energies of combustion processes (Wang et al., 2017; Vand 1943; Pitt 1962; Anthony et al., 1972; Miura, 1995; Bhavanam and Sastry, 2015). Hence, Coats–Redfern method Equation 3.8 was employed by plotting ln \left( \frac{-\ln(1-x)}{T^2} \right) versus 1/T to give a straight line of slope = -Eₐ/R (Quanrun et al., 2004; Coats and Redfern, 1964).

\[
\ln \left( \frac{-\ln(1-x)}{T^2} \right) = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E_a}{RT} \quad (3.7)
\]

where, \( x = \frac{m_t - m_i}{m_i - m_f} \)
\( m_t = \) mass at given moment of time during combustion
\( m_i = \) initial mass of sample
\( m_f = \) mass after combustion
\( T = \) temperature
\( E_a = \) Activation energy
3.3.5 Fourier-transform infrared (FT-IR)

Perkin Elmer 2000 FT-IR spectrometer (Figure 3.10) was used to investigate the functional groups of coal, microalgae and their blends. Each material was placed on the sample holder of a Perkin Elmer 100 ATR-IR. The samples were scanned from 400 to 4000 cm\(^{-1}\). All spectra were referenced against the background spectrum (the ATR with no sample). IR resolution software was used to analyse the spectra generated.

![Perkin Elmer 2000 FT-IR spectrometer](image)

**Figure 3. 10: Perkin Elmer 2000 FT-IR spectrometer.**

3.3.6 Scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS)

Samples of coal, Coalgae® blends and their ashes were prepared for scanning electron microscopy (SEM) by coating them in gold using a Balzers’ Sputtering device. The samples were viewed using a TESCAN Vega TS 5136LM typically operated at 20 kV at a working distance of 20 mm. Elemental analysis of samples using energy dispersive spectroscopy (EDS) was determined by using the same procedure as described for SEM.
analysis, except that no sample surface coating was needed. The samples of coal, Coalgae® and their ashes were imaged using a TESCAN Vega TS 5136LM scanning electron microscope (SEM). Before images were taken; samples were coated to prevent surface charging and to protect the surface material from thermal damage by the electron beam. For EDS analysis, no coating was required. EDX was used to qualitatively determine the elemental compositions. Coal ash contains typically Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr, which are reported as oxides by default (Fe₂O₃, Al₂O₃, MgO, MnO, V₂O₅, TiO₂, SiO₂, CaO, Na₂O, K₂O, P₂O₅, SO₃ and Cr₂O₃).

3.4 COMBUSTION TESTS USING A FIXED-BED REACTOR

3.4.1 Combustion procedure

A vertical down firing fixed-bed combustion reactor, as shown in Figure 3.11, was used to carry out the combustion experiments.

Figure 3. 11: Combustion setup using a fixed-bed reactor.
A 33 cm long fixed-bed reactor with an inner diameter of 4.1 cm and outer diameter of 4.9 cm was used to carry out the combustion experiments. The reactor was fitted with an air supply line situated below the grate. The flow of air into the reactor was regulated through a flow meter. Above the grate is the ignition inlet operated manually to ignite the fuel, suspended onto the grate, inside the reactor. During combustion, the flue gas was directed towards the chimney on top of the reactor. Also, at the top of the reactor there is a gas flow outlet from which flue gas was analysed using Lancom 4 portable flue gas analyser, and there is a hole where a thermocouple was inserted to take temperature readings throughout the combustion test.

To carry out the combustion experiments, 200 g of the fuel was loaded onto the grate in the reactor chamber as shown in Figure 3.12.

**Figure 3.12:** Schematic representation of a fixed-bed combustion reactor.
After loading the substrate, air was pumped into the reactor at a controlled flow rate. This was followed by manual ignition of the substrate which took approximate 3 to 6 minutes. During combustion experiment, the temperature inside the reactor (around the chimney) was measured, followed by measuring of the gases, CO₂ (%), O₂ (%), NOx (ppm) and SO₂ (ppm), as well as measuring the mass reduction (g). Gas emissions were measured at the flue gas outlet every minute using the Lancom 4 portable flue gas analyser shown in Figure 3.13. The same procedure was used for the co-firing tests of Coalgae® blends with minor adjustment to the mass loading. Each test was repeated three times to ensure reproducibility of the results.
The Lancom 4 portable flue gas analyser can measure up to eight flue gases in a range of combustion and emissions process. The technical specification of the gas analyser including only the gases measured in this study is presented in Table 3.3. The Lancom 4 gas analyser uses the infrared sensor to directly measure the CO₂ in flue gas. This CO₂ sensor combined with the measurement capability offered by the flow probe gives quantitative information on greenhouse gas emissions. The gas analyser draws the sample gas through a sample probe and hose connect it to the input connection on the side panel. The sample gas enters the water catchpot where residual water is removed, and then passes through a 0.1 micron particulate filter. Gas concentration readings are then recorded every minute. The gas analyser automatically performs a zero calibration every time it is switched on, and always purges the sensors with ambient air before switching off. This ensures maximum accuracy and sensor longevity. The Lancom 4 portable flue gas analyser was sent to experts for full calibration and maintenance every 6 months.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Min. range</th>
<th>Max. range</th>
<th>Accuracy % of range</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ % v/v</td>
<td>0 – 25</td>
<td>0 – 30</td>
<td>± 1</td>
</tr>
<tr>
<td>SO₂ ppm</td>
<td>0 – 100</td>
<td>0 – 4000</td>
<td>± 2</td>
</tr>
<tr>
<td>NO ppm</td>
<td>0 – 100</td>
<td>0 – 5000</td>
<td>± 2</td>
</tr>
<tr>
<td>NO₂ ppm</td>
<td>0 – 100</td>
<td>0 – 1000</td>
<td>± 2</td>
</tr>
<tr>
<td>CO₂ % v/v</td>
<td>0 – 25</td>
<td></td>
<td>± 2</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>Max. 600°C with standard probe and Max. 1400°C with high-temperature probe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient Temperature</td>
<td>-5°C</td>
<td>45°C</td>
<td></td>
</tr>
</tbody>
</table>
3.4.2 Ash analysis

Ash is an incombustible material which remains after a combustion test. SEM and EDX analysis were carried out as described in section 3.3.6 to characterize the morphology of ash and to detect metals that are contained in ash. Ash analysis was also carried out to determine the elemental composition using an XRF spectrometer (ARL9800XP SIM-SEQ) (shown in Figure 3.14).

![X-ray fluorescence (XRF) spectrometer (ARL9800XP SIM-SEQ).](image)

**Figure 3. 14: X-ray fluorescence (XRF) spectrometer (ARL9800XP SIM-SEQ).**

XRF analysis is a simple, non-destructive method which can quantitatively measure minor and trace elements in ash. The elements were determined by fusing the ash sample with lithium tetraborate and pressed into a glass disk. For quantification, the intensity of characteristic lines of the element to be analysed was measured. Coal ash contains typically Fe, Al, Mg, Mn, V, Ti, Si, Ca, Na, K, P, S and Cr, which are reported as oxides by default (Fe$_2$O$_3$, Al$_2$O$_3$, MgO, MnO, V$_2$O$_3$, TiO$_2$, SiO$_2$, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$, SO$_3$ and Cr$_2$O$_3$).
3.4.3 Calculations for required combustion air

Combustion is a chemical reaction of a fuel and oxidant. The amount of combustion air required to react with coal can be estimated by first determining the chemical equations expected. The reaction of nitrogen with oxygen is also taken into consideration in this study. Combustion equations used to calculate the stoichiometric mass of oxygen required to burn coal (CHNS) are shown in the following Equations:

Basis: 1 kg coal

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]  \hspace{1cm} (3.8)

\[ \rightarrow 12 \text{ kg C reacts with 32 kg O}_2 \text{ to form 44 kg CO}_2 \]

\[ \rightarrow 1 \text{ kg C reacts with 2.67 kg O}_2 \text{ to form 3.67 kg CO}_2 \]

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (3.9)

\[ \rightarrow 2 \text{ kg H}_2 \text{ reacts with 16 kg O}_2 \text{ to form 18 kg H}_2\text{O} \]

\[ \rightarrow 1 \text{ kg H}_2 \text{ reacts with 8 kg O}_2 \text{ to form 9 kg H}_2\text{O} \]

\[ \text{S} + \text{O}_2 \rightarrow \text{SO}_2 \]  \hspace{1cm} (3.10)

\[ \rightarrow 32 \text{ kg S reacts with 32 kg O}_2 \text{ to form 64 kg SO}_2 \]

\[ \rightarrow 1 \text{ kg S reacts with 1 kg O}_2 \text{ to form 2 kg SO}_2 \]
N + O₂ → NO₂  
(3.11)

\[ \text{14 kg N reacts with 32 kg O}_2 \text{ to form 46 kg NO}_2 \]

\[ \text{1 kg N reacts with 2.29 kg O}_2 \text{ to form 3.29 kg NO}_2 \]

Molecular mass of O₂ is 16 kg/mol, C is 12 kg/mol, CO₂ is 44 kg/mol, H₂ is 2 kg/mol, H₂O is 18 kg/mol, S is 32 kg/mol, SO₂ is 64 kg/mol, N is 14 kg/mol and NO₂ is 46 kg/mol.

### 3.4.3.1 Stoichiometric oxygen required

The stoichiometric amount of oxygen required to burn 1 kg of coal was calculated using proximate and ultimate analyses data presented in Chapter 4. It is necessary to calculate the amount of oxygen required to burn a fuel as this will prevent either too little or too much air and ultimately prevent poor combustion or loss of energy. Calculations of the stoichiometric oxygen required to burn coal are laid out in a tabular basis for better presentation (Table 3.4).

**Table 3.4: Stoichiometric oxygen required to burn 1 kg of coal.**

<table>
<thead>
<tr>
<th>Coal components (ad)</th>
<th>Mass (kg/kg)</th>
<th>O₂ required (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.6536</td>
<td>2.67 x 0.6536 = 1.745</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0504</td>
<td>8 x 0.0504 = 0.403</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0197</td>
<td>2.29 x 0.0197 = 0.045</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0049</td>
<td>1 x 0.0049 = 0.0049</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1213</td>
<td>-0.1213</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1501</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>1.000</td>
<td>2.198</td>
</tr>
</tbody>
</table>

The stoichiometric amount of oxygen required by each component of coal was determined independently and summed to obtain a total of 2.198 kg oxygen required to
burn 1 kg of coal. The stoichiometric amount of air (air to fuel ratio) required to burn 1 kg of coal was calculated by dividing oxygen amount required by mass fraction of oxygen in air:

$$\frac{A}{F} = \frac{2.198}{0.233} = 9.433 \text{ kg air/kg coal}$$

(Note: air consists of 21% O$_2$ and 79% N$_2$)

Mass fraction of oxygen in air was calculated as follows (Table 3.5):

<table>
<thead>
<tr>
<th>Components</th>
<th>Vol. fraction (Vf)</th>
<th>Vf * MW</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.21</td>
<td>6.72</td>
<td>6.72 / 28.84 = 0.233</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.79</td>
<td>22.12</td>
<td>22.12 / 28.84 = 0.767</td>
</tr>
<tr>
<td>Total</td>
<td>0.1</td>
<td>28.84</td>
<td>0.1</td>
</tr>
</tbody>
</table>

3.4.3.2 Excess air

When coal only reacts with theoretical air, this result in incomplete combustion, releasing toxic CO gas, soot and causes reduction in fuel efficiency. Complete combustion can be achieved by supplying extra air, known as “Excess Air”, which is the percentage of air in addition to the theoretical air required for complete combustion. In this study, excess air was calculated using Equation 3.12.

$$\% \text{ Excess air} = \frac{\% O_2 \text{ measured}}{20.9 - \% O_2 \text{ measured}} \times 100$$  \hspace{1cm} (3.12)

The oxygen (%$O_2$ measured) used in Equation 3.12 was measured using the Lancom 4 portable flue gas analyser during trial combustion runs (described in section 3.4.1). The actual A/F ratio of coal combustion at 30% excess air became:
Actual A/F = 9.433 × 1.3 = 12.263 kg air/kg coal

3.4.3.3 Air flow rate

The air flow rate (AFR) required to burn 200 g (0.2 kg) of coal in 180 min was calculated and expressed in l/min. Density of air was assumed to be 1.2 kg/m³.

\[
AFR = 12.263 \times \frac{0.2}{1.2 \times 180} = 0.0114 \frac{m^3}{min} = 11.4 \frac{l}{min}
\]

The air requirement calculations were also performed for Coalgae® blends 5%, 10%, 15% and 20%, following the same calculations and using their proximate and ultimate values in Chapter 4. Mass loading of 200 g was used for Coalgae® blends in calculating AFR. These calculations are presented in Appendix A. Air requirement values calculated for Coalgae® blends are depicted in Table 3.5.

**Table 3.6: Air requirement values of Coalgae® blends at 30% excess air.**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Air required (kg/kg)</th>
<th>A/F ratio (kg/kg)</th>
<th>Actual A/F ratio (kg/kg)</th>
<th>AFR (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coalgae® 5%</td>
<td>2.166</td>
<td>9.296</td>
<td>12.085</td>
<td>11.2</td>
</tr>
<tr>
<td>Coalgae® 10%</td>
<td>2.126</td>
<td>9.124</td>
<td>11.861</td>
<td>10.9</td>
</tr>
<tr>
<td>Coalgae® 15%</td>
<td>2.128</td>
<td>9.133</td>
<td>11.873</td>
<td>11.0</td>
</tr>
<tr>
<td>Coalgae® 20%</td>
<td>2.208</td>
<td>9.476</td>
<td>12.319</td>
<td>11.2</td>
</tr>
</tbody>
</table>

3.4.3.3 The O₂ referencing

The statutory guidelines stipulate that the concentration of SO₂ and NOx should be corrected or normalised for the diluting effect of excess air (Land Instruments
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International, 2004). The measured O₂, O₂ reference (3% or 6% are often used) and the amount of oxygen in the atmospheric air (20.9%) are used in Equation 3.13 to obtain normalised concentration of SO₂ and NOx. An O₂ reference of 6% was used to ensure readings were measure from the same reference.

\[
\text{Corrected ppm} = \text{measured ppm} \times \frac{20.9 - \text{O}_2 \text{ reference}}{20.9 - \text{O}_2 \text{ measured}} \tag{3.13}
\]
Chapter 4

4 FUEL CHARACTERIZATION RESULTS

In this chapter, the characterization of coal, *Scenedesmus* microalgae and their blends Coalgae® 5% - 20% which include proximate analysis, ultimate analysis, Thermogravimetric-Mass spectrometer analysis (TG-MS), Fourier-transform infrared (FTIR) and scanning electron microscopic analysis (SEM) and X-ray energy dispersive spectroscopic analysis (EDX) are provided.

4.1 PROXIMATE ANALYSIS

Proximate analysis was performed to evaluate the effect of blending coal and *Scenedesmus* microalgae on the chemical composition of Coalgae® blends (5% - 20%) with reference to coal and microalgae. Proximate analysis was performed to determine the weight percentages (wt.%) of moisture content, volatile matter content, ash yield and fixed carbon content, and their averages were reported. The proximate analysis results are presented in Table 4.1 on air dry (ad) basis.

Table 4. 1: Proximate analysis of coal, microalgae and Coalgae® blends (ad basis).

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Coal (100:0)</th>
<th>Coalgae® (95:5)</th>
<th>Coalgae® (90:10)</th>
<th>Coalgae® (85:15)</th>
<th>Coalgae® (80:20)</th>
<th>Micro-algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>M (wt.%)</td>
<td>4.61</td>
<td>4.68</td>
<td>4.78</td>
<td>4.85</td>
<td>5.36</td>
<td>5.88</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>24.52</td>
<td>26.89</td>
<td>29.07</td>
<td>31.66</td>
<td>34.87</td>
<td>77.34</td>
</tr>
<tr>
<td>A (wt.%)</td>
<td>15.01</td>
<td>14.92</td>
<td>14.67</td>
<td>13.88</td>
<td>12.99</td>
<td>5.6</td>
</tr>
<tr>
<td>FC* (wt.%)</td>
<td>55.86</td>
<td>53.51</td>
<td>51.48</td>
<td>49.61</td>
<td>46.78</td>
<td>11.18</td>
</tr>
<tr>
<td>Fuel ratio</td>
<td>2.28</td>
<td>1.99</td>
<td>1.77</td>
<td>1.57</td>
<td>1.34</td>
<td>0.14</td>
</tr>
<tr>
<td>Volatility</td>
<td>0.44</td>
<td>0.5</td>
<td>0.56</td>
<td>0.64</td>
<td>0.75</td>
<td>6.92</td>
</tr>
</tbody>
</table>

*Calculated by difference
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The fuel ratio and the volatility were calculated using Equation 4.1 and 4.2, respectively.

\[
\text{Volatility} = \frac{\text{Volatile matter (wt.\%)} }{\text{Fixed carbon (wt.\%)}} \quad (4.1)
\]

\[
\text{Fuel ratio} = \frac{\text{Fixed carbon (wt.\%)}}{\text{Volatile matter (wt.\%)}} \quad (4.2)
\]

The fixed carbon content and ash yield decreased with increasing microalgae ratio to coal from 55.86 wt.% to 46.78 wt.% and from 15.01 wt.% to 12.99 wt.%, respectively. The decreased fixed carbon content in Coalgae® blends was a clear indication that the blends have less energy value compared to coal. This will have a negative impact on the efficiency of combustion. The reduction in fixed carbon content was about 2 wt.% from each mixture, except for the 20% Coalgae® blend which decreased by 3 wt.% due to its high volatile matter content. The volatile matter content increased with increasing blending ratio from 24.52 wt.% to 34.87 wt.% The increased volatile matter content in Coalgae® blends indicates that the co-firing of coal and microalgae will have an improved ignition and prolonged flame compared to combustion of coal (Ekbote, 2016).

The proximate analysis results of coal obtained in this study are comparable to the results of a South African Waterberg bituminous coal reported by Sehume et al., (2017). They reported 51.8 wt.%, 34.2 wt.% and 10.9 wt.% for fixed carbon content, volatile matter content and ash yield, respectively. Falcon and Ham (1988) also reported a comparable 59.8 wt.%, 24.3 wt.% and 14.3 wt.% for fixed carbon content, volatile matter content and ash yield, respectively. Makgato and Chirwa (2017) reported a South African coal (from Waterberg coalfield) with a similar volatile matter content (24.7 wt.%) but very high ash yield (32.8 wt.%).

The fuel ratio (FC/VM) and volatility (VM/FC) are included in the proximate analysis and are plotted against the microalgae blending ratios in Figure 4.1. Fuel ratio (FC/VM) required for satisfactory combustion performance is greater than 1, while volatility (VM/FC) is less than 1 (Munir et al., 2011). Therefore, the decreased fuel ratio of
Coalgae® blends from 2.28 (coal) to 1.34 (Coalgae® 20%) was within the required ratio for satisfactory combustion. The fuel ratio of microalgae is 0.14 far less than 1 as expected, and this is an indication of poor combustion which could lead to low energy output. The volatility of Coalgae® blends also presented satisfactory combustion characteristics of <1 despite increase of the blending ratio. Microalgae on the other hand showed a volatility of 6.92 which is far higher than 1 and therefore unsatisfactory for combustion. The reduction in fuel ratio and increase in volatility have been previously reported,

![Graph showing fuel ratio and volatility comparison between Coalgae® blends and coal.](image)

**Figure 4.1: Comparison of fuel ratio and volatility Coalgae® blends and coal.**

This means that co-firing coal with microalgae biomass at ratios higher than 20% will result in unacceptable combustion characteristics or would have poor combustion performance compared to raw coal. Furthermore, the proximate analyses of the Coalgae® blends meet the characteristics required for good combustion due to relative low ash yields and high volatile matter contents (Vamvuka *et al.*, 2003).
4.2 ULTIMATE ANALYSIS

Ultimate analysis was performed to determine the weight % contents of carbon, hydrogen, oxygen, nitrogen and sulphur. Calorific value was determined to obtain the high heating value of fuels. The elemental composition and high heating value (HHV) of coal, *Scenedesmus* microalgae and Coalgae® blends (5% - 20%) are presented in Table 4.2. The average contents of carbon, hydrogen, nitrogen, sulphur and oxygen are presented in weight percentage (wt.%) on dry ash free (daf) basis and HHV in MJ/kg.

**Table 4. 2: Ultimate analysis of coal, microalgae and Coalgae® blends (daf basis).**

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th>Coal</th>
<th>Coalgae® 5%</th>
<th>Coalgae® 10%</th>
<th>Coalgae® 15%</th>
<th>Coalgae® 20%</th>
<th>Microalgae</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt.%)</td>
<td>80.63</td>
<td>78.16</td>
<td>76.08</td>
<td>74.91</td>
<td>74.17</td>
<td>55.77</td>
</tr>
<tr>
<td>H (wt.%)</td>
<td>5.58</td>
<td>5.59</td>
<td>5.62</td>
<td>5.75</td>
<td>6.05</td>
<td>10.68</td>
</tr>
<tr>
<td>N (wt.%)</td>
<td>2.43</td>
<td>3.39</td>
<td>3.40</td>
<td>3.45</td>
<td>3.71</td>
<td>9.31</td>
</tr>
<tr>
<td>S (wt.%)</td>
<td>0.60</td>
<td>0.58</td>
<td>0.49</td>
<td>0.48</td>
<td>0.45</td>
<td>0.33</td>
</tr>
<tr>
<td>O*(wt.%)</td>
<td>10.76</td>
<td>12.28</td>
<td>14.41</td>
<td>15.41</td>
<td>15.62</td>
<td>23.91</td>
</tr>
<tr>
<td>H/C ratio</td>
<td>0.069</td>
<td>0.072</td>
<td>0.074</td>
<td>0.077</td>
<td>0.082</td>
<td>0.192</td>
</tr>
<tr>
<td>O/C ratio</td>
<td>0.133</td>
<td>0.157</td>
<td>0.189</td>
<td>0.206</td>
<td>0.211</td>
<td>0.429</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>25.89</td>
<td>25.65</td>
<td>25.41</td>
<td>25.32</td>
<td>25.05</td>
<td>21.4</td>
</tr>
</tbody>
</table>

*Calculated by difference

Biomasses are often characterised by high hydrogen and oxygen contents and low carbon content which results in low energy value (Senneca, 2007). These characteristics are totally different from those of coal and when the two are blended, a newly formed material with different characteristics is expected. The contents of carbon and sulphur decreased with increasing blending ratio of coal to microalgae biomass from 80.63 wt.% – 74.17 wt.% and 0.60 wt.% – 0.45 wt.%, respectively. The content of carbon was reduced by
approximately 2% from the baseline coal to Coalgae® 5% and from Coalgae® 5% to Coalgae® 10% but decreased slightly thereafter. On the other hand, the contents of hydrogen, nitrogen and oxygen increased with increasing blending ratio from 5.58 wt.% – 6.05 wt.%, 2.43 wt.% – 3.71 wt.% and 10.76 wt.% – 15.62 wt.% respectively. The carbon, hydrogen and oxygen contents of coal are comparable to the results reported by Sehume et al. (2017) which were 80.9 wt.%, 5.5 wt.% and 10.4 wt.%, respectively. The oxygen content of coal is within the reported range of South African coals; 4.3 wt% - 14.9 wt% (Bada et al., 2015; Matjie et al., 2016; Makgato and Chirwa, 2017). Microalgae had lower carbon (55.77 wt.%) and sulphur (0.33 wt.%) contents and higher hydrogen (10.68 wt.%), nitrogen (9.31 wt.%) and oxygen (23.91 wt.%) contents compared to coal. The C, H, N, S and O contents of microalgae obtained in this study are comparable to the results reported by Baloyi and Dugmore (2019) which were 56.4 wt.%, 8.2 wt.%, 9.9 wt.%, 0.4 wt.% and 25.1 wt.%, respectively.

The decrease in carbon content resulted in decreased HHV of Coalgae® blends. However, the change in HHV was insignificant and reductions were between 0.9% – 3.2% for Coalgae® 5% – Coalgae® 20%, respectively. The decrease in energy values of Coalgae® blends can be attributed to lower energy value contained in C-H and C-O bonds compared to energy in C-C bonds (Munir et al., 2009). Nonetheless, the high oxygen content in Coalgae® blends represents higher thermo-chemical reactivity compared to coal (Gil et al., 2010). Therefore, co-firing of coal with microalgae is expected to have an improved ignition (Yanfen and Xiaoqian, 2010). Additionally, the decrease in carbon and sulphur contents in Coalgae® blends is expected to reduce the emissions of CO₂ and SO₂ during co-firing tests. The increase in nitrogen content of Coalgae® blends was due to nitrogen-containing nutrients used in growing microalgae.

Elemental composition of different carbonaceous materials is reported in a Van Krevelen diagram (Senneca, 2007) presented in Figure 4.2. Biomasses are generally deemed more reactive than coal upon pyrolysis, combustion and gasification (Senneca, 2007). The H/C
and O/C ratios of Coalgae® 5% – 20% have been inserted in the Van Krevelen diagram. It should be noted that all four Coalgae® blends are located within the coal region meaning their characteristics are like those of coal but will have an enhanced reactivity and probably lower emissions compared to coal. The H/C and O/C ratios of the Coalgae® blends (5% - 20%) increased with increasing blending ratio from 0.072 – 0.082 and 0.157 – 0.211, respectively. On the other hand, the H/C ratios of coal and microalgae were 0.069 and 0.192 while their O/C ratios were 0.133 and 0.429, respectively. The H/C ratios of coal and Coalgae® blends are below 0.1 while the O/C ratios are below 0.4 in the Van Krevelen diagram where most South African coals are located (Pokothoane, 2010; Bada et al., 2015; Matjiel et al., 2016; Makgato and Chirwa, 2017).

Figure 4. 2: Elemental analysis results incorporated in Van Krevelen diagram to compare with different carbonaceous materials (Senneca, 2007).

This plot is a convenient form of presenting the fuel rank. On this graph higher rank coals fall within bottom-left part of the plot, with the decrease of rank, fuels rise towards top-right corner. All investigated solid fuels seem to fit the plot according to H/C and O/C.
ratios (Figure 4.2). Further increase in microalgae blending ratio would shift the newly formed material to the biomass region and that would negatively affect the coal-firing boilers. Therefore, it is best to keep the blending ratio low as seen in literature, blending ratios have been kept to a maximum of 20% biomass loading (Tillman, 2000; Demirbas, 2003; Vamvuka et al., 2003; Holtmeyer et al., 2012). When increasing the microalgae biomass co-firing, the availability of biomass needs to be considered. It is also important to cultivate biomass in a sustainable manner and avoid the food versus fuel conflict.

4.3 SEM ANALYSIS

Scanning electron microscopy (SEM) is one of the most used techniques to characterize the physical morphology of coal and other fuels (Creelman and Ward 1996). It is important to understand the morphological characteristics of materials for combustion studies. SEM images of coal and other fuels are analysed based on common characteristics such as shape, wall thickness, fused and unfused structures, porosity and voidage (Dooley, 2017). Figure 4.3 presents the SEM images of coal and Coalgae® 5% - 20% at various magnifications (20 µm, 50 µm and 100 µm). The SEM images of coal (A, B, C), Coalgae® 5% (D, E, F), Coalgae® 10% (G, H, I), Coalgae® 15% (J, K, L) and Coalgae® 20% (M, N, O) all show the presence of mineral matter and solid organic matter. Mineral matter is indicated by a lighter grey to white colour while organic matter is indicated by dark grey colour (Lallier-Verges et al., 1991).

The apparent changes in the surface morphology of coal can be seen on Coalgae® images. From the SEM images, coal has more minerals and less organic matter compared to Coalgae® blends. The SEM image of coal (A) shows randomly distributed round-shaped particles. On the SEM images of Coalgae® blends (B-D), the round-shaped particles are stacked together to form agglomerates by the presence of microalgae and layered structures are observed. The layered structures are mainly observed on the SEM image of Coalgae® 20% and the layers are in an angled morphology.
Figure 4.3: SEM images of coal (A,B,C), Coalgae® 5% (D,E,F), Coalgae® 10% (G,H,I), Coalgae® 15% (J,K,L) and Coalgae® 20% (M,N,O).
4.4 EDX ANALYSIS

Energy Dispersive X-ray spectroscopy (EDX) analysis is a SEM accessory and a qualitative analysis technique used by many authors for identification of minerals in coal (Creelman and Ward, 1996; Kutchko and Kim, 2006; Manoj et al., 2009). Figure 4.4 – 4.8 show the elemental spectra of coal and Coalgae® 5% - 20% respectively, obtained from EDX analysis. The EDX analysis of coal and Coalgae® blends showed the presence of carbon (C), oxygen (O), nitrogen (N) and sulphur (S) and these results agree with the ultimate analysis results which showed the presence of the same elements. Additionally, magnesium (Mg), aluminium (Al) and silicon (Si) were also observed on the EDX spectra of coal and Coalgae® blends indicating the presence of dolomite, kaolinite and quartz.

The peak intensity of oxygen, nitrogen, aluminium and silicon were observed to increase with increasing proportion of Scenedesmus microalgae. However, it should be noted that the intensity of the peaks in the EDX spectra is not a quantitative measure of elemental concentration. The increase of the peak intensity in the above-mentioned elements was probably due to nutrients used in growing microalgae. The qualitative EDX results (weight percentages of coal and Coalgae® blends) are presented in Table 4.3. The EDX elemental proportions indicated higher Si, Mg and Al contents in Coalgae® blends, and lower S and C contents compared to coal.
Table 4.3: Qualitative elemental composition of coal and Coalgae® blends based on EDX results (mass %).

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>Elemental composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Coal</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>85.93</td>
</tr>
<tr>
<td>Mg</td>
<td>MgO</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>Al₂O₃</td>
<td>2.30</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>2.78</td>
</tr>
<tr>
<td>P</td>
<td>P₂O₅</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>K</td>
<td>K₂O</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>CaO</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO₂</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>FeO</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>91.34</td>
</tr>
</tbody>
</table>

Figure 4.4: EDX spectrum of coal.
Figure 4. 5: EDX spectrum of Coalgae® 5%.

Figure 4. 6: EDX spectrum of Coalgae® 10%.
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4.5 FT-IR ANALYSIS

Figure 4.9 presents ATR-FTIR spectra of coal, *Scenedesmus* microalgae and their blends (Coalgae® 5% - 20%). The locations of absorption bands for coal and Coalgae® blends are the same, suggesting that the functionalities of these materials are not much different. The broad absorption bands at 3500-3000 cm⁻¹ observed for *Scenedesmus* microalgae and
Coalgae® blends are ascribed to O-H vibration in water, phenol and alcohol. These bands are also ascribed to C-H stretching, confirming the presence of alkynes. The absorption band around 2800 cm\(^{-1}\) observed for all materials but stronger for microalgae, is ascribed to –O-CH\(_3\) and C-H stretching confirming the presence of methoxy and methyl ether from lipids. The prominent adsorption bands at 1700-1500 cm\(^{-1}\) which are stronger for microalgae, are ascribed to N-H bending, suggesting the presence of amide-I and amide-II bonding from proteins (Gai et al., 2015). These bands are also ascribed to alkenyl C=C stretching, -C=N open chain imino and carboxylates.

![Figure 4.9: FT-IR spectra of coal, microalgae and Coalgae® 5% - 20%](image)

The small absorption bands around 1500-1200 cm\(^{-1}\) which are stronger for microalgae are ascribed to C=C-C aromatic ring stretching, aromatic nitro compounds and carbonate ions at 1490 cm\(^{-1}\), O-H bending of phenols and tertiary alcohols, ammonium ions and organic sulphate at 1410 cm\(^{-1}\) and C-H stretching, C-N stretching, O-H bending and P-O stretching from organic phosphates at 1250 cm\(^{-1}\). The absorption bands around 1000 cm\(^{-1}\) is higher
for coal, followed by microalgae and Coalgae® blends in order with increasing microalgae proportion. These bands are ascribed to skeletal C-C vibrations, aromatic C-H in-plane bending, C-O stretching and Si-O-C organic siloxane or silicone. The absorption bands observed for coal and Coalgae® blends around 900 cm\(^{-1}\) are ascribed to P-OC stretching from aromatic phosphates, vinyl C-H out-of-plane bending and 1,3 disubstitution (meta). The absorption bands observed for coal and Coalgae® blends around 750 cm\(^{-1}\) are assigned to aromatic C-H out-of-plane bending. All the absorption bands at 700-490 cm\(^{-1}\), which are stronger for coal followed by Coalgae® blends, are ascribed to S-S stretching from polysulphides and aryl disulphides, and C-S stretching from disulphides.

Coal absorption bands dominate at the wavelength region (1000-490 cm\(^{-1}\)) that shows C-H functional groups, C-S (690-685 cm\(^{-1}\)), S-S (510-505 cm\(^{-1}\)), C=S (1040-1010 cm\(^{-1}\)) S-H (2400-2000 cm\(^{-1}\)) while microalgae absorption bands dominate at the wavelength region (3500-1200 cm\(^{-1}\)) where there are O-H and N-bonded compounds. Generally, intensities of \(\nu(OH)\), \(\nu(NH)\), \(\nu(C=O)\), \(\nu(C=N)\) and N-H bending frequencies increases in the order of coal <Coalgae® 5% <Coalgae® 10% <Coalgae® 15% <Coalgae® 20% <Scenedesmus microalgae. An increase in the band intensity of O-H was observed for Coalgae® blends as microalgae blending ratio increased.

4.6 TGA

It was of interest to examine possible interactions between microalgae biomass components with coal (Coalgae®). These experiments aimed to give a deeper understanding of the processes occurring during thermal combustion in the presence of air. Coal, microalgae and Coalgae® 5% - 20% were combusted. All the tests were performed on loose powdered sample fuels. The mass loss curves against temperature obtained during the combustion of these samples are shown in Figure 4.10. The first derivative of the mass loss with time versus temperature (DTG) is given in Figure 4.11.
Key temperatures, maximum mass loss rate and combustion residual mass are listed in Table 4.4.

Several activities can be identified from a combustion profile. The thermal breakdown of organic matters in a sample can be defined from the start to the end of a derivative thermogravimetric (DTG) curve. The combustion process of coal has been reported to occur in three stages; these are moisture evaporation and chemisorption of oxygen, combustion stage and burnout stage which are identified based on the weight and heat changes (Kastanaki and Vamvuka, 2006; Yanfen and Xiaoqian 2010; Moon et al., 2013).

It was observed that microalgae starts to decompose the earliest of all the evaluated samples (225-575°C) and reaches its maximum rate of conversion (the highest peak value) at 291°C. The degradation process of Coalgae® 20% is slower than that of microalgae, in the range of 250-580°C and reaches a maximum conversion rate at 531.09°C. Coalgae® 15% decomposition follows a similar path as Coalgae® 20% in the range of 252-581°C reaching maximum rate at 530.47°C. Coalgae® 10% decomposition was in the range of 273-582°C reaching maximum rate at 529.84°C. Coalgae® 5% decomposition was in the range of 275-583°C reaching maximum rate at 524.23°C. Coal presented a similar decomposition pattern with Coalgae® blends; however, decomposition was in the range of 350-584°C reaching maximum conversion rate at 521.74°C, which is similar to the peak maximum temperatures of low and medium rank coals.
Figure 4.10: TG profiles of coal, microalgae and their blends (Coalgae® 5% - 20%).

Coal presented a similar decomposition pattern to Coalgae® blends; however, three stages could be distinguished from the TG profile of coal combustion. The first stage spans from 43°C to around 150°C which was attributed to a loss of moisture. Then a net weight gain was observed from 150°C to 315°C due to chemisorption of oxygen which is represented by negative values on the DTG curve. The second stage with a drastic weight loss spans from 315°C to 620°C which is represented by a one strong peak on the DTG curve. This peak could be attributed to devolatilization and simultaneous combustion of volatile matter and char reaching a maximum conversion rate of 0.7307%/°C at 522°C. The last stage spans from 620°C to 650°C which was attributed to the burnout of char and about 15.18 wt.% ash remained. The ash yield determined from the proximate analysis was 15.01 wt.% and it is greatly comparable to the ash yield obtained from TGA with only 1% difference.

It was observed that Scenedesmus microalgae start to decompose the earliest of all the evaluated samples (250-510°C). This is similar to results reported by other researchers using different algae species (Chen et al., 2011; Tahmasebi et al., 2013; Miranda et al., 2014).
The first stage spans from 30°C to 120°C was attributed to the release of moisture. The second stage spans from 150°C to around 500°C which was attributed to the release and combustion of volatile matter. Stage two showed two zones of devolatilization; zone one (labelled peak 1 in Figure 4) was attributed to combustion of proteins and carbohydrates, and zone two was attributed to combustion of lipids. The third stage between 500°C and 600°C (peak 2) was attributed to the combustion of char. Similar results have been reported in literature (Agrawal and Chakraborty, 2013). The maximum weight loss rate reached was 0.5502%/°C at 291°C. The ash yield that remained after combustion was 7.23 wt.% for *Scenedesmus* microalgae which is 22% higher than the ash yield obtained from proximate analysis (5.6 wt.%) and this difference might be due to the poor combustion rate compared to coal.

The volatile matter released from microalgae during combustion accounts for 90% of the mass (dry basis). Microalgae are known to contain cellulose which decomposes on heating by two pathways (Simoneit, 2002). According to the well accepted Broido-Shafizadeh mechanism, at low temperatures <300°C a reduction in the degree of polymerization of cellulose with only a small weight loss takes place, leading to the formation of "active cellulose". At temperatures greater than 300°C, the decomposition proceeds through two competing pathways. The first includes a ring scission of cellulose to yield ash and gases, while the second includes a depolymerization of cellulose by end group depolymerization which yields primarily volatile products.

The co-combustion of coal and *Scenedesmus* microalgae blends (Coalgae®) shows different characteristics from those of the parent fuels. The TG and DTG curves of the Coalgae® blends lie between those of the individual fuels, and the contributions of coal and microalgae to these profiles are obvious. The DTG curves of the Coalgae® blends show one major peak between 400°C and 620°C which is due to the combustion of both coal and microalgae. The maximum weight loss rate reached was 0.7187%/°C, 0.7185%/°C, 0.6997%/°C and 0.6842%/°C for Coalgae® 5%, Coalgae®10%, Coalgae® 15% and Coalgae® 20%, respectively. For the Coalgae® blends, two separate
devolatilization regions can be distinguished (peaks at 300°C and 350°C (Figure 4.11)), with high volatile matter and relatively low ash yield. The presence of microalgae in the blends does appear to slightly affect the coal decomposition pattern (300-500°C). The ash yields after co-combustion of Coalgae® 5% - 20% are 15.15 wt.%, 15.31 wt.%, 14.41 wt.% and 14.74 wt.%, respectively. The ash yields of Coalgae® 5% - 20% from TGA are comparable to the ash yields that were obtained from the proximate analysis with a difference of 1.5%, 4.2%, 3.7% and 11.9%, respectively. The higher ash yield difference for Coalgae® 20% can be attributed to poor combustion due to relative low higher heating value.

Figure 4.11: DTG curves of coal, Scenedesmus microalgae and their blends (Coalgae® 5% - 20%).

Looking in more detail at the DTG peak temperatures collated in Figure 4.11 and Table 4.4, it can be noted that the Coalgae® blends reached their maximum conversion rate 3-
10°C later than coal. These results suggest possible interaction between chars of each constituent of the Coalgae® blends, as microalgae char combustion (peak 2) was observed 20°C higher than coal. This negatively impacted the maximum conversion rate of the Coalgae® blends. The ash quantities (Wr) summarised in Table 4.3, also indicate additive yields for the Coalgae® blends compared to the ash yields obtained with proximate analysis and this might be due to the negative effect of microalgae on the combustion rate.

**Table 4.4: Characteristic parameters for the combustion profiles of coal, microalgae and Coalgae® 5% - 20%**.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_i$ (°C)</th>
<th>$T_{p1}$ (°C)</th>
<th>$T_{p2}$ (°C)</th>
<th>DTG$_{\text{max}}$ (%/°C)</th>
<th>Wr (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>448.22</td>
<td>-</td>
<td>521.74</td>
<td>0.7307</td>
<td>15.28</td>
</tr>
<tr>
<td>Coalgae® 5%</td>
<td>444.62</td>
<td>-</td>
<td>524.23</td>
<td>0.7187</td>
<td>15.15</td>
</tr>
<tr>
<td>Coalgae® 10%</td>
<td>439.37</td>
<td>-</td>
<td>529.84</td>
<td>0.7185</td>
<td>15.11</td>
</tr>
<tr>
<td>Coalgae® 15%</td>
<td>436.6</td>
<td>-</td>
<td>530.47</td>
<td>0.6997</td>
<td>14.66</td>
</tr>
<tr>
<td>Coalgae® 20%</td>
<td>433.67</td>
<td>-</td>
<td>531.09</td>
<td>0.6842</td>
<td>14.44</td>
</tr>
<tr>
<td>Microalgae</td>
<td>301.17</td>
<td>291.07</td>
<td>541.06</td>
<td>0.5502</td>
<td>7.23</td>
</tr>
</tbody>
</table>

$T_i$- Ignition temperature  
$T_{p}$- Peak temperature  
DTG$_{\text{max}}$- Maximum weight loss rate  
Wr- Residual mass
4.6.1 Combustion Kinetics

Combustion kinetic evaluation of results for coal and Coalgae® blends was performed. The kinetic parameters obtained show changes in the activation energies, when rates derived for the blends were compared to that of coal. The activation energy calculated for the coal peak combustion was 161.3 kJ/mol, while a significant decrease of up to 27 kJ/mol was observed when 20% by mass microalgae (Coalgae® 20%) was added to coal. The lowering of activation energy could be attributed to the presence alkaline elements and oxidative volatiles. The presence of higher amount of microalgae influences coal combustion/decomposition by lowering its energy requirement to initiate the combustion process. The first order volatilization rates of coal and Coalgae® blends are presented in Figure 4.12 – 4.16. Activation energy and Arrhenius parameters are presented in Table 4.5. The activation energies of Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20% are 160.4 kJ/mol, 159.6 kJ/mol, 151.2 kJ/mol and 134.2 kJ/mol, respectively, so the requirement for temperature and energy necessary to initiate the combustion reaction reduces as biomass content increases.

<table>
<thead>
<tr>
<th>Fuels</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\ln A$ ($s^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>301</td>
<td>2.06</td>
<td>0.9707</td>
</tr>
<tr>
<td>Coalgae® 5%</td>
<td>279</td>
<td>2.51</td>
<td>0.9857</td>
</tr>
<tr>
<td>Coalgae® 10%</td>
<td>247</td>
<td>2.04</td>
<td>0.9767</td>
</tr>
<tr>
<td>Coalgae® 15%</td>
<td>241</td>
<td>1.96</td>
<td>0.9673</td>
</tr>
<tr>
<td>Coalgae® 20%</td>
<td>207</td>
<td>1.47</td>
<td>0.9965</td>
</tr>
</tbody>
</table>

Table 4.5: Devolatilization kinetics of activation energies of Coalgae® 5% - 20%.
Greenhouse gas emissions reduction through the co-firing of coal and microalgae biomass: An experimental evaluation
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Figure 4.12: Plot of $\ln \left[ -\ln(1-x) \right] / T^2$ versus 1/T of coal combustion calculated by one step integral method.

Figure 4.13: Plot of $\ln \left[ -\ln(1-x) \right] / T^2$ versus 1/T of Coalgae® 5% combustion calculated by one step integral method.
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Figure 4.14: Plot of $\ln \left[ \frac{-\ln(1-x)}{T^2} \right]$ versus $1/T$ of Coalgae® 10% combustion calculated by one step integral method.

Figure 4.15: Plot of $\ln \left[ \frac{-\ln(1-x)}{T^2} \right]$ versus $1/T$ of Coalgae® 15% combustion calculated by one step integral method.
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4.7 MS ANALYSIS

The effect of co-firing coal and *Scenedesmus* microalgae was also studied on CO$_2$, NO$_x$ and SO$_2$ emissions measured during co-combustion of Coalgae® 5% - 20% using a TGA-MS system. Gas emissions analysed were CO$_2$ (m/e 44), NO$_x$ (m/e 30 and 46) and SO$_2$ (m/e 64). Figure 4.20 shows the MS results of CO$_2$ gas emissions evolved during combustion of coal, *Scenedesmus* microalgae and Coalgae® 5% - 20% in a TGA. Similarly to the observations with DTG, CO$_2$ release for microalgae combustion shows two events. The first release of CO$_2$ occurs at a temperature range of 250°C to 400°C, and the second stage between 500°C to 620°C. This shows that CO$_2$ was released at both peak temperatures during the combustion of volatile matter and during the combustion of fixed carbon with the second peak having a higher CO$_2$ released than the first one. Coal and the Coalgae® blends, also presents similar curves as DTG, only one peak is observed at temperatures around 300°C and 620°C. This means that the release of CO$_2$ occurs
simultaneously during the combustion of volatile matter and fixed carbon. The CO₂ peak strength decreases with increasing proportion of Scenedesmus microalgae in coal (Figure 4.20). Similar findings have been reported with co-combustion of coal and biomass fuels (Otero et al., 2011; Zhang et al., 2013).

Again, in Figure 4.21, the release of NO for microalgae combustion is shown by two peaks around 250°C to 350°C and around 500°C to 600°C. While the combustion of coal and the Coalgae® blends shows one peak around 470°C to 600°C. The release strength of NO for microalgae is higher than coal and the Coalgae® blends lie between the two parent materials. Microalgae have a lower heating value, high oxygen content and high moisture content. Low amounts of NO and NO₂ were detected (Figures 4.21 and 4.22). The amount of NO₂ released (peak between 400°C and 600°C, Figure 4.22) is higher for coal compared to microalgae. This is because coal has a higher heating value and therefore
has a higher chance of complete combustion where NO is further oxidised to NO₂, compared to microalgae.

Figure 4. 18: MS curves of NO evolved during combustion of coal, microalgae and Coalgae® 5% - 20%.

Figure 4. 19: MS curves of NO₂ evolved during combustion of coal, microalgae and Coalgae® 5% - 20%.
The combustion of sulphur resulted mostly in the formation of SO$_2$ (Figure 4.22), however, the amount of sulphur in coal, microalgae and Coalgae® blends was very low (0.49 – 0.29 wt.%) such that the MS plot of SO$_2$ is noisy. According to general expectation, SO$_2$ should decrease with increasing microalgae co-firing ratio due to lower sulphur content of microalgae compared to coal (Van Loo et al., 2002). Some of the SO$_2$ is captured by alkaline ash, causing further reductions on the SO$_2$ emissions (Wieck-Hansen et al., 2000; Robinson et al., 2003).

Figure 4. 20: MS curves of SO$_2$ evolved during combustion of coal, microalgae and Coalgae® 5% - 20%.
Chapter 5

5 COAL AND MICROALGAE CO-FIRING RESULTS

The mass reduction curve and flue gas temperature measured during the co-firing of Coalgae® 5%, 10%, 15% and 20% with reference to combustion of coal, are provided in this chapter. The effect of co-firing Scenedesmus microalgae and coal on CO₂, SO₂ and NOx emissions was investigated, and the results are provided in this chapter. Ash analysis is also provided in this chapter, including ash residue, SEM/EDX, XRF as well as combustion efficiency and mass balance. It should be noted that in this study Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20% refers to the mass ratio of coal to microalgae biomass 95:5, 90:10, 85:15 and 80:20, respectively.

During the combustion of each fuel, several stages may be distinguished. At the beginning, when the sample is exposed to the flame, moisture is released, then, during the pyrolysis stage, volatile matter is burned, and a flame appears above the fuel. Finally, the char combustion takes place and the end product of ash is formed. Some ash elements remain as a residue in the sample basket, others evolve as a fly ash or aerosol.

5.1 MASS REDUCTION

The mass loss readings were recorded every minute during the combustion of coal and co-firing of Coalgae® blends at an air flow rate of 17.5 l/min and the results are depicted in Figure 5.1. It should be noted that the mass reduction was plotted as a function of time (Figure 5.1) and not temperature as temperature itself was measured against time (Figure 5.2) during the combustion experiments. From the coal and Coalgae® curves (Figure 5.1), three combustion stages were distinguished. The first weight loss can be attributed to moisture loss and release of volatiles which occurs around 0 – 55 min for coal, 0 – 35 min for Coalgae® 5% and 10%, and 0 – 10 min for Coalgae® 15% and 20%. The second
weight loss can be attributed to the combustion of volatiles and char which occurs around 55 – 128 min for coal, 35 – 80 min for Coalgae® 5% and 10%, and 10 – 70 min for Coalgae® 15% and 20%. The third weight loss can be attributed to ashing which occurs around 128 – 165 min for coal, 80 – 120 min for Coalgae® 5% and 10%, and 70 – 85 for Coalgae® 15% and 20%. The mass residues after the combustion of coal and Coalgae® 5% - 20% were 33.4 g, 32 g, 30.8 g, 29 g and 27.2 g, respectively. When dividing the mass residues by the mass of sample (200 g) burned and multiply by 100 (according to Equation 3.6), the ash yields of coal and Coalgae® 5% - 20% become 16.7 wt.%, 16 wt.%, 15.4 wt.%, 14.5 wt.% and 13.6 wt.%, respectively. These ash yields are comparable to the ash yields obtained from proximate analysis and TGA with a difference of up to 1.8 wt.%.

![Mass reduction curves of coal and Coalgae® 5% - 20%](image)

**Figure 5.1: Mass reduction curves of coal and Coalgae® 5% - 20%**.

The volatiles and char seem to have been combusted simultaneously. The combustion of Coalgae® is faster than that of coal and becomes faster as microalgae proportion was
increased. The fast combustion of Coalgae® blends is shown by mass loss curves which shift down by few minutes as microalgae is increased. Additionally, this was also proven by increasing fuel consumption rate, which was calculated by averaging the mass difference per time interval. The co-firing tests showed a fuel consumption rate of 2.17 g/min, 2.21 g/min, 2.37 g/min and 2.62 g/min for Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20%, respectively. The reference coal showed a fuel consumption rate of 1.48 g/min. The combustion of coal was longer (took about 2.75 hours) than the co-firing of Coalgae® blends which took about 1.4 – 2 hours (Figure 5.1). The fast combustion of Coalgae® blends can be associated to comparative high volatility. The release of volatiles leaves the char more accessible to all possible reactants (Li et al., 2012). The high volatiles in Coalgae® blends made the ignition easy and quick compared to coal when fire was introduced to the sample during combustion experiments, and this is advantageous for industrial scale as it would save energy.

5.2 COMBUSTION TEMPERATURE

The temperature of the flue gas exiting the reactor was measured using a thermocouple for all the Coalgae® combustion tests and compared to coal combustion as a reference. Three different stages of combustion were typically established in the reactor. The first stage was associated with ignition and release of volatiles shown by a rapid increase in temperature. The second stage was associated with the drastic reduction in mass as a result of the conversion of the solid fuel to gaseous products which is due to (stable) combustion combustion of volatiles and char. The third stage was associated with char burnout (ashing) shown by a large decrease in temperature. These three stages of combustion using different combustion systems have been reported in literature (Gil at al., 2010; Muthuraman et al., 2010; Agrawal and Chakraborty, 2013). The different temperature curves of Coalgae® 5% - 20% with coal as a reference at an air flow rate of 17.5 l/min are depicted in Figure 5.2.
A rapid temperature increase was observed with Coalgae® blends and became faster as microalgae loading increased, reaching the first peak at 287°C for Coalgae® 5%, 296°C for Coalgae® 10%, 317°C for Coalgae® 15% and 352°C for Coalgae® 20%. The first peak can be attributed to the ignition and release of volatile matter and was reached in 19, 17, 14 and 12 minutes with Coalgae® 5% - 20%, respectively. The ignition of Coalgae® became faster as the microalgae blending ratio increased compared to coal and this can be associated with the increase in relative volatility. Similar results that show fast ignition of biomass have been reported on co-firing of coal sawdust and grass (Pokothoane, 2010). In the case of coal, only one peak was observed which suggests that the devolatilization and combustion stages occurred simultaneously. Since coal has lower volatile matter content than microalgae, the devolatilization stage occurred slowly at higher temperatures. These results suggest that Coalgae® blends are more reactive than coal due to high volatile matter content and high oxygen content.
The second rise in temperature (second peak) was attributed to the combustion of volatile compounds and char. This reaction occurred very fast for Coalgae® blends and this was shown by a sharp peak. The peak temperatures reached for Coalgae® 5% - 20% were 438°C, 453°C, 498°C and 510°C. Coal burned very slowly showing one broad peak with a peak temperature of 419°C. The slower combustion of coal compared to biomass has been reported in literature when co-firing coal with different biomasses including algae (Wang et al., 2009; Gil et al., 2010; Chen et al., 2011; Tahmasebi et al., 2013). The peak temperatures were observed around 60 minutes (Figure 5.2) and are plotted against excess air in Figure 5.3 to determine the effect of microalgae co-firing on peak temperature at varied excess air.

![Graph showing the effect of microalgae co-firing on peak temperature.](image)

**Figure 5.3: Effect of microalgae co-firing on peak temperature.**

Peak temperatures increased with increasing microalgae co-firing ratio at higher excess air (50%, 70% and 100%). However, peak temperatures at lower excess air (0%, 10% and 30%) increased with increasing microalgae co-firing ratio up to Coalgae® 10% and decreased thereafter. The decrease in peak temperatures of Coalgae® 15% and 20% at lower excess air might be due to relative increasing moisture content.
The hypotheses that coal blended with microalgae will have better combustion behaviour than raw coal can be accepted based on the above results, which showed faster devolatilization and ignition leading to overall faster combustion for Coalgae® blends compared to coal. However, the significant temperature increase observed at an excess air of 100% for Coalgae®15% and Coalgae® 20% might not be good for the boilers. These high temperatures are likely to cause swelling of the particles, resulting in bubble-like ash and could cause fouling and clinkering on the boilers depending on ash fusion temperatures (Van Alphen, 2005). Therefore, Coalgae® 10% is recommended to be used as an alternative source for energy generation in existing boilers.

5.3 COMBUSTION EMISSIONS

Experimental data obtained from the combustion tests of Coalgae® blends at an air flow rate of 17.5 l/min with coal as a reference are depicted in Table 5.1. This data shows average concentrations of CO₂, O₂, SO₂ and NOx as well as calculated excess air and measured peak temperature. Excess air notably increased with increasing microalgae cofiring ratio from 50% (coal) to 65% (Coalgae® 20%) and this was expected relative to oxygen content which was readily available in Coalgae® blends.

Table 5.1: Experimental data obtained during combustion of coal and Coalgae®
5% - 20%.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Coal</th>
<th>Coalgae® 5%</th>
<th>Coalgae® 10%</th>
<th>Coalgae® 15%</th>
<th>Coalgae® 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_p (°C)</td>
<td>417</td>
<td>438</td>
<td>453</td>
<td>498</td>
<td>510</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>14.96</td>
<td>12.73</td>
<td>12.05</td>
<td>11.45</td>
<td>10.27</td>
</tr>
<tr>
<td>O₂ (% dry)</td>
<td>6.97</td>
<td>7.01</td>
<td>7.44</td>
<td>7.59</td>
<td>8.24</td>
</tr>
<tr>
<td>Excess air (%)</td>
<td>50.0</td>
<td>50.5</td>
<td>55.3</td>
<td>57.0</td>
<td>65.1</td>
</tr>
<tr>
<td>SO₂ (ppm)</td>
<td>144.2</td>
<td>141.5</td>
<td>128.9</td>
<td>121.4</td>
<td>117.9</td>
</tr>
<tr>
<td>NOx (ppm)</td>
<td>132.2</td>
<td>102.6</td>
<td>97.7</td>
<td>100.0</td>
<td>109.9</td>
</tr>
</tbody>
</table>
5.3.1 Emissions of CO₂

The effect of microalgae co-firing on CO₂ concentration is depicted in Figure 5.4. The data presented in Figure 5.4 shows CO₂ concentration measured over time during the combustion tests of the four Coalgae® blends with coal as a reference.

![Graph showing CO₂ concentration over time](image)

**Figure 5.4: CO₂ concentration measured over time.**

The CO₂ curves follow the same trend as the temperature curves, meaning CO₂ concentration increased with increasing temperature, stabilized as stable combustion was reached and then decreased as temperature decreased. The maximum CO₂ concentration slightly shifted towards lower concentrations as the microalgae co-firing ratio increased. Inversely, the O₂ concentration (Figure 5.5) decreased as temperature and CO₂ concentration increased. This means that high temperatures destruct the chemical structure of the fuel, making it accessible for oxygen (fuel O₂ and atmospheric O₂) to bind onto carbon, hydrogen, nitrogen and sulphur (Shen, 2009).
Blending coal with microalgae showed positive results as CO₂ emissions decreased with the increasing microalgae co-firing ratio regardless of changing air flow rate, as can be seen in Figure 5.6. The mass (g) of CO₂ from the combustion of coal increased with increasing air flow rate from approximately 547 g (8.6 l/min) to 837 g (14.6 l/min), and slightly decreased thereafter. The calculations of the mass of CO₂ are shown in Appendix C. However, the mass of CO₂ from the co-firing of Coalgae® 5%, 10% and 15% showed almost linear trends meaning varying air flow rate did not have much effect. Coalgae® 20% increased with increasing air flow rate up to 11.2 l/min and decreased thereafter. This means that higher air flow rates results in poor combustion, hence the lower emissions of CO₂.
Figure 5.6: Effect of air flow rate on CO$_2$ formed from co-firing coal and microalgae.

The effect of co-firing microalgae and coal on CO$_2$ is better presented in Figure 5.7 which shows average CO$_2$ concentrations versus microalgae co-firing ratios. Average CO$_2$ concentrations measured were 12.73%, 12.05%, 11.45% and 10.27% for Coalgae® 5%, Coalgae® 10% and Coalgae® 15% and Coalgae® 20%, respectively. Reference coal had an average CO$_2$ concentration of 14.96%. The decrease in CO$_2$ concentration was associated with decrease in comparative carbon content which decreased from 80.63 wt.% – 74.17 wt.% from coal to Coalgae® 20%. Comparable results with decreasing CO$_2$ have been reported in literature for microalgae co-firing and biomass co-firing (Kadam, 2002; Gani et al., 2005; Pokothoane, 2010).
Reductions in average CO₂ concentrations achieved with Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20% were 14.9%, 19.5%, 23.5% and 31.4%, respectively. These reductions are depicted in Figure 5.8. The CO₂ reduction increased proportionally with increasing microalgae co-firing ratio.
Conclusions regarding CO₂ in this study were made using statistical analysis to compare CO₂ concentration from the co-firing of Coalgae® blends to that measured from the combustion of coal. This was done to prove whether the CO₂ reduction was significant, or it was just caused by experimental error. When analysing all the five materials using Anova: Single Factor, it showed that the CO₂ reductions are significant as the p-value was below 0.05 (p-value 0.000934). Therefore, the hypotheses that blending microalgae with coal will reduce CO₂ emissions can be accepted for Coalgae® 5% - 20% as this was statistically proven. The reduction of CO₂ emissions was mainly associated to the differences in the carbon content and combustion behaviour of Coalgae® blends and coal. As Pokothoane (2010) stated, CO₂ can either increase or decrease, but what is important is the source of CO₂ (whether it is fossil or can be recycled).
5.3.2 Emissions of SO$_2$

Both combustion of coal and co-firing of Coalgae® resulted in the formation of sulphur dioxide (SO$_2$) due to the oxidation of sulphur in their fuel structures. Most biomasses contain lower amount of sulphur compared to coal which results in decreased amounts of SO$_2$ during combustion (Fernando, 2012; Yang et al., 2015). Reductions in SO$_2$ may also be caused by presence of higher alkali and alkaline earth compounds in biomass ash compared to coal ash, which capture considerable fractions of sulphur in the ash (Fernando, 2012). The concentrations of SO$_2$ during the co-firing of Coalgae® blends was measured over time and the results are depicted in Figure 5.9 including coal as a reference.

![Graph showing SO$_2$ concentration over time](image)

**Figure 5.9: SO$_2$ concentration measured over time.**

The concentration of SO$_2$ decreased as the portion of microalgae was increased to 20%. The SO$_2$ formation is due to the oxidation of the fuel sulphur with oxygen and its
maximum peaks corresponded to maximum temperature peaks. Coal and Coalgae® 5% showed one peak of SO₂ due to spontaneous combustion of volatiles and char. As the microalgae loading increased, the SO₂ formation from volatile combustion and char combustion separated showing two individual peaks, particularly with Coalgae® 20%. This is because Coalgae® 20% have a volatile matter content of 34.87 wt.% which is 10% higher than Coalgae® 15%.

The mass of SO₂ is presented in Figure 5.10 at different air flow rates to show the effect of air flow rate on SO₂ formation from coal and microalgae co-firing. The mass of SO₂ decreased with increasing microalgae co-firing ratio at almost all flow rates, despite for Coalgae® 20%. The co-firing of Coalgae® 20% released higher SO₂ compared to other Coalgae® blends and this result was not expected. Since the sulphur content decreased with increasing microalgae loading, SO₂ was expected to follow the same trend as stated by Van Loo et al. (2002).

The mass of SO₂ for coal increased with increasing air flow rate up to 12.9 l/min, and then decreased thereafter. Changing air flow rate during combustion tests of Coalgae® 5%, Coalgae® 10 and Coalgae® 15% did not show much effect on the formation of SO₂ as there was no clear trend observed for these fuels (the plots are almost linear). Only Coalgae® 20% showed an increasing mass of SO₂ as air flow rate increased up to 11.2 l/min but decreased beyond.
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Figure 5.10: Effect of air flow rate on SO$_2$ formed from co-firing coal and microalgae.

The effect of co-firing microalgae and coal on SO$_2$ is further presented in Figure 5.11 which shows the average SO$_2$ concentration versus microalgae co-firing ratio. The average SO$_2$ concentration is the average of the SO$_2$ concentration readings measured every minute with the Lancom 4 portable flue gas analyser during the stable combustion stage of each material. The SO$_2$ concentration was corrected to 6% O$_2$ to account for the dilution effect of excess O$_2$. 
Emissions of SO$_2$ decreased with increasing microalgal loading, corresponding to relative decrease in the fuel sulphur. The SO$_2$ concentrations measured from the co-firing of Coalgae® 5% - 20% were 141.5 ppm, 128.9 ppm, 121.4 ppm and 117.9 ppm, respectively. Reference coal formed higher SO$_2$ concentration (144.2 ppm) compared to Coalgae® blends. The SO$_2$ reductions achieved with Coalgae® 5% - 20% were 1.9%, 10.6%, 15.8% and 18.2%, respectively. These are depicted in Figure 5.8, which shows that SO$_2$ reductions increased with increasing microalgal co-firing ratio. The reductions in SO$_2$ emissions could also be attributed to sulphur being retained in the alkaline ash of Coalgae® blends. This was shown by presence of sulphur in Coalgae® ash which increased with increasing microalgal co-firing ratio as depicted in Table 5.3. The effect of self-desulphurisation of coal co-fired with different biomasses including microalgae has been reported in literature (Kadam, 2002; Robinson et al., 2003; Kucukvar and Tatari, 2011; Yang et al., 2015).
To conclude on whether the SO$_2$ emissions were reduced by co-firing coal and microalgae or the difference was just due to experimental error, statistical analysis had been performed. The Anova: Single Factor analysis showed that the SO$_2$ reductions are significant within experimental error as the p-value was less than 0.05 (1.92E-10). Therefore, the null hypotheses, which states that SO$_2$ emissions will be reduced by co-firing small portion of microalgae with coal can be accepted.

5.3.3 Emissions of NOx

Most biomasses contain lower content of nitrogen compared to coal and therefore result in lower NOx formation (Fernando, 2012; Li et al., 2012; Saikaew et al., 2012). However, biomasses with higher nitrogen content have also been reported to decrease the levels of NOx (Daoed et al., 2013). The formation of NOx is complicated and difficult to predict. NOx may increase, decrease or remain the same depending on the biomass type, blending ratio, co-firing conditions and operating conditions. Fuel NOx in biomass co-firing evolve as volatile compounds and results in reduced levels of NOx while thermal NOx depends on combustion temperature (Fernando, 2012). Fuel NOx forms when the nitrogen bound in the fuel reacts with the oxygen in the combustion air. Thermal NOx forms when the nitrogen and oxygen in the combustion air combine with one another at high temperatures in a flame.

The concentrations of NOx were measured during the co-firing of Coalgae® blends with coal combustion as a reference; results are depicted in Figure 5.12. The concentration of NOx measured throughout the combustion of coal appears as one broad peak. However, this was different for Coalgae® blends because the NOx concentration appears as two peaks. The first peak can be associated to the formation of fuel NOx from microalgae evolving during the devolatilization stage. The second peak can be associated to the formation of fuel NOx from coal evolving during the stable combustion stage as it appears around 50 minutes where simultaneous combustion of volatiles and char takes place (Figure 5.2).
Figure 5.12: NOx concentration measured over time.

The effect of an air flow rate on NOx emissions from the co-firing of coal and microalgae is shown in Figure 5.13. Coal combustion has a higher mass of NOx compared to the Coalgae® blends regardless of varying the air flow rate. However, varying the air flow rate showed no effect on the mass of NOx for the Coalgae® blends as no clear trends were observed. The mass of NOx for coal increased with increasing air flow rate up to 14.6 l/min, and then decreased thereafter. The increase in NOx emissions as air flow rate increased could be associated to the increase in combustion temperature (Figure 5.3). Although the temperatures measured at the reactor exit were below 1000°C, the flame temperature at the exact combustion area might be higher enough to produce thermal NOx via the Zeldovitch mechanism (Moron and Rybak, 2015).
The effect of co-firing coal and microalgae on NOx emissions was investigated and the results are depicted in Figure 5.14. The emissions of NOx were normalised to 6% oxygen for the dilution effect of excess oxygen. Average NOx concentrations of 102.6 ppm, 97.7 ppm, 100 ppm and 109.9 ppm were measured for Coalgae® 5%, 10%, 15% and 20%, respectively. Average NOx concentration of 132.2 ppm was obtained from the combustion of coal. The average concentration of NOx decreased as the microalgae co-firing ratio increased and then slightly increased after a co-firing ratio of 10% was reached. However, NOx emitted by each Coalgae® blend was still lower compared to NOx emitted by coal. The reduction of NOx might be also due to the formation of NHx during the oxidation of nitrogen-bound in the fuel which is further decomposed to N₂ (Williams et al., 2001; Kubica et al., 2001).
Figure 5.14: Effect of microalgae co-firing on NOx emissions.

Microalgae biomass reduced NOx emissions from the baseline coal by 22.4%, 26.1%, 24.4% and 16.9% for Coalgae® 5%, 10%, 15% and 20%, respectively. NOx reductions are shown in Figure 5.8, which increased as the microalgae co-firing increased up to Coalgae® 10% and decreased thereafter. These results show that lower NOx emission levels can be achieved with fuel containing higher nitrogen content compared to coal. Therefore, suggesting that the fuel nitrogen has little influence in the production of NOx as suggested by (Gani et al., 2005; Kazagic and Smajevic, 2009; Pokothoane, 2010). Most of the NOx evolved as volatile compounds due to high volatility in Coalgae® blends and this further explains the reduction in NOx emissions as Fernando (2012) reported. However, the role of higher nitrogen content in Coalgae® blends compared to coal started showing at Coalgae® 15% and 20% as NOx started increasing slightly. This means that further co-firing ratio of microalgae beyond 20% could possibly result in higher NOx emissions compared to coal as Kucukvar and Tatari (2011) reported at blending ratios of up to 100% microalgae.
The reductions of NOx emissions from the baseline coal were statistically proven by Anova: Single Factor analysis to make conclusions. A p-value of less than 0.05 (p-value = 6.54E-05) was achieved when analysing the five materials, which proves that the NOx reductions achieved were significant. The minimal reductions beyond Coalgae® 10% show possibilities that further increase in microalgae loading might results in increased NOx formation as Kucukvar and Tatari (2011) reported increased levels of NOx at higher microalgae blending ratios. However, the hypotheses that microalgae co-firing will reduce NOx emissions from baseline coal can be accepted for all Coalgae® blends.

5.4 IMPLICATIONS IN POLLUTANT REDUCTION IN FIXED BED CO-COMBUSTION

The co-utilisation of coal and biomass in fixed bed boilers results in pollutant reduction. Most notable is the impact on the emissions of NOx, SO2 and CO2. The NOx and SO2 emissions can be explained not only in terms of lower N and S contents in the biomass compared to the coal, but also to competitive char burnout and influence of mineral matter on S capture, respectively.

Some speculation for the influence of co-combustion on pollutant formation via route complete breakdown of the volatiles to smaller fragments such as acetylene followed by C2/C4 addition to form larger PAH and soot can be made. During the co-combustion of coal and biomass, the effect of biomass addition to coal combustion (Ross et al, 2007). The effect of biomass addition to coal combustion has been seen in this work whereby earlier ignition of microalgae biomass assists the ignition of coal.

Studies of temperatures in a domestic fixed bed (Ross et al, 2007) found that biomass burns at a lower temperature, and adding biomass to coal reduces the temperatures both above and within the bed. It was proposed that this was mainly a result of the lower calorific value of the fuel. However, in this study the addition of microalgae biomass to coal increased the peak temperature (Figure 5.3) and this was associated to higher volatiles compared to coal. Therefore it is possible that this, combined with the large
amounts of oxygenated volatiles (from the biomass) increases the production of volatile
organic compounds and PAH/soot via the C2/C4 addition route.

Combustion studies indicate that strong interaction can be observed. The combustion tests
showed that, ignition of biomass char in the blend aids the ignition of the coal char. As a
result, mixtures reach maximum temperatures faster than seen for coal.

5.5 ASH ANALYSIS

Ash residues that remained after combustion tests of coal and Coalgae® were weighed
and analysed. Ash analysis was performed to give a partial view on the effect of ash on
deposition. SEM and EDX analyses were performed to characterize the morphology of
ash and detect metals that exist in ash. Elemental composition of ash was analysed to
determine the content of unburned carbon as well as combustion efficiency of coal and
Coalgae®. XRF analysis was performed to determine the mineral composition of coal
and Coalgae® ash.

5.5.1 Ash residue

The initial mass of coal and Coalgae® blends of 5% - 20% burned, as well as the mass of
ash obtained after combustion tests are given in Table 5.2. The ash content (%) of each
material was calculated using Equation 5.1 and compared with the ash content which was
determined by proximate analysis in Chapter 4.

\[
\text{%Ash} = \frac{\text{mass of ash (g)}}{\text{mass of fuel (g)}} \times 100
\] (5.1)
Table 5.2: Mass of fuels burned and mass of ash after combustion tests.

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Mass burned (g)</th>
<th>Mass of ash (g)</th>
<th>% Ash (calculated)</th>
<th>% Ash (Proximate analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>200</td>
<td>32.2</td>
<td>16.1</td>
<td>15.01</td>
</tr>
<tr>
<td>Coalgae® 5%</td>
<td>200</td>
<td>30.0</td>
<td>15.0</td>
<td>14.92</td>
</tr>
<tr>
<td>Coalgae® 10%</td>
<td>200</td>
<td>29.2</td>
<td>14.6</td>
<td>14.67</td>
</tr>
<tr>
<td>Coalgae® 15%</td>
<td>200</td>
<td>28.6</td>
<td>14.3</td>
<td>13.88</td>
</tr>
<tr>
<td>Coalgae® 20%</td>
<td>200</td>
<td>27.8</td>
<td>13.9</td>
<td>12.99</td>
</tr>
</tbody>
</table>

The ash content calculated from the ash residues after combustion of coal and Coalgae® 5% - 20% was slightly higher than the one determined with proximate analysis. However, the difference is very minimal (up to 1.09) and could be caused by the presence of unburned carbon in ash residue as shown in Table 5.4.

5.5.2 SEM/EDX analysis of ash from coal and Coalgae® blends

Figure 5.15 and 5.16 present the SEM images of ash from coal and Coalgae® 5% - 20% at various degrees of magnification (20 µm, 50 µm and 100 µm). The SEM images of coal (A,B,C), Coalgae® 5% (D,E,F), Coalgae® 10% (G,H,I), Coalgae® 15% (J,K,L) and Coalgae® 20% (M,N,O) all show the presence of mineral matter and solid organic matter. Mineral matter (labelled M in Figure 5.15-A) is indicated by a lighter grey to white colour...
while organic matter (labelled O in Figure 5.15-A) is indicated by dark grey colour (Lallier-Verges et al., 1991). Combusted Coalgae® blends produce more volatiles and char combustion peaks compared to coal. The heat released from volatiles combustion accelerates the char combustion, so that these two stages are overlapping forming the resulting ash. For example, in the Coalgae® blends, there is a possibility of swelling of the particle during volatiles combustion and the ash is seen to bubble at the end of experiment (Figures 5.15 and 5.16). The swelling might be due to higher fluxing elements (Ca and Mg) in Coalgae® blends compared to coal as shown by EDX data in Table 5.3. At lower co-firing ratios (Coalgae® 5% and 10%) the bubble is not very visible as compared to the higher co-firing ratios (Coalgae® 15% and 20%) which have low carbon, e.g. oxygenated species released at the early stage of conversion. XRF data presented in Figure 5.22 confirms an increase in fluxing elements (Ca, Mg) as microalgae to coal ratio increases. Coal on the other hand shows no bubble in the ash as lower Ca and Mg are shown by EDX (Table 5.3) and XRF (Table 5.4) analyses.
Figure 5.15: SEM images of ash of coal (A,B,C) and ash of Coalgae® 5% (D,E,F).
Figure 5.16: SEM images of ash of Coalgae® 10% (G,H,I), ash of Coalgae® 15% (J,K,L) and ash of Coalgae® 20% (M,N,O).
Figure 5.17 – 5.21 show the elemental spectra of coal and Coalgae® 5% - 20% respectively, obtained from electron dispersive X-ray spectrophotometer (EDX). The elemental identification by EDX of coal and Coalgae® 5% - 20% showed strong peaks of aluminium (Al), silicon (Si), oxygen (O) and titanium (Ti) could be observed within the ashes of coal and Coalgae® blends. Carbon (C), nitrogen (N), sulphur (S), magnesium (Mg), iron (Fe), phosphorus (P), potassium (K), calcium (Ca) and chlorine (Cl) were also found in ashes of coal and Coalgae® blends. These elements were also identified and quantified from XRF analysis. The presence of catalytic elements such as K and Ca which influences combustion of solid fuels (Svoboda et al., 2000; Safar et al., 2019) was further confirmed through EDX. As shown in Figure 5.1, Coalgae® blends burned faster than coal.

Table 5.3: Qualitative elemental composition of ash based on EDX results.

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>Elemental composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Coal</td>
</tr>
<tr>
<td>Mg</td>
<td>MgO</td>
<td>0.45</td>
</tr>
<tr>
<td>Al</td>
<td>Al₂O₃</td>
<td>10.45</td>
</tr>
<tr>
<td>Si</td>
<td>SiO₂</td>
<td>10.47</td>
</tr>
<tr>
<td>P</td>
<td>P₂O₅</td>
<td>2.61</td>
</tr>
<tr>
<td>K</td>
<td>K₂O</td>
<td>1.17</td>
</tr>
<tr>
<td>Ca</td>
<td>CaO</td>
<td>2.78</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO₂</td>
<td>0.90</td>
</tr>
<tr>
<td>Fe</td>
<td>FeO</td>
<td>5.59</td>
</tr>
</tbody>
</table>

Coal and Coalgae® blends are characterised by high proportions of Al- and Si-bearing minerals (associated with kaolinite and quartz) which decrease with increasing microalgae to coal ratios and low proportions of Ca-Mg compounds, Fe (pyrite) and Ca (calcite) which increase with decreasing microalgae to coal ratios. Ti (rutile) was also found in minor proportions (Table 5.3- qualitative EDX and 5.4- quantitative XRF).
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Figure 5. 17: EDX spectrum of coal ash.

Figure 5. 18: EDX spectrum of Coalgae® 5% ash.
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Figure 5.19: EDX spectrum of Coalgae® 10% ash.

Figure 5.20: EDX spectrum of Coalgae® 15% ash.
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Figure 5.21: EDX spectrum of Coalgae® 20% ash.

5.5.4 XRF analysis

The elemental analysis of ash which remained after the combustion tests of Coalgae® blends with coal as a reference is shown in Table 5.4.

Table 5.4: Elemental composition of ash of coal and Coalgae® blends by XRF.

<table>
<thead>
<tr>
<th>Elements (%)</th>
<th>Coal</th>
<th>Coalgae® 5%</th>
<th>Coalgae® 10%</th>
<th>Coalgae® 15%</th>
<th>Coalgae® 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>27.726</td>
<td>25.719</td>
<td>24.13</td>
<td>19.475</td>
<td>18.191</td>
</tr>
<tr>
<td>SiO</td>
<td>45.989</td>
<td>38.601</td>
<td>33.748</td>
<td>31.063</td>
<td>27.828</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.992</td>
<td>4.113</td>
<td>4.744</td>
<td>5.813</td>
<td>7.912</td>
</tr>
<tr>
<td>SO₃</td>
<td>_</td>
<td>0.172</td>
<td>0.179</td>
<td>0.207</td>
<td>0.216</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.051</td>
<td>1.219</td>
<td>2.151</td>
<td>3.029</td>
<td>3.134</td>
</tr>
<tr>
<td>CaO</td>
<td>5.624</td>
<td>7.987</td>
<td>9.818</td>
<td>11.451</td>
<td>12.714</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>TiO</th>
<th>5.861</th>
<th>5.741</th>
<th>5.575</th>
<th>5.526</th>
<th>5.151</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrO</td>
<td>0.106</td>
<td>0.116</td>
<td>0.117</td>
<td>0.121</td>
<td>0.129</td>
</tr>
<tr>
<td>MnO</td>
<td>0.076</td>
<td>0.120</td>
<td>0.152</td>
<td>0.248</td>
<td>0.285</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.048</td>
<td>0.054</td>
<td>0.238</td>
<td>0.274</td>
<td>0.291</td>
</tr>
<tr>
<td>SrO</td>
<td>0.772</td>
<td>0.917</td>
<td>1.044</td>
<td>1.052</td>
<td>1.208</td>
</tr>
<tr>
<td>ZrO</td>
<td>0.143</td>
<td>0.156</td>
<td>0.167</td>
<td>0.186</td>
<td>0.221</td>
</tr>
<tr>
<td>MgO</td>
<td>_</td>
<td>0.395</td>
<td>0.440</td>
<td>0.459</td>
<td>0.569</td>
</tr>
<tr>
<td>B/A</td>
<td>0.189</td>
<td>0.270</td>
<td>0.356</td>
<td>0.468</td>
<td>0.568</td>
</tr>
</tbody>
</table>

*B/A - base/acid ratio = (Mg+K+Ca+Fe)/ (Al+Si+Ti) (5.1)*

The ash residues of all the five materials tested in this study are composed mainly of SiO and Al<sub>2</sub>O<sub>3</sub> followed by Fe<sub>2</sub>O<sub>3</sub>, CaO, TiO, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O. Other elements were present in minor quantities and therefore this section will focus on these seven significant elements. The ash of coal composed mostly of SiO and Al<sub>2</sub>O<sub>3</sub> which were 45.989% and 27.726% respectively. The coal ash contained minor quantities of fluxing elements Fe<sub>2</sub>O<sub>3</sub> (8.358%), CaO (5.624%), K<sub>2</sub>O (1.051%) and MgO (0%); therefore, ash is relatively refractory and is unlikely to cause slagging and fouling (Van Alphen, 2005). Similarly, the ash of Coalgae® blends composed mostly of SiO and Al<sub>2</sub>O<sub>3</sub> but these elements decreased with increasing microalgae co-firing ratio. This can be seen clearly in Figure 5.22 showing the major elements of the five materials studied. On the other side, the fluxing elements (Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, CaO and MgO) increased with increasing microalgae co-firing ratio, resulting in increased base/acid ratio from 0.189 with baseline coal up to
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0.568 with Coalgae® 20%. P₂O₅ also increased significantly from baseline coal (1.99%) to Coalgae® 20% (7.91%), while TiO decreased insignificantly.

![Elemental analysis in ash of coal and Coalgae® blends](image)

**Figure 5.22: Elemental analysis (reported as oxides) in ash of coal and Coalgae® 5% - 20%.

The increase of fluxing elements in ash of Coalgae® blends is likely to cause fouling on the grate. Additionally, the formation of clinkers was experienced with the ash residues from the co-firing of Coalgae®15% and Coalgae® 20%. The ash clinkers formed with Coalgae® 20% are demonstrated in Figure 5.23 (b) and coal ash (a) for reference.
Although the Coalgae® ash clinkering did not cause damage to the fixed-bed combustion system (on the lab-scale) used in this study, this may result in considerable effects on large boilers as mass loading are large and the temperature gets very high. Even though Coalgae® 15% and 20% showed significant emission reductions of CO₂, SO₂ and NOx, co-firing ratios beyond 10% are not recommended for future work due to potential risks of fouling caused by ash deposition.

### 5.6 COMBUSTION EFFICIENCY

The co-firing of microalgae biomass and coal is a potential way of reducing net CO₂ emissions in coal power plants. Biomass co-firing may result in increased or decreased combustion efficiency compared to coal depending on the characteristics of different blends and combustion environments (McIlveen-Wright et al., 2011; Sahu et al., 2014). Combustion efficiency, also referred to as burnout of carbon, was calculated using the Equation 5.2 (Diez et al., 2015). Combustion efficiency calculated in this study refers to the measure of how well coal and Coalgae® blends burned during the combustion tests.

\[
n_c(\%) = 1 - \frac{C_{\text{unburned}}}{C_{\text{initial}}} \times 100
\]  

(5.2)
Where;

\[ n_c = \text{the combustion efficiency in } \% \]
\[ C_{\text{unburned}} = \text{the content of unburned carbon in ash fraction} \]
\[ C_{\text{initial}} = \text{the content of carbon in coal and Coalgae® blends} \]

The data used to calculate combustion efficiency is shown in Table 5.5. \( C_{\text{initial}} \) is the carbon content in Figure 4.2 (ultimate analysis) but on a dry basis and \( C_{\text{unburned}} \) was calculated from carbon content in initial samples and carbon content in ash samples (Equation 5.3).

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Carbon in fuel (%, db)</th>
<th>Carbon in ash (%, db)</th>
<th>Combustion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>68.54</td>
<td>9.32</td>
<td>86.40</td>
</tr>
<tr>
<td>Coalgae® 5%</td>
<td>66.57</td>
<td>1.96</td>
<td>97.06</td>
</tr>
<tr>
<td>Coalgae® 10%</td>
<td>65.07</td>
<td>0.99</td>
<td>98.48</td>
</tr>
<tr>
<td>Coalgae® 15%</td>
<td>64.65</td>
<td>0.67</td>
<td>98.96</td>
</tr>
<tr>
<td>Coalgae® 20%</td>
<td>64.40</td>
<td>0.71</td>
<td>98.90</td>
</tr>
</tbody>
</table>

The carbon which remained unburned in ash residue and combustion efficiency/carbon burnout of coal and Coalgae® blends are depicted in Figure 5.24 and Figure 5.25, respectively. The unburned carbon is inversely proportional to combustion efficiency. The carbon in ash was determined by elemental analysis using the method in Section 3.3.2. The percentage unburned carbon was calculated from the data in Table 5.4, using Equation 5.3.
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\[ \% \text{Unburned carbon} = \frac{\text{Carbon in fuel}}{\text{Carbon in ash}} \times 100 \] (5.3)

Figure 5.24: Effect of microalgae co-firing on unburned carbon.

The unburned carbon decreased with increasing microalgae co-firing ratio and this positively affected the combustion efficiency/carbon burnout of Coalgae® blends which increased by up to 14% from baseline coal to Coalgae® 20%. The increase in combustion efficiency in Coalgae® blends was associated with their reactivity (high volatile matter) compared to coal. The structure of coal is very complex and makes it difficult to combust completely due to less reactivity, hence the high unburned carbon compared to Coalgae® blends.
Figure 5.25: Effect of microalgae co-firing on combustion efficiency.

The combustion efficiency increased insignificantly from Coalgae® 10% to Coalgae® 15% (increased by 0.6%) and slightly decreased at Coalgae® 20%. This shows that microalgae co-firing ratio beyond 10% are not necessary as these result in decreased combustion efficiency due to increase in moisture content. High moisture content in biomass blends is one of the factors that can affect the efficiency of combustion (McIlveen-Wright et al., 2011; Sahu et al., 2014). Another factor which negatively impacts the burnout of carbon is the increased composition of fluxing elements (CaO, Fe₂O₃ and K₂O) (Li et al., 2009) in Coalgae® blends as was shown in Table 5.3.

The addition of biomass to coal reduces the ash fusion temperature of coal due to increased fluxing elements (Pokothoane, 2010). The 0.06% decrease in combustion efficiency of Coalgae® 20% from Coalgae® 15% suggests that the high combustion temperature (Figure 5.3) affects the rate of char reaction. The presence of an inorganic-rich layer on the char surface acts as a barrier of oxygen diffusion to the reacting surface (Li et al., 2009). This ash layer may form when the char is oxidized on or near the external surface of the particle, leaving mineral constituents on the char surface (Lunden et al.,...
The fluxing elements melt at high temperatures during the late stage of combustion as these minerals get exposed when most of the char conversion has occurred, whereas during early combustion stage these minerals are protected by carbon as carbon does not melt at typical temperatures. This melting of minerals blocks the oxygen access to the active site of carbon and reduces the availability of carbon on the char matrix (Lunden et al., 1998; Li et al., 2009).

The combustion efficiency plot shows that Coalgae® 10% burned more efficiently compared to coal and Coalgae® 5% and that it is not necessary to increase the microalgae co-firing ratio beyond 10% as the was no significant change thereafter. Although Coalgae® 15% and Coalgae® 20% showed better ignition properties than coal, Coalgae® 5% and Coalgae® 10%, the fluxing compounds had a significant effect in the combustion efficiency of these fuels due to partial or total carbon encapsulation by molten ash.

5.7 MASS BALANCE

Mass balances were determined for the combustion of four coal and Scenedesmus microalgae blends: Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20%. In addition, the mass balance for the combustion of lumpy coal was included as a reference. Equation 5.4 shows the mass balance used in a thermochemical conversion system of the five fuels. Mass inputs include the mass contents of an element $i$ both in the Coalgae® fuels and in the combustion air. On the other side, mass outputs include the mass contents of the element $i$ in the flue gas and bottom ash.

\[ m_{i,\text{fuel}} + m_{i,\text{air}} = m_{i,\text{gas}} + m_{i,\text{ash}} \] (5.4)

Where $m_{i,j}$ is the mass fraction of an element $i$ in a constituent $j$: the constituents are the fuel (Coalgae® blends and coal), the combustion air, the flue gas and the bottom ash. In this study, the mass balance of the combustion of the Coalgae® blends and coal was determined for three major elements: carbon (C), nitrogen (N) and sulphur (S). Mass balance was performed relative to 200 g of fuels burned. The ashes and tars that were
trapped inside the combustion system were neglected when calculating the mass balance. The fly ash was not measured in this study and therefore it was also neglected when calculating the mass balance.

Figure 5.26 summarises the recovered mass of the major elements (C, N and S) in the gas and ash from 200 g of the fuels burned. The C, N and S amounts in the ash were measured using an elemental analyser (ultimate analysis) while the C, N and S amounts in the gas were calculated from CO₂, NOx and SO₂ measured using a Lancom 4 portable gas analyser (calculations attached as a separate document for clarity, last page).

<table>
<thead>
<tr>
<th>Fuels (g)</th>
<th>C</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>131</td>
<td>0.98</td>
<td>3.04</td>
</tr>
<tr>
<td>Coal/5%</td>
<td>127</td>
<td>0.95</td>
<td>5.48</td>
</tr>
<tr>
<td>Coal/10%</td>
<td>124</td>
<td>0.79</td>
<td>5.52</td>
</tr>
<tr>
<td>Coal/15%</td>
<td>123</td>
<td>0.78</td>
<td>5.56</td>
</tr>
<tr>
<td>Coal/20%</td>
<td>122</td>
<td>0.74</td>
<td>6.43</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gases (g)</th>
<th>C</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>129</td>
<td>0.96</td>
<td>0.41</td>
</tr>
<tr>
<td>Coal/5%</td>
<td>117</td>
<td>0.38</td>
<td>0.21</td>
</tr>
<tr>
<td>Coal/10%</td>
<td>96</td>
<td>0.31</td>
<td>0.24</td>
</tr>
<tr>
<td>Coal/15%</td>
<td>119</td>
<td>0.34</td>
<td>0.19</td>
</tr>
<tr>
<td>Coal/20%</td>
<td>105</td>
<td>0.25</td>
<td>0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash (g)</th>
<th>C</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>2.99</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>Coal/5%</td>
<td>0.29</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>Coal/10%</td>
<td>0.26</td>
<td>0.19</td>
<td>0.01</td>
</tr>
<tr>
<td>Coal/15%</td>
<td>0.19</td>
<td>0.21</td>
<td>0.01</td>
</tr>
<tr>
<td>Coal/20%</td>
<td>0.09</td>
<td>0.33</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 5.26: Mass balance of major elements (carbon, nitrogen and sulphur).
Carbon presented an expected combustion reaction process. Almost all carbon was recovered in the flue gas as CO$_2$ emissions. Recovery of carbon as CO$_2$ emissions ranged between 96 – 119 g for Coalgae® blends randomly. On the other hand, carbon recovered as CO$_2$ emissions from coal combustion was 129 g. The insufficient carbon on the flue gas may have been due to lack of precision in the measurements of gas flow rate at the chimney, emissions of CO and formation of CHx radical. The recovery of carbon in the ash residue decreased with increasing microalgae co-firing ratio from 2.99 g for baseline coal to 0.09 g for Coalgae® 20%. Therefore, this means that the more microalgae biomass is added to coal, the higher is the consumption of carbon during the combustion process. Furthermore, higher consumptions of carbon during a combustion reaction could be associated to higher reactivity of Coalgae® blends compared to coal.

Similarly, sulphur presented expected combustion reaction process. In the case of sulphur, the recovery of sulphur in the flue gas as SO$_2$ emissions ranged between 0.25 – 0.96 g from baseline coal to Coalgae® 20%. The sulphur recovered in the flue gas was quite low compared to the starting sulphur. This may have been caused by the presence of radicals formed such as H· and CHx·, leading to SO$_2$ reduction due to H$_2$S and H$_2$O formation (Merryman and Levy, 1967; Wielgosinski, 2012). In the ash residue, sulphur increased with increasing microalgae co-firing ratio from 0.06 g with baseline coal to 0.33 g with Coalgae 20%. These results are in agreement with the XRF results as the increasing sulphur was observed in the form of SO$_3$. This further explains the reductions in SO$_2$ emissions as sulphur was retained in ash due to presence of high alkaline compounds.

Nitrogen on the other hand presented an unexpected combustion reaction process. The nitrogen recovered from both flue gas and ash residue was extremely low. The recovery of nitrogen as NOx ranged between 0.17 – 0.41 g in the flue gas and 0.10 – 0.01 g in the ash residue. The low recovery of nitrogen was associated to a complex mechanism of nitrogen oxidation during the combustion reaction. Figure 5.27 shows that during the nitrogen oxidation, radicals such as NHx and HCN are formed which are further decomposed to N$_2$ at high temperatures (Williams et al., 2001; Kubica et al., 2001). Hence
nitrogen is much lower in the product side compared to the nitrogen in the starting material.

Figure 5. 27: Schematic representation of coal and Coalgae® combustion showing the major combustion steps together with NOx reaction pathways (Williams et al., 2001; Kubica et al., 2001).
Chapter 6

6 SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 SUMMARY

The motivation to conduct this study was the increasing environmental challenges emanating from the utilization of fossil fuels, particularly coal. The study encourages the utilization of green energy to minimize the environmental burden and diversify the energy supply, particularly in South Africa. The study was conducted to evaluate the effect of co-firing microalgae and coal on greenhouse gas emissions. Coal fines were blended with Scenedesmus microalgae slurry at mass ratios of 95:5, 90:10, 85:15 and 80:20 to form Coalgae® 5%, Coalgae® 10%, Coalgae® 15% and Coalgae® 20%, respectively. Properties of the newly formed Coalgae® blends were determined and compared to properties of coal. Coalgae® combustion tests were performed in a bed-fixed reactor and through TG-MS analysis. Mass reduction, combustion temperature and emissions of CO₂ (%), SO₂ (ppm), and NOₓ (ppm) were measured during combustion tests. Characterisation analysis conducted in this study included SEM/EDX, FT-IR and XRF.

The results presented in this study showed better combustion behaviour when coal was co-fired with microalgae at low mass ratios. The addition of microalgae to coal significantly increased the volatile matter which resulted in faster ignition compared to pristine coal. The ash content, which is one of the combustion setbacks, was reduced by up to 13.5% from baseline coal to Coalgae® 20%. The results also showed emission reductions with all the Coalgae® blends. CO₂ emission reductions of up to 31.5% were achieved with Coalgae® 20% blend, followed by 23.5%, 19.5% and 14.9% which were achieved with Coalgae® blends of 15%, 10% and 5%, respectively. SO₂ emissions were significantly reduced by up to 18.2% with Coalgae® 20%, followed by 15.8%, 10.6% and 1.9% achieved with co-firing ratios of 15%, 10% and 5%, respectively. Even though
Coal, *Scenedesmus* microalgae and their blends (Coalgae® 5% – 20%) were successfully characterized and subjected to combustion. The co-combustion of coal and microalgae confirmed a synergistic effect due to different combustion characteristics of coal and microalgae. The ignition temperature and the burnout temperature of the mixed char decrease with the increase of the microalgae mixture ratio, thus, improving the combustion performance of the blends (Coalgae® 5% – 20%). The combustion process of coal consists of one reaction, whereas, for microalgae and the Coalgae® blends, the process consists of three reactions. The addition of microalgae biomass improves the combustion behaviour and efficiency of coal. The activation energy decreased significantly from baseline coal (161.3 kJ/mol) to Coalgae® 20% (134.2 kJ/mol) relative to increasing microalgae proportion. From the results obtained in this study, it is evident that the co-firing of coal and microalgae biomass significantly reduces the emissions of CO₂, SO₂, and NOx. The CO₂, SO₂ and NOx emissions were reduced by up to 31.5%,
18.2% and 26.1%, respectively. The decrease in the emissions of CO\textsubscript{2} and SO\textsubscript{2} was due to the relative decrease in carbon and sulfur content. Additionally, the reduction of NOx was attributed to the complex combustion mechanism of NOx in the presence of radicals resulting in shorter combusting time. The ash of Coalgae\textsuperscript{®} blends showed characteristic of slagging and fouling as observed by their dense and bubble like surface resulting from higher amounts of Ti, Fe, Ca and K obtained as compared to coal. The aim of this research was achieved, and the objectives set were relevant, therefore, the hypothesis of this study is accepted.

6.3 RECOMMENDATIONS

To declare the coal and microalgae co-firing technology successful and for it to be possible to be implemented, the following recommendations were made during the study:

- It is recommended that a full scale test on a boiler be done in order to determine the required ignition time, stoker speed, boiler output and possible clinker formation or fouling.
- It is recommended to test the coal and microalgae co-firing technology on a large-scale to test combustion factors such as slagging and fouling as these were not detected in a laboratory-scale fixed-bed reactor used in this study.
- Microalgae co-firing ratios beyond 10% are not recommended for existing boilers as ratios of 15% and 20% showed possibly slagging and fouling characteristics. However, a study which will focus on ash deposition during coal and microalgae co-firing is recommended as it would give a clear indication as up to what maximum blending ratio can microalgae biomass be co-fired with coal.
- To grow microalgae with flue gas obtained from coal and microalgae co-firing, to further decrease levels of CO\textsubscript{2} and NOx emissions is also recommended. The nitrogen in NOx would be recycled and consumed as a nutrient and likewise with CO\textsubscript{2}. This would also lower the costs of microalgae cultivation.
• Life Cycle Assessment study is recommended to ensure that other possible environmental burdens are taken into consideration and not only the energy conversion impact.
REFERENCES


Western Climate Initiative (2007). Coal meeting the climate challenge: Technology to reduce greenhouse gas emissions.


APPENDICES

Appendix A: Stoichiometric air required to burn Coalgae® blends at 30% excess air

A.1 Stoichiometric calculations for Coalgae® 5%

Stoichiometric calculations for the amount of oxygen required to burn Coalgae® 5% are laid out in a tabular basis for better presentation (Table A.1).

<table>
<thead>
<tr>
<th>Coalgae® 5% (ad)</th>
<th>Mass (kg/kg)</th>
<th>O₂ required (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.6339</td>
<td>2.67 \times 0.6339 = 1.693</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0506</td>
<td>8 \times 0.0506 = 0.405</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0274</td>
<td>2.29 \times 0.0274 = 0.063</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0047</td>
<td>1 \times 0.0047 = 0.0047</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1342</td>
<td>-0.1342</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1492</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>1.000</td>
<td>2.166</td>
</tr>
</tbody>
</table>

The stoichiometric oxygen of each component of Coalgae® 5% was determined independently and summed to obtain a total of 2.166 kg oxygen required to burn 1 kg of Coalgae® 5%. The stoichiometric air (air to fuel ratio) required to burn 1 kg of Coalgae® 5% was calculated by dividing oxygen required by mass fraction of air:

\[
A/F = \frac{2.166}{0.233} = 9.296 \text{ kg air/kg Coalgae® 5%}
\]

(Note: air consist of 21% O₂ and 79% N)

Excess air of 30% was used and the actual A/F ratio became:

\[
\text{Actual } A/F = 9.296 \times 1.3 = 12.085 \text{ kg air/kg Coalgae® 5%}
\]

Air flow rate (AFR) required to burn 200 g (0.2 kg) of Coalgae® 5% in 180 min was calculated and expressed in l/min. Density of air was assumed to be 1.2 kg/m³.
A.2 Stoichiometric calculations for Coalgae® 10%

Stoichiometric calculations for the amount of oxygen required to burn Coalgae® 10% are laid out in a tabular basis for better presentation (Table A.2).

<table>
<thead>
<tr>
<th>Coalgae® 10% (ad)</th>
<th>Mass (kg/kg)</th>
<th>O₂ required (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.6182</td>
<td>2.67 x 0.6182 = 1.651</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0510</td>
<td>8 x 0.0510 = 0.408</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0276</td>
<td>2.29 x 0.0276 = 0.063</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0040</td>
<td>1 x 0.0040 = 0.0040</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1525</td>
<td>-0.1525</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1467</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.000</strong></td>
<td><strong>2.126</strong></td>
</tr>
</tbody>
</table>

The stoichiometric oxygen of each component of Coalgae® 10% was determined independently and summed to obtain a total of 2.126 kg oxygen required to burn 1 kg of Coalgae® 10%. The stoichiometric air (air to fuel ratio) required to burn 1 kg of Coalgae® 10% was calculated by dividing oxygen required by mass fraction of air:

\[
A/F = \frac{2.126}{0.233} = 9.124 \text{ kg air/kg Coalgae® 10%}
\]

(Note: air consist of 21% O₂ and 79% N)

Excess air of 30% was used and the actual A/F ratio became:

\[
\text{Actual } A/F = 9.124 \times 1.3 = 11.861 \text{ kg air/kg Coalgae® 10%}
\]

Air flow rate (AFR) required to burn 200 g (0.2 kg) of Coalgae® 10% in 180 min was calculated and expressed in l/min. Density of air was assumed to be 1.2 kg/m³.

\[
\text{AFR} = 11.861 \times \frac{0.2}{(1.2 \times 180)} = 0.011 \text{ m}^3/\text{min} = 11.0 \text{ l/min}
\]
A.3 Stoichiometric calculations for Coalgae® 15%

Stoichiometric calculations for the amount of oxygen required to burn Coalgae® 15% are laid out in a tabular basis for better presentation (Table A.3).

**Table A. 3: Stoichiometric oxygen required to burn 1 kg of Coalgae® 15%**.

<table>
<thead>
<tr>
<th>Coalgae® 15% (ad)</th>
<th>Mass (kg/kg)</th>
<th>O₂ required (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.6139</td>
<td>2.67 x 0.6139 = 1.639</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0525</td>
<td>8 x 0.0525 = 0.420</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0283</td>
<td>2.29 x 0.0283 = 0.065</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0039</td>
<td>1 x 0.0039 = 0.0039</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1626</td>
<td>-0.1626</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1388</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.000</strong></td>
<td><strong>2.128</strong></td>
</tr>
</tbody>
</table>

The stoichiometric oxygen of each component of Coalgae® 15% was determined independently and summed to obtain a total of 2.128 kg oxygen required to burn 1 kg of Coalgae® 15%. The stoichiometric air (air to fuel ratio) required to burn 1 kg of Coalgae® 15% was calculated by dividing oxygen required by mass fraction of air:

$$\frac{A/F}{\text{kg air/kg Coalgae® 15%}} = \frac{2.128}{0.233} = 9.133$$

(Note: air consist of 21% O₂ and 79% N)

Excess air of 30% was used and the actual A/F ratio became:

$$\text{Actual A/F} = 9.133 \times 1.3 = 11.873 \text{ kg air/kg Coalgae® 15%}$$

Air flow rate (AFR) required to burn 200 g (0.2 kg) of Coalgae® 15% in 180 min was calculated and expressed in l/min. Density of air was assumed to be 1.2 kg/m³.

$$\text{AFR} = 11.873 \times (0.2/ (1.2 \times 180)) = 0.0109 \text{ m}^3/\text{min} = 10.9 \text{ l/min}$$
A.4 Stoichiometric calculations for Coalgae® 20%

Stoichiometric calculations for the amount of oxygen required to burn Coalgae® 20% are laid out in a tabular basis for better presentation (Table A.4).

Table A. 4: Stoichiometric oxygen required to burn 1 kg of Coalgae® 20%

<table>
<thead>
<tr>
<th>Coalgae® 20% (ad)</th>
<th>Mass (kg/kg)</th>
<th>O₂ required (kg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.6108</td>
<td>2.67 x 0.6108 = 1.686</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.0561</td>
<td>8 x 0.0561 = 0.449</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0302</td>
<td>2.29 x 0.0302 = 0.069</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0037</td>
<td>1 x 0.0037 = 0.0037</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1693</td>
<td>-0.1693</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1299</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>1.000</td>
<td>2.208</td>
</tr>
</tbody>
</table>

The stoichiometric oxygen of each component of Coalgae® 20% was determined independently and summed to obtain a total of 2.208 kg oxygen required to burn 1 kg of Coalgae® 20%. The stoichiometric air (air to fuel ratio) required to burn 1 kg of Coalgae® 20% was calculated by dividing oxygen required by mass fraction of air:

\[
A/F = \frac{2.208}{0.233} = 9.476 \text{ kg air/kg Coalgae® 20%}
\]

(Note: air consist of 21% O₂ and 79% N)

Excess air of 30% was used and the actual A/F ratio became:

\[
\text{Actual } A/F = 9.476 \times 1.3 = 12.319 \text{ kg air/kg Coalgae® 20%}
\]

Air flow rate (AFR) required to burn 200 g (0.2 kg) of Coalgae® 20% in 180 min was calculated and expressed in l/min. Density of air was assumed to be 1.2 kg/m³.

\[
\text{AFR} = 12.319 \times (0.2/ (1.2 \times 180)) = 0.0114 \text{ m}^3/\text{min} = 11.4 \text{ l/min}
\]
Appendix B: Experimental data for emissions

B.1 Emissions of CO₂ at different air flow rates

![Graph showing CO₂ concentrations over time for different air flow rates and fuel types.](image)

**Figure B1.1:** CO₂ concentrations measured over time.

![Graph showing CO₂ concentrations over time for different air flow rates and fuel types.](image)

**Figure B1.2:** CO₂ concentrations measured over time.
Figure B1. 3: CO₂ concentrations measured over time.

Figure B1. 4: CO₂ concentrations measured over time.
Figure B1. 5: CO₂ concentrations measured over time.

B.2 Emissions of SO₂ at different air flow rates

Figure B2. 1: SO₂ concentrations measured over time.
Figure B2. 2: SO$_2$ concentrations measured over time.

Figure B2. 3: SO$_2$ concentrations measured over time.
Figure B2. 4: SO$_2$ concentrations measured over time.

Figure B2. 5: SO$_2$ concentrations measured over time.
B.3 Emissions of NOx at different air flow rate

Figure B3.1: NOx concentrations measured over time.

Figure B3.2: NOx concentrations measured over time.
Figure B3. 3: NOx concentrations measured over time.

Figure B3. 4: NOx concentrations measured over time.
Figure B3. 5: NOx concentrations measured over time.
Appendix C: Mass balance calculations

The C, N and S values in fuel (g) were calculated as follows:

CNS (ultimate analysis) * initial mass of fuel (used for combustion in a fixed bed reactor)

For C, N and S values in ash (g);

Ash (values from ultimate analysis)/ 100)*mass of ash (residue left after combustion in a fixed bed reactor)

Then C, N, S values in gas (g) were calculated from CO₂, SO₂ and NOx (concentration readings from the Lancom 4 portable gas analyser) as follows;

First convert the concentrations of CO₂, SO₂, and NOx (ppm) into grams as follows;

For CO₂: CO₂ (ppm) *1.84 = mg/m³ * (air flow rate/1000) = mg/1000 = g then sum the mass of measured readings Total mass/ MW (CO₂) * MW (C) = g of C
For SO₂: \((21 - 6) / (21 - \text{O}_2 \text{measured}) \times \text{SO}_2 \text{ (ppm)} \times 2.86 = \text{mg/m}^3 \times (\text{air flow rate/1000}) = \text{mg/1000} = \text{g}\) then sum the mass of measured readings Total mass/ \(\text{MW (SO}_2) \times \text{MW (S)}\) = g of S

For NOx: \((21 - 6) / (21 - \text{O}_2 \text{measured}) \times \text{NOx \ (ppm)} \times 2.05 = \text{mg/m}^3 \times (\text{air flow rate/100}) = \text{mg/1000} = \text{g}\) then sum the mass of measured readings Total mass/ \(\text{MW (NOx)} \times \text{MW (N)}\) = g of N
IT WAS NOT EASY! BUT, IT WAS WORTH IT!!!

I THANK YOU LORD FOR THE WISDOM, STRENGTH AND UNCONDITIONAL LOVE!!!