

Co-combustion of coal and biomass in a fluidised bed reactor

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Eduardo Garcia,
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*Dedicated to **Tilia***

Not everything that can be counted counts, and
no everything that counts can be counted.

Albert Einstein

Abstract

For decades coal has been the main energy source for electricity generation in many parts of the world. Coal combustion is the most intensive producer of CO_2 , the main greenhouse gas (GHG) in the atmosphere. The continued dominance of fossil fuels, particularly coal, in the energy mix has been going on for decades due to the slow uptake of low-carbon technologies. Among others, co-combustion of coal and biomass is quite a promising alternative in the short-term to achieve major cuts in GHG and pollutant emissions. Nevertheless, the current inability to address technical factors linked to the characteristics of biomass in terms of ash issues during combustion or modification of ash quality limits the increase of biomass ratio in co-combustion. The pursuit of new resources to substitute coal has prompted consideration of the use of woody materials, herbaceous biomass or waste from the agro-industrial sector.

The aim of this research was to investigate the combustion behaviour of coal and biomass blends using a pilot-scale bubbling fluidised bed reactor. The blends were prepared with a traditionally used biomass fuel (i.e. wood) and selected rich in alkali-metals biomass fuels (i.e. wheat straw and spent coffee grounds (SCG)) to investigate the potential of SCG as a fuel and the effect of ilmenite on agglomeration tendency when used as an additive and alternative bed material. To elucidate the interaction between the fuels in the blends and the effect of ash composition, thermogravimetric and ash fusibility studies were performed looking at both the parent fuels and blends.

Initially, thermogravimetric studies focused on understanding the thermal decomposition of coal blended with by-products (spent coffee ground (SCG), and coffee husk (CH)) of coffee crop. Blends with wood were included for comparison purpose. The blends were prepared by blending coal with biomass at 10, 30 and 50 wt%. The experiments were performed under inert and oxidising conditions to elucidate the thermal behaviour and fuel interactions. The results showed that the inclusion of either spent coffee grounds or coffee husk in coal combustion can enhance the combustion performance.

Indeed, the blends with spent coffee grounds were found to be more reactive than those with coffee husk and with similar characteristics to the blends with wood. It was attributed to the existence of synergistic effects. These results offer compelling evidence of the potential of by-products from the coffee crop, especially spent coffee ground for energetic applications.

The study of ash fusibility characteristics investigated the ash fusibility temperatures under oxidising conditions of coal ash blended with ash from spent coffee grounds. Blends with wheat straw ash were included for comparison purpose. Particular attention was paid to the blending ratio effect on ash fusibility temperatures. The results showed that SCG is an interesting fuel in co-processing due to the low ash content and high ash fusibility temperatures when blended with coal. The high ash fusibility temperatures of the blends were attributed to the high content of CaO , MgO , and P_2O_5 in SCG with negligible content of SiO_2 and Cl , complementing the high content of Al_2O_3 and Fe_2O_3 in coal. Evidence from this study suggests that the high ash fusion temperatures in the blends of coal with spent coffee grounds can reduce the common operational issues related to biomass ash such as agglomeration. This can also provide confidence for large scale thermochemical conversion systems fuelled by such kind of coal and biomass blends to be able to maintain long-term stable operation.

The final part of this research focused on co-combustion experiments in a pilot-scale BFB aiming to investigate the potential of SCG as a fuel, and ilmenite as an additive and alternative bed material. For comparison purpose blends of coal with wheat straw and wood pellets were also combusted in the same BFB reactor under similar combustion conditions. Similarly, kaolin and bauxite, and silica sand were compared to ilmenite when used as an additive and alternative bed material, respectively. The inclusion of biomass in coal combustion showed marked differences in the temperature profiles, gas emissions, and combustion performance. The results showed that coal and SCG blends can be combusted for energy applications with improved combustion efficiency compared to wheat straw and wood commercial pellets. Nevertheless, high N content in SCG represents a challenge in terms of NO_x emissions that should be addressed.

The results from experiments using ilmenite showed improved combustion performance due to reduced values of unburnt carbon in ash and CO emissions when ilmenite was used in comparison with the reference case. It was attributed to the improved oxygen transport capacity of ilmenite. Nevertheless, higher NO_x emissions in comparison with the reference case were found when ilmenite was used as alternative bed material. Ilmenite showed to have potential to reduce the risk of agglomeration when used as an additive and alternative bed material. SEM/EDX and XRF analysis of agglomerates and ash showed the predominantly presence of K and Si in the binder region in all cases, with other refractory elements (i.e. Ca , Al , Mg , and Ti) to a lesser extent. This indicates the existence in the binder of K-Ca-silicates, K-Al-silicates, K-Mg-silicates, K-Ca/Mg silicates, and Fe- Ti-bearing compounds with higher melting temperatures.

Keywords: Co-combustion, Spent Coffee Grounds, Bituminous Coal, Thermogravimetric Analysis, Ash Fusibility Temperatures, Fluidised Bed Combustion, Ilmenite, Agglomeration, Synergistic Effects.

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Chapter 1

Introduction

1.1 Decarbonisation Scenarios Background

For decades fossil fuels have been the main energy source worldwide. These fuels represented over 80 % of the total primary energy use worldwide in 2015 [Agency for Natural Resources and Energy, 2017]. Among the fossil fuels coal is the main resource for electricity generation in many parts of the world. It represented approximately 28 % of the world's total primary energy supply (TPES) in 2015, corresponding to electricity production and emitting 8.56 Gt of carbon dioxide (CO_2) emissions (45 % of the global emissions) [IEA, 2017]. The large worldwide reserves of coal make it attractive for its proven stability in supply and cost.

Coal combustion is the most intensive producer of CO_2 , the main greenhouse gas (GHG) in the atmosphere. The continued dominance of fossil fuels, particularly coal, in the energy mix has been going on for decades due to the slow uptake of low-carbon technologies [IEA, 2017] [IEA, 2016b] [Gupta et al., 2014]. Fossil fuel combustion, mainly coal, has led to a significant increase in CO_2 concentration in the atmosphere over the past century. In the pre-industrial era, the average concentration of CO_2 was about 280 parts per million (ppm). In 2016, the average concentration of CO_2 (403 ppm) was about 40 % higher than values in the mid-1800s. Similar growing trends have also been observed in the level of methane (CH_4) and nitrous oxide (N_2O) [IEA, 2017]. By 2030, it is predicted a CO_2 global annual emission

of approximately 60 Gt, which will represent about double the 2005 level of 27.8 Gt [IEA, 2017]. The environmental impact of high levels of CO_2 , NO_x , SO_2 , heavy metals and particulate emissions from coal combustion have triggered several research efforts to decrease the amount of pollutants emitted in terms of the energy produced.

Most of the research activities have been focused on thermal efficiency improvements, use of alternative fuels, or carbon capture and storage (CCS) technologies. The use of biomass in co-combustion with coal is considered a feasible alternative in the short-term to achieve major pollutant emission reductions from the coal power sector due to the neutral CO_2 nature of biomass [Guo and Zhong, 2018] [Sirisomboon and Kuprianov, 2017] [Karampinis et al., 2014] [Reddy, 2014] [Agbor et al., 2014]. Co-combustion may allow the use of fuels with reduce quality and low prices by their blending with better quality and more expensive fuels for balancing purpose [Morris et al., 2018]. Indeed, the use of biomass in co-combustion with coal provides an alternative to decrease GHG emissions from coal fired power plants, with higher efficiencies than dedicated biomass power plants [Nuamah et al., 2012b].

In recent decades, more than 200 power and combined heat and power (CHP) plants using co-combustion in pulverised coal (PC) and fluidised bed boilers (FBB) have shown promising results with reduced impact on boiler efficiencies [Agbor et al., 2014] [Karampinis et al., 2014]. So far, most of the biomass used comes from wood crops, but other resources such as straw, miscanthus and wastes have been considered to a less extent. Nevertheless, the maximum ratio of wood in the fuel blend in most commercial applications has been up to 5 - 10 % (energy basis). Currently, 20 % is feasible and more than 50 % is technically achievable [Reddy, 2014] [IRENA, 2013]. Despite a higher biomass ratio means lower GHG emissions, the current inability to address technical factors linked to the characteristics of biomass in terms of ash issues during combustion or modification of ash quality limits the increase of biomass ratio in co-combustion.

Co-combustion in FBB allows higher biomass ratios when compared to PC boilers. The capacity to operate with bigger particles size and handle a broader range of solid fuels may reduce operational costs when FBB are the selected option. In addition, higher efficiency could be achieved in FBB due to the improved mixing, reduced unburned carbon in the ash and the possibility to operate at temperatures below the ash sintering of most of the fuels ash. Nonetheless, there is still a need for addressing major challenges which are not widely understood such as the interactions of the fuels during the process and agglomeration of ash.

1.2 Problem Statement and Research Motivation

Co-combustion of coal and biomass is quite a promising alternative in the short-term, but it still faces unsolved challenges. Higher biomass ratios of either woody materials or herbaceous biomass in FBB could have a negative effect on combustion efficiency and GHG emissions. Additionally, the high level of alkali-metals in biomass ash could increase the severity of the agglomeration phenomenon and lead to bed defluidisation even at low ratios. The pursuit of new resources to substitute coal has prompted consideration of the use of waste from the agroindustrial sector such as oil palm shells, rice husk or olive oil industry by-products.

Recently, spent coffee grounds (SCG), a by-product from the coffee industry, has drawn attention to be used as a substitute of coal [Kourmentza et al., 2018] [Le et al., 2017]. Its availability in large quantities, higher heating value in comparison with other biomass resources and ease for densification due to reduced particle size and high lignin content make this resource potentially viable for co-combustion applications. SCG shows higher content of nitrogen and high alkali-metals content in ash compared to other traditionally used biomass resources [Wei et al., 2018] [Jeguirim et al., 2016] [Campos-Vega et al., 2015]. This raises a number of challenges about GHG emissions, and ash sintering and agglomeration. A few studies have investigated the co-combustion of coal with SCG in fluidised beds, this alternative is not completely understood yet and further research is needed.

The use of additives and alternative bed materials is one of the most effective measures to reduce the ash agglomeration phenomenon [Morris et al., 2018]. Several natural minerals such as kaolin, bauxite, dolomite, and alumina have shown good results in decreasing agglomeration tendency when biomass is used [Niu et al., 2016a] [Dahlquist, 2013]. Recently, as part of a novel concept called Oxygen Carrier-Aided Combustion (OCAC) used in fluidised beds, another natural mineral namely ilmenite, has shown potential to improve the combustion efficiency while decreasing the ash issues originated from the alkali-metals in the biomass [Thunman et al., 2013]. Most of the attention has been on the effect on combustion efficiency and GHG emissions with promising results. Nevertheless, few researchers have investigated the effect of ilmenite on agglomeration tendency when used as an additive or alternative bed material. This particular area remains unclear for co-combustion of coal and biomass blends.

This research aimed to investigate the combustion behaviour of coal and biomass blends using a pilot-scale bubbling fluidised bed reactor. The blends were prepared with a traditionally used biomass fuel (i.e. wood) and selected rich in alkali-metals biomass fuels (i.e. wheat straw and spent coffee grounds (SCG)) to investigate the potential of SCG as a fuel and the effect of ilmenite on agglomeration tendency when used as an additive and alternative bed material.

The specific objectives of this research were as follows:

- To investigate the potential of spent coffee grounds as a biomass fuel in co-combustion with coal in terms of most representative flue gas emissions (CO_2 , CO , and NO_x), combustion performance, agglomeration tendency, and ash behaviour compared to blends of coal with wood and wheat straw at the same ratio (i.e. 40 wt%) in a pilot-scale fluidised bed reactor.
- To investigate the effect of ilmenite on agglomeration tendency and ash behaviour, most representative flue gas emissions (i.e. CO_2 , CO ,

and NO_x), and combustion performance when used as an additive at 10 wt% compared to kaolin and bauxite at the same ratio and as alternative bed material compared to silica sand using coal blended with wheat straw at 40 wt% as fuel in a pilot-scale fluidised bed reactor.

- To study the thermal behaviour of coal blended with by-products (spent coffee grounds and coffee husk) of coffee crop at 10, 30, and 50 wt% compared to blends with wood at the same ratios using thermogravimetric analysis (TGA), studies were performed looking at both the parent fuels and blends.
- To study the ash fusibility temperatures (AFT) of coal blended with spent coffee grounds at 40, 60, and 80 wt% compared to blends with wheat straw at the same ratios, studies were performed looking at both the parent fuels and blends.

Due to the complexity of the pilot-scale fluidised bed reactor facility and operating procedures (it took more than 12 hours to complete one run of experiment), limited numbers of the tests were planned and performed, as shown in Chapter 6.

1.3 Thesis Structure

This work is divided into seven chapters:

Chapter 1 - Introduction

This chapter gives a brief overview background of information regarding the present research project, coal use future scenarios, benefits and challenges of co-combustion as a short-term alternative to reduce *GHG* emissions from coal combustion and the aim and objectives.

Chapter 2 - Literature review

This chapter provides a thorough literature review on classification and properties of solid fuels (coal and biomass), conventional and low-carbon combustion technologies, co-combustion pathways, insights into the combustion

of coal and biomass blends considering pollutant emissions, agglomeration characteristics, detection techniques, and counteraction strategies.

Chapter 3 - Experimental methods

This chapter describes the experimental methods that were implemented in this research to investigate the co-combustion of coal and biomass. It includes a detailed description of the samples preparation, experimental techniques, operational parameters, and analysis of results.

Chapter 4 - Thermogravimetric analysis of blends of coal and biomass with high alkali-metals content

This chapter presents the results from the thermogravimetric analysis (TGA) studies of the thermal decomposition behaviour of coal blended with wood, spent coffee grounds and coffee husk under inert and oxidising atmospheres. The analysis was based on fuel interactions and the occurrence of synergistic effects.

Chapter 5 - Ash fusibility analysis of blends of coal and biomass with high alkali-metals content

This chapter presents the results from the ash fusibility temperatures (AFT) studies of ash blends from coal with wheat straw and spent coffee grounds. The analysis was based on the effect of biomass ash ratio on the fusibility temperatures of the ash blends under oxidising conditions.

Chapter 6 - Co-combustion of bituminous coal and biomass with high alkali-metals content in a fluidised bed combustor

This chapter describes the experimental investigation using blends of coal and biomass in a pilot-scale 30 kW bubbling fluidised bed combustor. The effect of different biomass resources (wood, wheat straw and spent coffee grounds) on *GHG* emissions, combustion performance and agglomeration tendency was studied. Furthermore, several experiments were carried out to study ilmenite as an additive in comparison with kaolin and bauxite, and

as alternative bed material in comparison with silica sand in terms of GHG emissions, combustion performance and agglomeration tendency.

Chapter 7 - Conclusions and Future Work

This chapter summarises the main conclusions regarding the behaviour of coal and biomass blends under co-combustion conditions and ash agglomeration tendency from this research. Outline recommendations for future work are included.

Supplementary information and results necessary to understand this work in detail can be found in the Appendixes.

Chapter 2

Literature Review

This chapter gives an overview of solid fuels used in power generation, coal combustion technologies, and strategies to lessen the environmental impact. Descriptions of the level of deployment, advantages, and disadvantages along with challenges, research needs and future work are included. Special attention is paid to co-combustion in fluidised beds and emerging pathways such as Oxygen-Carrier-Aided combustion (OCAC) concept and the use of non-woody agroindustrial residues as a fuel resource.

It is considered that coal will remain as a key component of the energy electricity generation fuel mix in the coming decades for most of this century [IEA, 2016a] [World Energy Council, 2016] [Lackner et al., 2010] [Nersesian, 2016]. Nevertheless, coal has been proved as one of the most polluting fuels increasing greenhouse gas (GHG) atmosphere concentration and contributing to global warming and climate change significantly [IEA, 2017] [Strezov and Evans, 2015]. Large emissions reductions cannot be achieved as quickly as it is required through decreasing energy use or by substitution of fossil fuels with alternative sources which emit a reduced amount or no CO_2 [Rubin et al., 2012]. Therefore, achieving GHG emissions reduction targets require additional technological approaches such as improving generation efficiency and enhanced energy management through the implementation of clean solid fuels, and low-carbon technologies.

2.1 Solid Fuels

Despite coal being the most popular solid fuel for power and electricity generation at industrial scale, biomass has received attention in recent decades. This is due to concerns about the environmental impact caused by the use of fossil fuels [IRENA, 2013] [Loo and Koppejan, 2008]. The interest in biomass is prompted by the pursuit of alternatives to reduce GHG emissions from power generation [Basu et al., 2011] [Akpulat et al., 2010]. At present, increases in the efficiency and sustainability of energy production technologies from conventional (i.e coal) and alternative (i.e biomass) energy resources are sought to meet the ever-increasing demand [Gupta et al., 2014][Leung et al., 2014] [Miller, 2011] [Loo and Koppejan, 2008]. Both kinds of resources show significant differences in terms of chemical and physical characteristics which determine process efficiency, GHG emissions, and potential use of the by-products obtained.

2.1.1 Biomass

Biomass is an organic material originating from living or recently living (non-fossil) material [Lukasik, 2017], and the only renewable organic resource [Baskar, 2015]. The sources of biomass include whole or parts of plants and trees, animals and micro-organisms. Among the different resources, lignocellulosic materials such as agriculture and forestry residues represent the bulk of terrestrial biomass [Bajpai, 2016]. This kind of biomass is composed mainly by three natural polymers, hemicellulose, cellulose and lignin, along with smaller amounts of pectin, protein, extractives and ash. It can be used as a direct source of energy achieving a dual purpose of energy generation and environmentally friendly disposal [Baskar, 2015].

It is considered that biomass has a reduced contribution to atmospheric GHG emissions [Vassilev et al., 2015]. The CO_2 released during biomass combustion is the same as the CO_2 fixed through photosynthesis during the lifetime of the plant, which is again converted into carbon-rich compounds for reconversion into energy [Strezov and Evans, 2015] [Baskar, 2015]. Nevertheless,

the wide variability in biomass resources is one of the main challenges to use it as a fuel. The biomass composition within a single plant can change with age, stage of growth, cropping season and other conditions. Although challenging variability, using lignocellulosic biomass as a feedstock for renewable carbon represents a promising and sustainable alternative to coal [Lukasik, 2017]. Table 2-1 shows differences in biomass resources in terms of constituents.

Table 2-1: Cellulose, hemicellulose and lignin content in lignocellulosic biomass [Bajpai, 2016].

	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Wheat straw	30	50	15
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Switch grass	45	31.4	12

From Table 2-1, it is evident the variability of hemicellulose, cellulose, and lignin for different groups of sources such as woody, non-woody or agro-industrial residues. In fact, resources from the same kind of source such as hardwood or softwood, show different content of these compounds. This variability is also significant in other compounds found in biomass such as the mineral matter in ash [Bajpai, 2016].

2.1.2 Coal

Coal is an organic sedimentary rock in which the main organic components found are macerals [Speight, 2015]. In coal, macerals are analogous to minerals in inorganic rocks [Robl et al., 2017]. Coal is formed by the decomposition and alteration of fossilised carbon that originates from ancient organic material (i.e. trees, plants, leaves, roots, branches, pollen, and spores) by compaction, temperature, and pressure [Speight, 2015]. Over time, massive amounts of vegetative matter are cyclically accumulated in a saturated envi-

ronment, which provides suitable acidic and anaerobic conditions to prevent full decay leading to peat formation [Robl et al., 2017] [Reddy, 2014].

As decomposition proceeds, degraded components in organic material, such as cellulose and hemicellulose, are the first to be consumed by microorganisms, whilst the more resistant lignin remains [Robl et al., 2017]. As a result of the continued deposition of sediment layers, the peat is compacted and transformed into lignite (brown coal), the initial step in coalification. Moisture within the chemical structure, volatile matter (primarily CH_4) and CO_2 are reduced as pressure compacts organic material into a denser solid [Miller, 2011]. With time, heat and pressure; lignite matures into sub-bituminous coal, then into bituminous coal, and eventually into anthracite. The various stages that occur over time result in the conversion of volatile matter into fixed carbon, leading to an increase in energy density. Coal rank is the term used to define the extent to which the organic matter has progressed [Speight, 2015]. Table 2-2 shows differences in coal ranks in terms of elemental composition and heating value.

Table 2-2: Representation of coalification process in terms of the rank of coal (adapted from [Robl et al., 2017] [Speight, 2015] [Osborne, 2013]).

Rank	Composition, wt%			High Heating Value (MJ/kg) *mmf
	Carbon	Hydrogen	Oxygen	
Peat	48-50	6-8	42-46	<14.65
Lignite	68-72	4.5	24-26	14.65-19.3
Subbituminous coal	74-76	5-6	18-22	19.3-26.75
Bituminous coal	84-90	5-6	8-12	26.75-32.5
Anthracite	92-95	3-4	1-3	>32.5

*moist mineral-matter-free basis

From Table 2-2, it is evident the increase in carbon content and the decrease in oxygen content to the extent the rank moves from lignite to anthracite with the consequent increment in heating value. This characteristic along with the mineral matter found in coal determines the end use of the different coal ranks in the industry.

2.1.3 Coal and Biomass Differences

One of the main differences between coal and biomass is the higher volatile matter content in biomass. It reduces the ignition temperature of biomass. Moreover, biomass contains less carbon and more oxygen, leading to reduced heating values. To determine the potential use of solid fuels and their probable behaviour, there are analysis techniques such as the proximate analysis (moisture, fixed carbon, volatile matter, and ash) and the elemental analysis [Baukal, 2013]. These techniques provide information that can be used to deduce resultant emission precursors (N, S, and Cl) and ash forming elements (K, Na, Ca, Mg, Al, Si, P). Subsequently, this information can be used to analyse potential effects on slagging, fouling and sintering tendency during the process [Leckner, 2007]. In general, coal and biomass differ in several of these properties [Bartels et al., 2008] [Loo and Koppejan, 2008].

Table 2-3: Comparison of physicochemical properties of biomass and coal [Nuamah et al., 2012a].

Property	Coal	Peat	Wood without bark	Bark	Forest residues	Straw	Reed canary grass
Ash db	8.5 - 10.9	4-7	0.4-0.5	2-3	1-3	5	6.2-7.5
Moisture	6-10	40-55	5-60	45-65	50-60	17-25	15-20
LHV (MJ/kg)	26-28.3	20.9-21.3	18.5-20	18.5-23	18.5-20	17.4	17.1-17.5
C (% db)	76-87	52-56	48-52	48-52	48-52	45-47	45.5-46.1
H (% db)	3.5-5	5-6.5	6.2-6.4	5.7-6.8	6-6.2	5.8-6	5.7-5.8
N (% db)	0.8-1.5	1-3	0.1-0.5	0.3-0.8	0.3-0.5	0.4-0.6	0.65-1.04
O (% db)	2.8-11.3	30-40	38-42	24.3-40.2	40-44	40-46	44
S (% db)	0.5-3.1	<0.05-0.3	<0.05	<0.05	<0.05	0.05-0.2	0.08-0.13
Cl (% db)	<0.1	0.02-0.06	0.001-0.03	0.01-0.03	0.01-0.04	0.14-0.97	0.09
K (% db)	0.003	0.8-5.8	0.02-0.05	0.1-0.4	0.1-0.4	0.69-1.3	0.3-0.5
Ca (% db)	4-12	0.05-0.1	0.1-0.5	0.02-0.08	0.2-0.9	0.1-0.6	9

db, dry basis

LHV, low heating value

Table 2-3 shows how the properties of biomass and coal vary significantly, especially in terms of heating value, ash and mineral matter content. Although biomass has a lower heating value, the emission of CO_2 , NO_x , SO_x from biomass are much less compared to coal due to the lower carbon, nitrogen, and sulfur contents [Baskar, 2015]. To illustrate the significance of carbon content, Figure 2-1 depicts the difference between biomass and coal by the Van Krevelen diagram in terms of O:C and H:C ratios on the heating value.

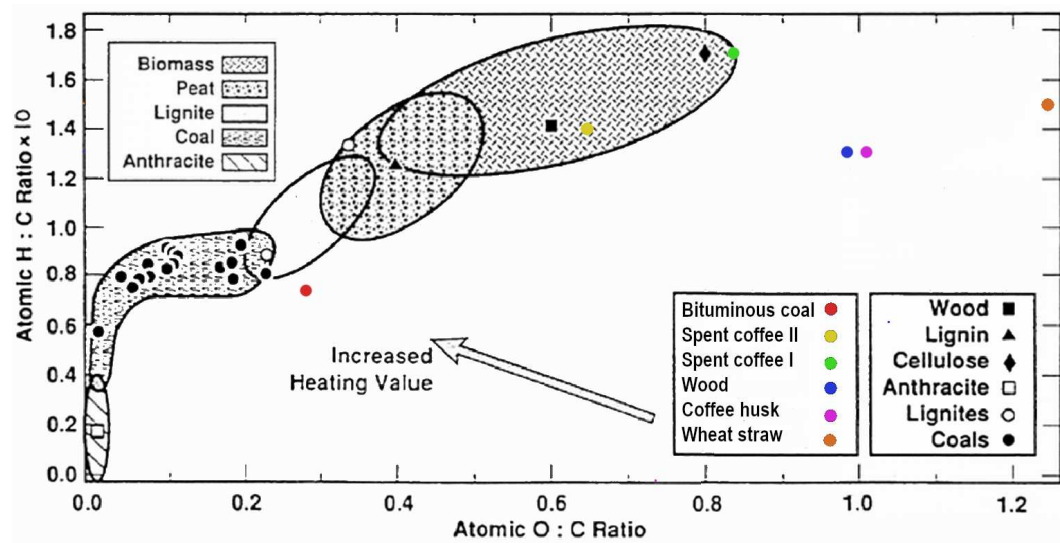


Figure 2-1: Van Krevelen diagram for various solid fuels [Dahlquist, 2013] (coloured dots correspond to the fuels studied in this research).

Figure 2-1 indicates that higher proportions of oxygen reduce the energy value of biomass in comparison to coal. Similarly, to the extent the coal rank move from lignite to anthracite the ratios of H and O reduce compared to C. It is mainly due to the carbon fixation during the coalification process.

2.2 General Principle of Combustion

Combustion is a complex process consisting of consecutive homogeneous and heterogeneous reactions where a fuel material burns directly in the presence of air or oxygen to produce heat [Lackner et al., 2010] [Baukal, 2013]. The main process stages include drying, devolatilisation, volatile combus-

tion, char combustion and gas phase reactions [Basu, 2015]. The oxidation of C and H contained in the fuel are considered the basic reactions leading to the formation of carbon dioxide and water. The determining factors in the process are the composition and physicochemical characteristics of the fuel, and the operational temperature and excess air in the combustion system.

2.3 Coal Combustion Technologies

Coal combustion technologies fall into three principal categories namely fixed bed (i.e. stokers), suspension burning (i.e. pulverised coal) and fluidised beds [Miller, 2011]. Stokers (oldest technology, 1700s) are considered outdated technologies [Cheremisinoff, 2012]. They are mainly used for small and medium industrial scale applications and generally not taken into account when building new coal-fired plants [Robl et al., 2017] [Cheremisinoff, 2012]. This technology uses coarse coal (roughly 95 % less than 32 mm) fed onto a grate, in which coal is heated, dried, devolatilised, and burned, leaving ash material at the bottom of the bed. Although stokers have evolved over the years from a simple design to sophisticated devices, technical challenges such as segregation of fuels, high fly ash carry over and considerable combustible heat loss have led to the reduction of great part of their traditional market to fluidised beds [Lackner et al., 2010] [Loo and Koppejan, 2008].

In suspension burning (pulverised coal, 1910s), based on the combustion of air-entrained pulverised coal (70 - 80 % smaller than $75\text{ }\mu\text{m}$), higher efficiencies can be achieved [Cheremisinoff, 2012]. This technology is by far the most common method of coal burning at large scale [Robl et al., 2017] [Cheremisinoff, 2012]. Among its advantages are the high reliability, adaptability to all coal ranks, full automation, and excellent capacity for increasing unit size. The main disadvantages are the high energy consumption for pulverising coal, high particulate emissions, and high SO_2 and NO_x emissions [Lackner et al., 2010]. Figure 2-2 depicts a schematic diagram of fixed bed and suspension burning of coal combustion technologies.

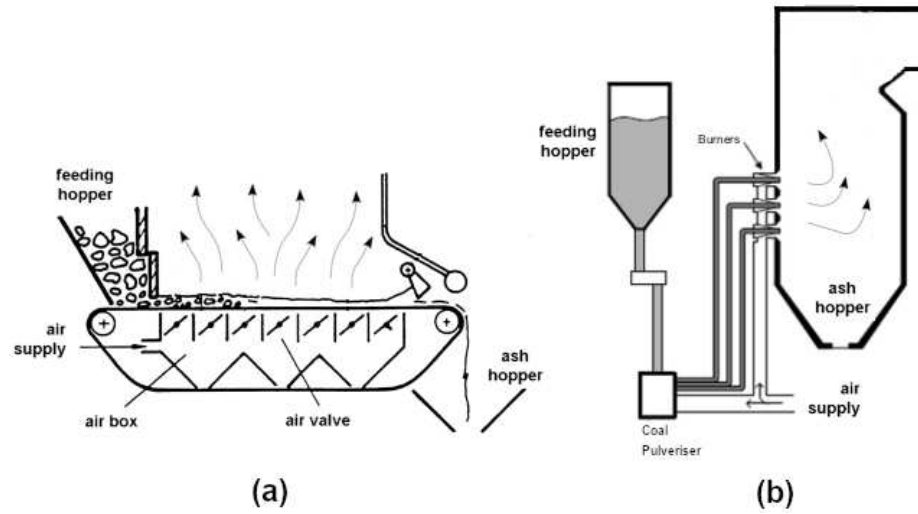


Figure 2-2: Working principle of stoker (a) and pulverised coal (b) combustors (adapted from [Cheremisinoff, 2012], [Miller, 2011] and [Lackner et al., 2010]).

In the last decades, more emphasis has been given to advanced coal technologies with higher thermodynamic efficiency and inherent emission control for reducing SO_x , NO_x , or CO_2 [Robl et al., 2017]. Some of the most promising of these technologies include fluidised bed technologies, both atmospheric and pressurised for coal combustion and gasification [Cheremisinoff, 2012] [Lackner et al., 2010]. Fluidised bed combustion (FBC) of coal is a mature technology that is considered an alternative to building new PC power plants [Cheremisinoff, 2012]. The following section gives further details of the advantages of fluidised bed technology over fixed bed and suspension burning technologies.

2.3.1 Fluidised Bed Combustion Technologies

Fluidised bed systems were implemented to improve the available technology for removing pollutants and to increase the combustion efficiency. These systems have been applied since 1960 for combustion purpose [Lackner et al., 2010] [Loo and Koppejan, 2008]. The fluidised bed technology could be considered between a fixed bed where the fuel particles are rather fixed in the combustor and an entrained flow where the fuel particles are in a state of pneumatic transport [Gupta et al., 2014]. In FBC technology, the fuel par-

ticles are mixed with an inert and granular bed material, which represents more than 90 % of the material in the bed and can contribute to stabilising the combustion process acting as a heat storage medium giving thermal inertia [Gupta et al., 2014] [Lackner et al., 2010].

During the process, the bed material is kept in a state of fluidisation similar to a fluid by the combustion air, which comes from below to fluidise the fuel together with the bed material [Loo and Koppejan, 2008] [Reddy, 2014]. As a result of the vigorous fluidisation and increased mixing level high heat transfer rates are obtained along with improved combustion rates and high efficiencies [Robl et al., 2017] [Gupta et al., 2014].

A fluidised bed combustor can burn coal of any quality including coal with a high ash and sulfur content, biomass or a mixture of both [Nersesian, 2016] [Loo and Koppejan, 2008]. The increased heating rates and combustion efficiencies in fluidised beds allow the design of more compact units than fixed bed and suspension burning technologies, reducing operating and maintenance costs. Lower NO_x and SO_x emissions compared to pulverised coal combustion are due to the operating temperatures (800 - 900 °C) below those required for thermal NO_x formation [Nuamah et al., 2012b]. Furthermore, using added limestone or dolomite to the bed material eliminates the need for a downstream flue-gas treatment as they remove SO_2 during combustion [Robl et al., 2017] [Lackner et al., 2010]. Table 2-4 describes the principal advantages and disadvantages of fluidised bed combustion systems.

Fluidised bed systems could be classified according to the operating pressure and fluidisation velocity. They can be atmospheric fluidised bed (AFB), or pressurised fluidised bed (PFB) systems. Fluidised bed combustion normally operates at atmospheric pressure, however in recent years, PFB has drawn more attention due to the potential to achieve extremely low levels of emissions [Nersesian, 2016] [Lackner et al., 2010]. Classified by the fluidisation velocity, there are two kinds of fluidised systems, bubbling fluidised bed (BFB) and circulating fluidised bed (CFB) [Reddy, 2014] [Nuamah et al., 2012b] [Cheremisinoff, 2012] [Loo and Koppejan, 2008].

Table 2-4: Advantages and disadvantages of fluidised bed combustion systems, (adapted from [Nersesian, 2016] [Reddy, 2014] [Scala, 2013] [Cheremisinoff, 2012] [Miller, 2011] [Lackner et al., 2010] [Spliethoff, 2010] [Basu, 2006] [Oka, 2004]).

Advantages
Fuel flexibility and ability to use a wide range of different fuels.
High heat transfer rates in the bed.
Increased combustion efficiency.
Less fouling and corrosion of furnaces.
Lower temperature operation.
Evenly distributed temperatures, resulting in reduced NO_x emissions.
Substantial reduction of SO_x emissions.
Easy to handle and usefully employed by-product material.
Disadvantages
Relatively large amounts of solid residues generated.
Erosion of combustor walls and heat transfer surfaces.
Higher carbon-in-ash levels than those from pulverised-coal combustion.
Increased N_2O formation, due to the lower combustion temperatures.
Low melting mixtures could lead to agglomeration and latter defluidisation of the bed.
Generation and elutriation of fines and power consumption due to pumping are inevitable.
Higher power demand for fluidisation.

Bubbling Fluidised Bed (BFB)

In a BFB, the bed stays stationary but fluidised in the combustion chamber. The gas velocities range between 1.5 and 2.5 m/s [Reddy, 2014] [Basu, 2006] [Kunii and Levenspiel, 1991]. BFB is a preferred solution in cases of low capacities or where fuels have low heating values, and hence low adiabatic combustion temperatures, as it is the case with biomass [Spliethoff, 2010]. BFB's are normally operated at gas velocities several times higher than the minimum fluidisation velocity [Spliethoff, 2010]. The minimum fluidisation and the terminal velocities of the bed particles limit the air velocity range of a combustor using a BFB [Spliethoff, 2010]. Erosion and corrosion of combustor walls and the in-bed heat transfer surfaces are a problem of the bubbling fluidised beds, and one explanation for them being superseded by circulating systems [Spliethoff, 2010]. A schematic diagram of a BFB

combustor is shown in Figure 2-3b. It consists of a chamber where the fuel is fed into the combustor and fluidised along with the bed material by the air passing through the distribution plate located at the bottom part of the reactor.

Circulating Fluidised Bed (CFB)

A CFB requires a much higher fluidisation velocity of air. The gas velocities range between 4 and 6 m/s [Basu, 2015]. The fluidisation velocity for circulating fluidised beds lies above the terminal velocity, in the transition range to pneumatic transport [Spliethoff, 2010]. As a result, solids continuously leave the combustor. It leads to have a much less dense bed than that in the bubbling fluidised bed but it extends to the top of the chamber [Khan et al., 2009]. In CFB the fluidised bed is circulating between the chamber, which is in the form of a riser then separated usually by a cyclone from the gas and fed back via the return leg into the riser, that is, the fluidised bed is circulating [Gupta et al., 2014]. As a result, the solids are vigorously back-mixed allowing to reach fairly uniform temperatures in the chamber, in the range of 800 - 900°C for optimum combustion and emission control. A generalised schematic of a CFB combustor is shown in Figure 2-3c.

Overall, the operational principle of fluidised combustion technology can be explained in the distinguishing features of all fluidised beds, velocity of air through the chamber and bed expansion, as illustrated in Figure 2-3. For comparison purpose, schematics of a fixed bed and a transport reactor are included, see Figures 2-3a and 2-3d, respectively. In general terms, BFB's have lower fluidisation velocities tending to prevent the solid elutriation from the bed, whilst CFB's use higher velocities to promote the solids elutriation.

At low velocities, the air flows through the void spaces between the solid particles and the bed remains fixed (see Figure 2-3a). When the gas velocity increases to a value higher than the minimum fluidisation velocity, the air flows through the bed as bubbles and the system behaves alike to an agitated fluid, the bed stays stationary but fluidised in the combustion chamber

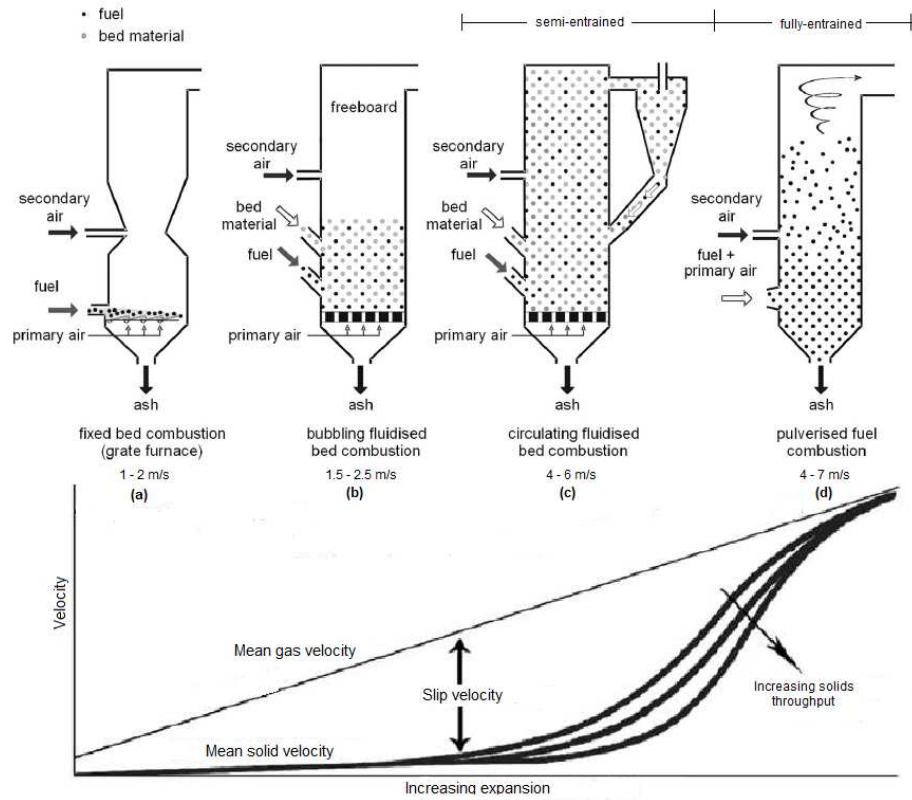


Figure 2-3: Comparison of velocities regimes versus bed expansion, fixed bed (a), bubbling fluidised bed (b), circulating fluidised bed (c), and transport reactor (d), (adapted from [Basu, 2015] [Lackner et al., 2010] and [Miller, 2011] and [Loo and Koppejan, 2008]).

(see Figure 2-3b). When the gas velocity approaches or slightly exceeds the terminal velocity of average particles, the fuel particles are entrained out of the reactor, collected in cyclones, and fed back into the chamber. In this case, the bed fills the entire furnace volume, although most of the mass is still in the lowest third of the bed (see Figure 2-3c). When the fuel particles are in a state of pneumatic transport, the particles are entrained out of the reactor immediately (see Figure 2-3d).

In Figure 2-3, the chart describing the relationship between the velocity and increasing expansion depicts how as long as the gas velocity increases from one regime of operation to another, the solids velocity does not increase that much. This feature leads to an increase in the gas-solid slip velocity. Nevertheless, for a fully entrained bed, the slip velocity drops suddenly to

about the terminal velocity of particles. In general terms, in CFB's the air flow rate is adjusted to that extent that the fuel particles will leave the reactor before they are completely combusted, then collected in a cyclone, and fed back into the combustor. For BFB's, the air flow rate is adjusted to that extent that it is low enough to allow the complete combustion without any need of feeding back into the combustor.

2.3.2 Carbon Capture Technology

The technology of carbon capture and storage (CCS) has arisen as a potential method to reduce carbon dioxide CO_2 emission, which is the principal *GHG* linked to climate change [Ballerat-Busserolles et al., 2018] [Rubin et al., 2012] [Lackner et al., 2010]. The purpose of CO_2 capture technology is to isolate or preconcentrate CO_2 from its high volume sources in a form suitable for transport and subsequent sequestration or long-term storage [Cheremisinoff, 2012] [Miller, 2011] [Spliethoff, 2010]. CCS technology is believed to be a key mitigation technology option to reduce CO_2 emissions from anthropogenic sources [Feron, 2016] [Bhown, 2014]. Although some of the CO_2 capture technologies have been demonstrated with promising results, their implementation and further diffusion in power generation systems still face considerable challenges [Ballerat-Busserolles et al., 2018] [Feron, 2016] [Smit et al., 2014]. The implementation of CCS could contribute around 70 - 80 % of the total cost of a full CCS system including capture, transportation, and storage [Leung et al., 2014]. A lot of research efforts have still to be made to develop affordable technologies allowing generalisation of CO_2 capture facilities throughout the world [Ballerat-Busserolles et al., 2018].

CO_2 capture technologies are classified according to the stage when the CO_2 is captured (see Figure 2-4), pre-combustion (CO_2 capture refers to carbon removal from the fuel prior to combustion, e.g. gasification), post-combustion (CO_2 capture refers to a standard combustion process in a boiler where CO_2 is removed from the flue gas, e.g. amine-based scrubbing systems), and oxy-fuel combustion (refers to coal burning in an atmosphere of oxygen and CO_2 , rather than air) [Ballerat-Busserolles et al., 2018] [Feron,

2016] [Reddy, 2014] [Smit et al., 2014] [Baukal, 2013] [Rubin et al., 2012] [Miller, 2011] [Spliethoff, 2010] [Kavouridis and Koukouzas, 2008]. Other approaches such as chemical looping combustion (CLC) incorporate novel oxygen combustion methods avoiding the need for separation of oxygen from air [Ballerat-Busserolles et al., 2018] [Smit et al., 2014] [Reddy, 2014].

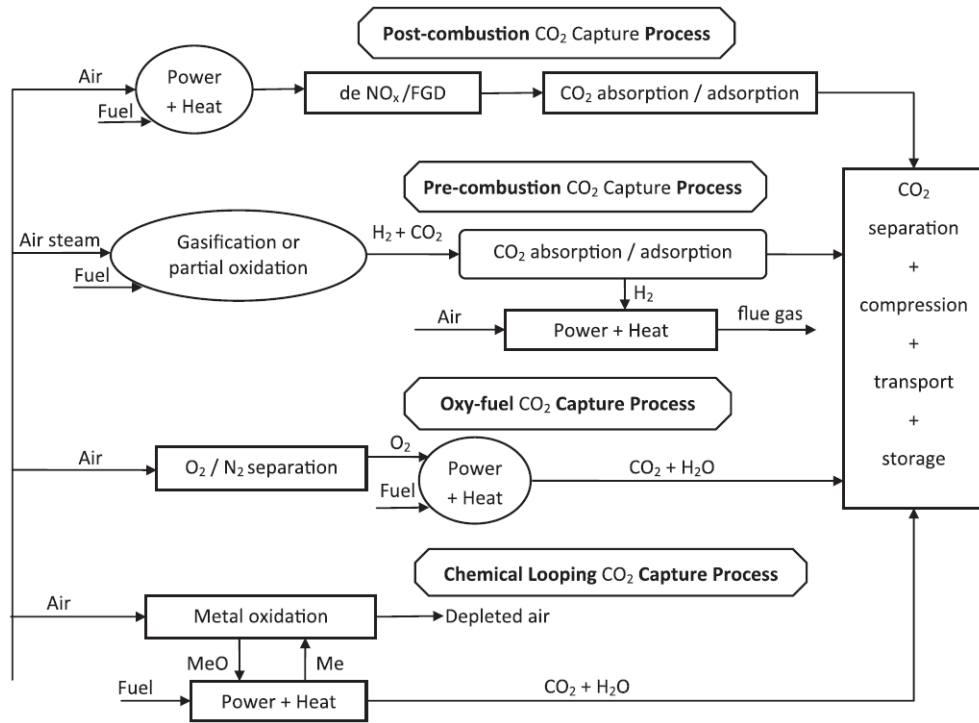


Figure 2-4: CO₂ capture technologies [Leung et al., 2014].

Table 2-5 compares the main advantages and disadvantages of the currently available CO₂ capture technologies and their areas of application. It illustrates CO₂ capture technologies potential to face this problematic situation. Nevertheless, most of them are feasible alternatives to long-term CO₂ reduction such as oxy-combustion and chemical looping combustion [Cheremisinoff, 2012] [Basu et al., 2011]. All these technologies are mainly in the early to mid-stages of development [Ballerat-Busserolles et al., 2018] [Feron, 2016] [Reddy, 2014]. In contrast, partial replacement of coal with biomass in combustion process known as co-combustion is a well-proven technology, which reduces considerably CO₂ and other harmful emissions [Basu, 2013] [Nuamah et al., 2012a] [Saidur et al., 2011] [Shao et al., 2010].

Table 2-5: Advantages and disadvantages of current CO_2 capture technologies, adapted from [Leung et al., 2014] [Miller, 2011].

Capture process	Application Area	Advantages	Disadvantages
Pre-combustion	Solid fuel gasification plants	High CO_2 concentration in flue gas ($> 20\%$) Opportunity to retrofit existing plants	High capital and operating cost
Post-combustion	Solid and gas fired plants	Mature technology Easy retrofitting into existing plants	Low CO_2 concentration in flue gas (7-14 % coal fired; 4 % gas fired)
Oxy-fuel combustion	Solid and gas fired plants	Very high CO_2 concentration, 80 - 98 % due to the use of nearly pure O_2 (95 - 99 %) Mature air separation technology Reduced volume of gas to be treated	High efficiency drop and energy penalty Costly O_2 Production Corrosion problems may arise

Co-combustion has arisen as a short-term alternative for reducing the deleterious effect of coal in electricity and heat production and probably the least complicated and one of the most advantageous ways of utilising biomass for replacement of fossil fuels for stationary energy conversion [Robl et al., 2017] [Tchapda and Pisupati, 2014] [IRENA, 2013] [Khodier et al., 2012]. Among other advantages, co-combustion in comparison with exclusive coal use allows the reduction of harmful emissions such as CO_2 , NO_x , SO_x ,

CO ; lower costs of adapting existing dedicated coal facilities than building new dedicated biomass facilitates [Sahu et al., 2014]. Additionally, co-combustion of coal and biomass might prevent the need for permanent biomass supply because the plant could burn coal if biomass is not available [Nuamah et al., 2012b] [Dai et al., 2008]. Nevertheless, the use of two different fuels raises concerns about the increased complexity of combustion with significant technical and regulatory challenges [IRENA, 2013] [Hupa, 2012].

As regards technical challenges, these are mainly related to the difference between biomass and coal regarding energy density, chemical and physical properties in terms of devolatilisation behaviour, char reactivity, and ash characteristics [Sahu et al., 2014] [Khodier et al., 2012]. These differences have a relevant influence on the amount of coal to be replaced by biomass.

2.4 Co-combustion Opportunities, Drawbacks and Challenges

Co-combustion has been successfully demonstrated in over 150 installations worldwide for a broad variety of feedstocks in several combustor types including pulverised coal, stokers and fluidised beds [Sahu et al., 2014] [Miller, 2011] [Loo and Koppejan, 2008]. Many of these demonstrations have confirmed the possibility to replace up to 20 % and 10 % (energy basis) of the total energy input when woody or herbaceous biomass is used, respectively [Karampinis et al., 2014]. The results have shown that the main modifications have been required in the feeding systems and burners without any relevant influence on the availability of the combustor [Reddy, 2014] [Miller, 2011]. Furthermore, it has been proved that due to fuel flexibility, fluidised bed boilers can substitute higher levels of biomass than pulverised coal or stokers combustors [Miller, 2011]. Negligible effect on the combustion efficiency has been reported for a modest level of replacement of either raw biomass (3 - 5 wt%) or relatively dry biomass (10% $\geq$ moisture) [Karampinis et al., 2014] [Loo and Koppejan, 2008]. Blends with more than 20 % (energy

basis) biomass may require more complex control and additional technical consideration [IRENA, 2012].

Current co-combustion technologies could be classified as direct, indirect and parallel co-combustion [Wladyslaw, 2017]. Figure 2-5 depicts the schematic pathways of these alternatives.

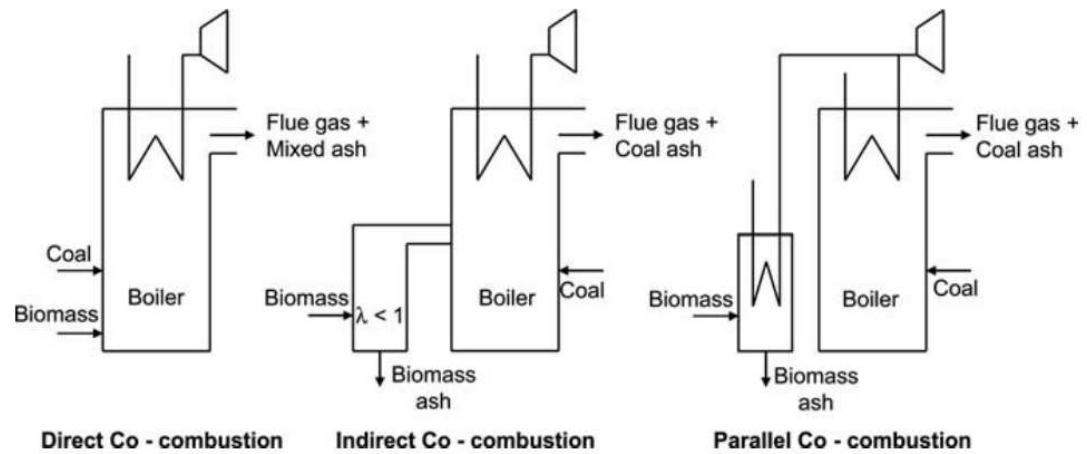


Figure 2-5: Co-combustion technologies pathways [IRENA, 2012] [Spliethoff, 2010].

- **Direct co-combustion:** it is the simplest, cheapest and most common option because of the required modifications are kept to a minimum [Karampinis et al., 2014]. It involves the direct feeding of coal and biomass into the combustor. In this approach, the heat balance should be considered, and high levels of biomass require more sophisticated equipment and fuel handling control systems [IRENA, 2012] [Loo and Koppejan, 2008].
- **Indirect co-combustion:** it is the least common option. This approach first gasifies the biomass, then later combusts the product fuel gas. High levels of fuel flexibility can be used whilst avoiding the use of complex cleaning systems [Nuamah et al., 2012a] [Dai et al., 2008].
- **Parallel co-combustion:** it implies separate biomass combustion, resulting in higher conversion efficiencies. In this approach, the common concerns about biomass ash issues are avoided because the flue

gas from the separate combustor is not in contact with any element of the existing combustor [Karampinis et al., 2014] [IRENA, 2012] [Basu et al., 2011] [Al-Mansour and Zuwala, 2010].

Co-combustion of coal and biomass offers several environmental benefits such as reductions in SO_2 , NO_x , and GHG emissions. In studies to assess carbon emissions for biofuel production and electricity from biomass, it has been reported there is significantly less carbon displacement when producing liquid fuels [Miller, 2011]. It shows that in terms of reducing carbon emissions, it is better to use biomass to produce electricity or heat; especially if carbon from biomass is captured and sequestered. Technical challenges related to fuel preparations, NO_x formation, and ash issues should be considered when co-combustion of biomass with coal is performed [Lackner et al., 2010]. Addressing these challenges is a key factor to achieve higher biomass ratios in the blends.

Combustion of biomass differs from coal combustion due to chemical and physical composition [Karampinis et al., 2014] [Nuamah et al., 2012a] [Chirone et al., 2008]. Biomass is mainly composed by cellulose, hemicellulose, lignin, ash, and other minor compounds. The concentration of each type of compound varies depending on environmental conditions during growing and harvesting [Khan et al., 2009]. Several studies addressing the behaviour of coal and biomass blends under combustion conditions have shown patterns completely different, even for the same species of biomass from a different source [Hupa, 2012]. In fact, compounds in the fuel ash from the blend could interact in a surprising way increasing dramatically operational issues [Zhu et al., 2018b].

2.5 Properties of Fuel Blend

The properties of the blend are influenced by the ratio of biomass in the blend. The chemical and physical characteristics of biomass play a key role in assessing the effect of biomass addition on coal combustion efficiency, emissions, and ash sintering and agglomeration tendency [Luo and Agraniotis,

2017] [Robl et al., 2017][Scala, 2013] [Loo and Koppejan, 2008] [Bartels et al., 2008] [Leckner, 2007]. Table 2-6 shows the physical and chemical characteristics of biomass feedstock and their effects on combustion.

Table 2-6: Physical and chemical characteristics of biomass and their effects on combustion [Nuamah et al., 2012a] [Dai et al., 2008].

	Property	Effects
Physical properties	Moisture content	Storage durability, Low LHV
	Bulk density	Fuel logistics (storage, transport, handling) and feeding problems
	Ash content	Dust, particulate emission, ash utilisation problems and disposal costs
	Particle size, size distribution and shape	Determine fuel feeding, dust formation, operational safety during fuel conveying
Chemical composition	Carbon (C)	HHV
	Hydrogen (H)	HHV (positive)
	Oxygen (O)	HHV (negative)
	Chlorine (Cl)	Corrosion, release of K and Na
	Nitrogen (N)	NO_x , N_2O , HCN emissions
	Sulphur (S)	SOx emissions, corrosion
	Fluorine (F)	HF emissions, corrosion
	Potassium (K)	Lowering of ash melting temperatures, aerosol formation, ash utilisation
	Sodium (Na)	Lowering of ash melting temperatures, aerosol formation
	Magnesium (Mg)	Increase of ash melting temperature, ash utilisation
	Calcium (Ca)	Increase of ash melting temperature, ash utilisation
	Phosphorus (P)	Increase of ash melting point, ash utilisation
	Heavy metals	Emission of pollutants, ash utilisation and disposal issues, aerosol formation

LHV, low heating value

Certain elements in biomass have higher influence during combustion; these include chlorine (Cl), potassium (K), sulphur (S) and silicon (Si). These elements could be in small quantities as low as 1 wt% dry matter, but occasionally much higher than this. In comparison with coal, biomass usually has more Si, Cl, and K and reduced content of iron (Fe), titanium (Ti), aluminium (Al) and sulphur (S), and sometimes more calcium (Ca) [Khan et al.,

2009]. The severity of the effect of these elements on co-combustion varies in different ways according to the blended fuel and its characteristics. In general terms, there is a mutual influence between the components of several fuels [Leckner, 2007]. Figure 2-6 shows the most influential interacting species and their effects.

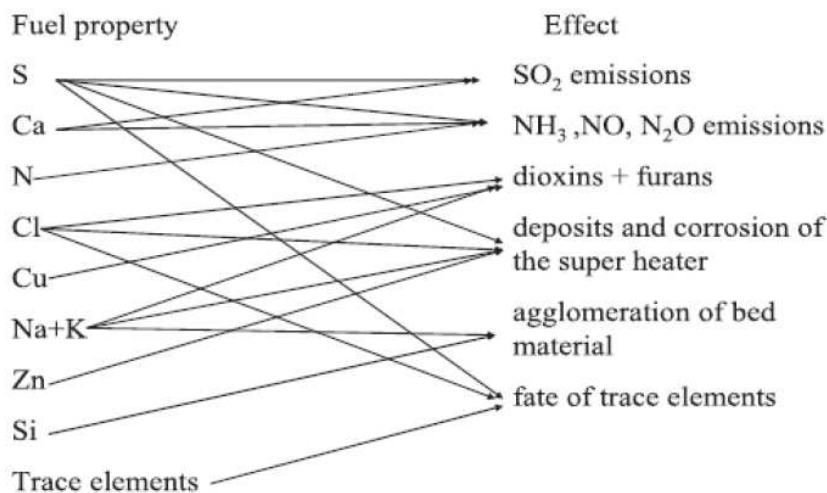


Figure 2-6: Most influential interacting species and their effects during coal and biomass co-combustion [Leckner, 2007].

Figure 2-6 shows that the most relevant elements in terms of effects are S, K, Na, and Cl. These elements represent technical and operational challenges that may compromise the availability of combustors. According to the technology implemented, different effects require more attention than others. In fluidised bed technology, unlike formation of deposit and corrosion of hot surfaces which is a result of extended operation, the risk of agglomeration of the bed material due to higher alkali metals (e.i. K and Na) content in biomass compared to coal represents a technical challenge that could lead to the collapse of the process after a few hours of operation.

2.6 Combustion of Coal-biomass Blends

Combustion consists of several subsequent steps which determine efficiency, by-products, and emissions. The main process steps are drying, devolatilization,

sation, and char oxidation [Baukal, 2013]. All of them consist of consecutive heterogeneous and homogeneous reactions [Hupa, 2012] [Nussbaumer, 2003]. Drying is the expelling of non-chemically bound moisture in the fuel, this has a non-energetic benefit in the process [Lackner et al., 2010]. Furthermore, high moisture contents may affect the quality of combustion due to the possibility of poor ignition, delay in volatiles release and reduction in the combustion temperature [Dai et al., 2008].

The release of volatile matter (VM) is the main aspect in devolatilisation. Higher VM in biomass in comparison to coal leads to higher reactivity and causes different behaviour during combustion [Khan et al., 2009] [Loo and Koppejan, 2008]. Devolatilisation of biomass occurs at a lower temperature than in coal and produces more light gases and tar [Sahu et al., 2014]. In co-combustion, higher VM content in biomass may promote the combustion of coal with high carbon content, creating a counterbalance between each fuel; it might provide better combustion than that for the single fuel [Khan et al., 2009] [Leckner, 2007]. High VM fractions in biomass, requires longer residence times at high temperatures zone for complete combustion, hence higher freeboard heights [Lackner et al., 2010]. When the biomass ratios are low there is no need for significant modification in the combustor.

After the devolatilisation, the remaining solid fraction left as carbonaceous residue is known as char. According to the characteristics of each fuel in the blend and combustion parameters, the char and its reactivity can vary [Sahu et al., 2014]. Inorganic elements and porous structure of char from biomass causes a higher reactivity than that from coal [Loo and Koppejan, 2008]. It may contribute to promote the combustion of char from coal [Dai et al., 2008]. Nevertheless, complex interactions during char combustion may be influenced by process parameters, operating conditions and combustion technology [Sahu et al., 2014]. Additionally, the interaction of char from biomass and coal during co-combustion has a significant effect on emissions and characteristics of the remaining solid fraction after char oxidation known as ash [Scala, 2013] [Dahlquist, 2013] [Loo and Koppejan, 2008].

Co-combustion still has major unsolved technical challenges [Guo and Zhong, 2018] [Fuller et al., 2018] [Karampinis et al., 2014] [Scala, 2013] [Moon et al., 2013] [Liu et al., 2013b]. These challenges include among others, NO_x emissions, particulate matter, deposit and corrosion problems, and ash issues [Karampinis et al., 2014]. Although woody resources are the preferred option for co-combustion in existing coal power plants due to its low ash content and reduced alkali metals, their use raises some concerns about high-intensity use of land and water resources in the crops [Spliethoff, 2010]. Recent developing trends aim to increase the use of herbaceous and other considered troublesome biomass resources [Karampinis et al., 2014], as well as torrefied biomass, which has been identified as a promising alternative to reduce operational costs and facilitate an increase in the biomass ratio in the blends [Chen et al., 2015].

2.6.1 Gaseous Pollutant Emissions

The emissions from solid fuels combustion are mainly CO_2 , CO , NO_x , SO_2 and to a less extent other minor emissions such as volatile organic compounds and particulate matter. Among these pollutants, CO_2 is the major gaseous product, originating from the carbon in the fuel but considered neutral in terms of GHG emissions when biomass is burned [Vassilev et al., 2015] [Lackner et al., 2010]. SO_2 tend to decrease because of lower sulphur content in biomass, while NO_x may increase, decrease, or remain the same, depending on fuel and operating conditions [Khan et al., 2009]. Therefore, the characteristics of the biomass and its ratio in the blend are critical to the emissions obtained under co-combustion conditions as are the operating conditions.

CO_2 and CO Emissions

In co-combustion to keep the same heat input as coal, higher amounts of biomass are required, resulting in no relevant changes in the CO_2 emissions in comparison with the combustion of pure coal. Nevertheless, the CO_2 emitted from biomass does not contribute to the net increase in the CO_2 level of the atmosphere due to the carbon-neutral nature of biomass [Vas-

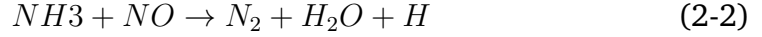
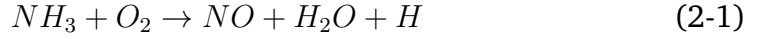
silev et al., 2015] [Dahlquist, 2013]. Although CO emissions are generally produced in trace amounts in combustion, it is a product of incomplete combustion which depends on fuel reactivity, combustion technology, and operation mode [Scala, 2013] [Baukal, 2013] [Lackner et al., 2010]. Among the factors influencing CO emissions are inadequate fuel/air mixing and insufficient residence time for combustion [Miller, 2011].

NO_x Emissions

Nitrogen compounds from solid fuel combustion, commonly known as NO_x , consist of nitrogen oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) [Baukal, 2013] [Miller, 2011]. Commonly, more than 90 % of the NO_x is in the form of NO , approximately 20 to 300 ppm as N_2O and the balance as NO_2 [Reddy, 2014] [Dahlquist, 2013] [Miller, 2011]. NO_x formation is complex and influenced by several factors linked to combustion technology and fuel properties [Loo and Koppejan, 2008]. For instance, NO_x emissions formed during coal combustion are between 90 g/GJ_{LHV} (fluidised bed) to 540 g/GJ_{LHV} (fixed bed) [Reddy, 2014]. NO_x is responsible for causing acid rain and in combination with hydrocarbons leading to ground-level ozone pollution (also called urban smog) [Reddy, 2014]. These pollutants have deleterious effects on both the environment and on the health of humans and animals [Baukal, 2013] [Spliethoff, 2010].

In co-combustion of coal and biomass, NO_x emissions show a more complicated pathway with potential for either less or higher emissions than those from dedicated coal combustion [Karampinis et al., 2014]. The devolatilisation of bituminous coal produces mostly tarry compounds that at high temperatures decay rapidly to hydrogen cyanide (HCN) [Tchapda and Pisupati, 2014] [Glarborg et al., 2003]. In contrast, biomass exhibits a nitrogen conversion behaviour closer to that of low-rank coals, forming mainly ammonia (NH_3), which reduces NO to molecular nitrogen (N_2) (see Equations 2-1 and 2-2) [Sahu et al., 2014]. In general, co-combustion reduces the NO_x emissions in comparison with coal combustion due to the lower nitrogen content of biomass, along with lower conversion rates of NH_3 to NO compared

to HCN , the main product of coal fuel nitrogen [Karampinis et al., 2014] [Xie et al., 2007].



There are three mechanisms for NO_x formation. (1) fuel NO_x : a result of reactions involving the oxidation of organically bound nitrogen in the fuel, (2) prompt NO_x : the fixation of atmospheric nitrogen by hydrocarbon fragments mostly under very low air-fuel ratios, and (3) thermal NO_x : a product of a high-temperature process that requires sufficiently high temperatures for dissociation of the atmospheric diatomic species N_2 and O_2 [Baukal, 2013]. In fluidised bed combustion, in addition to the technical advantage due to enhanced energy efficiency of 45 % compared to 35 % for a pulverised combustion technology, the operational temperatures are insufficient for the formation of thermal NO_x , accounting for a reduction of about 40 - 75 % in NO_x emissions [Nersesian, 2016]. Therefore, the primary contributor of NO_x is the nitrogen in the fuel [Dahlquist, 2013].

The process of formation and reduction of NO_x from fuel nitrogen is complex with many homogeneous and heterogeneous intermediate reactions shown in Figure 2-7. When fuel particle combustion begins, fuel nitrogen is divided between the volatiles phase, mainly NH_3 , HCN and tars-N, and the remaining carbonaceous solid phase known as char, which also contain nitrogen. This partition of fuel nitrogen between char and volatiles, as well as the volatile nitrogen composition, depends on char structure and temperature [Glarborg et al., 2003]. Similarly, it determines the outcome of the subsequent reactions because those for the char nitrogen are completely different from those for the volatile nitrogen [Scala, 2013]. Certainly, compared to coal, biomass fuels produce higher levels of volatile species and lower levels of char, which has a catalytic effect on NO_x formation and reduction due to the availability of a catalytic surface from the char for the NO reduction by CO . Indeed, it is problematic to reduce CO and NO_x simultaneously be-

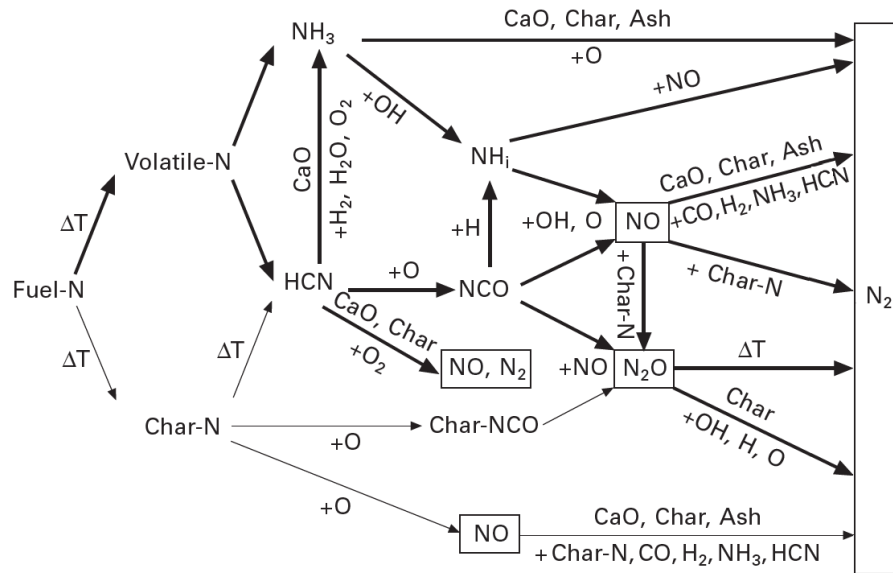


Figure 2-7: Simplified mechanism of NO and N_2O formation. The bold arrows represent the privileged paths for biomass with high volatile matter content that produce very low char nitrogen (Char-N) content, relative to coals [Scala, 2013].

cause decreasing one may result in an increase of the other [Baukal, 2013]. Overall, NO_x forming pathways in coal are therefore completely different from those in biomass fuels [Scala, 2013].

2.6.2 NO_x Reduction Techniques in Fluidised Bed Combustion

Fluidised beds intrinsically produce reduced NO_x due to the lower operating temperatures. Therefore the nitrogen in the fuel is the main source for NO_x emissions. When necessary, additional combustion modifications or flue gas treatment NO_x control can also be adopted [Reddy, 2014] [Miller, 2011]. NO_x reduction techniques applied to FBC include flue gas recirculation, air staging, fuel reburning, low excess air, and reduced air preheat [Miller, 2011] [Spliethoff, 2010]. The most effective measure to limit NO_x emissions in fluidised bed combustion is to decrease excess air [Spliethoff, 2010].

Air staging has proven to be successful to reduce NO_x emissions. It consists of introducing less than the theoretical amount of combustion air through the

distributor plate as primary air and adding the remainder of the combustion air several levels above the dense bed as secondary air [Spliethoff, 2010]. As a result, the nitrogen that is liberated from the fuel in the deficient oxygen zone tends to recombine to inert N_2 and the balance of the air guarantees complete burnout of the fuel and reduces the temperature of the combustion products [Baukal, 2013]. Although air staging allows some of the fuel nitrogen compounds to decompose into N_2 rather than forming NO_x due to the reducing atmosphere in the bed, char and CO concentrations in the bed may increase mainly because CO is formed preferentially to NO under reducing conditions [Baukal, 2013] [Miller, 2011].

2.7 Ash Sintering and Agglomeration

In the thermochemical processing of solid fuels in fluidised bed reactors, one of the most important factors is ash sintering and agglomeration of the bed material. This phenomenon could lead to the loss of fluidisation and compromise the continuity of the process [Singh, 2014] [Heyne and Liliedahl, 2013]. The inclusion of biomass, especially herbaceous biomass, in coal combustion may intensify the technical challenge and complicate even more the combustion due to high alkali metals content of biomass [Coda Zabetta et al., 2013] [Chirone et al., 2008]. In biomass, the alkali metals are homogeneously dispersed in the fuel and may be readily vaporised due to being present in ionic forms or organically bound rather than associated with minerals [Teixeira et al., 2012]. It could lead to easy interactions with the bed material during thermal degradation, originating agglomeration problems or forming deposits on the convective sections of the combustors [Silvennoinen and Hedman, 2013] [Lin and Tsai, 2012]. Appropriate fuel blend control is required by the quality of biomass feedstock and its ratio in the blend to minimise severe impact from this phenomenon [Nuamah et al., 2012b].

Silica sand is the most used bed material for solid fuels combustion [Silvennoinen and Hedman, 2013] [Hupa, 2012]. When the bed material consists of silica sand, alkali metals and silica sand can react forming low-melting silicates, characterised by a lower melting point than the individual compo-

nents [Shao et al., 2010]. It could lead to sintering, a process by which the contact between loosely attached ash particles is increased or strengthened by the diffusion of surface matter across particle boundaries [Morris et al., 2018], and subsequent adhesion of small ash particles on the sand particles [Teixeira et al., 2012]. As a result, the sand particles are coated with a sticky surface that then grows to larger agglomerates due to the formation of permanent bonds upon collisions [Khadilkar et al., 2014][Davidsson et al., 2008]. This process, known as agglomeration, is a major problem in solid fuels thermochemical processing in fluidised beds due to difficult recognition and eventual propagation to the whole reactor, resulting in an unscheduled shutdown for replacement of bed material, which impacts on cost and reliability of the process [Corcoran et al., 2018b] [Gómez-Hernández et al., 2016] [Niu et al., 2016a] [Akram et al., 2015a] [Thy et al., 2010]. Figure 2-8 illustrate the schematic transformation of ash and the formation of agglomerates in a fluidised bed.

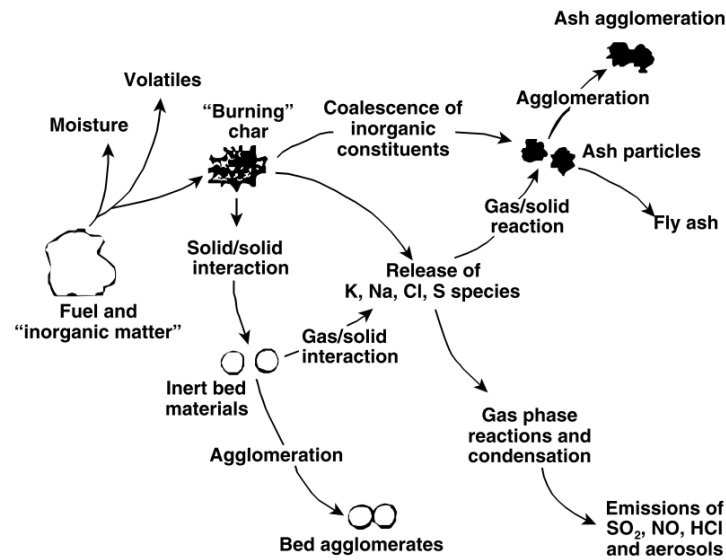


Figure 2-8: Illustration of transformation of ash and formation of agglomerates in fluidised bed combustion [Lackner et al., 2010].

Furthermore, the use of biomass along with coal could impose limitations in ash use due to constituents in biomass. High alkali metals content in biomass may hinder the use of ash in building materials due to undesired changes in ash composition [Fuller et al., 2018] [Saidur et al., 2011]. Simi-

larities in bulk chemical composition of biomass resources of the same kind, may show different behaviour with different ash composition during their thermochemical conversion due to diverse modes of element existence in biomass [Vassilev et al., 2013].

2.7.1 Mechanisms of Agglomeration in a Fluidised Bed at High Temperature

Fluidisation involves transport phenomena and chemical reactions, agglomeration at high temperatures increases the complexity. These two aspects should be considered because agglomeration can affect the hydrodynamics of the bed, and combustion itself involves chemical reactions and migration of material at high temperatures.

Agglomeration may be classified into two kinds: melt-induced agglomeration and coated-induced agglomeration [Morris et al., 2018] [Scala, 2018] [Niu et al., 2016a] [Ninduangdee and Kuprianov, 2015a]. Both mechanisms show similar steps of progression by which the bed particles are covered in an ash layer, building up until a critical thickness is reached, leading to agglomeration [Morris et al., 2018] [Gatternig and Karl, 2015]. In the combustion of solid fuels, the most common mechanism is the coated-induced agglomeration [Gatternig and Karl, 2015] [Mettanant et al., 2009]. The melt-induced mechanism is more relevant when herbaceous biomass is used due to the high alkali metals and silicon content [Ninduangdee and Kuprianov, 2016] [Gatternig and Karl, 2015] [Kaknics et al., 2015].

Figure 2-9 shows the schematic process of the agglomeration mechanisms. The difference between the two mechanisms of agglomeration is based on the fact that in the melt-induced mechanism, the ash is already molten before it deposits over the bed particles, whilst in the coating-induced mechanism the ash is solid and a melt is only formed after a critical eutectic composition is reached in the layer coating the particle [Morris et al., 2018] [Scala, 2018] [Niu et al., 2016a].

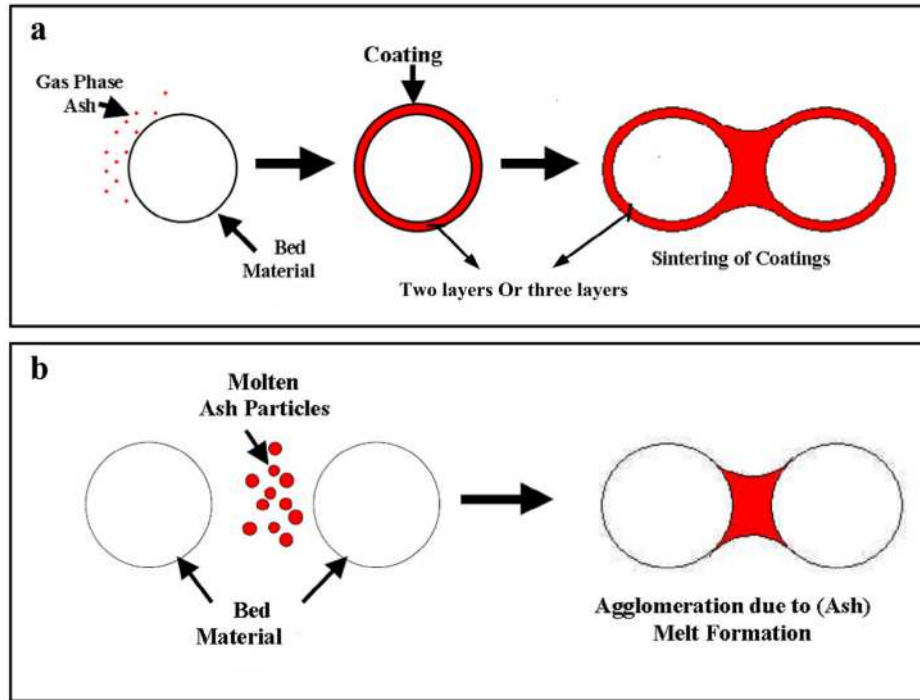


Figure 2-9: Agglomeration mechanisms of bed materials, (a) coated-induced agglomeration and (b) melt-induced agglomeration (adapted from [Niu et al., 2016a]).

Melt-induced Agglomeration

This mechanism is characterised by the formation of melts and later agglomeration due to the interaction of alkali metals and the silica available in the fuel ash [Morris et al., 2018]. Therefore, if the fuel ash contains high quantities of alkali metals, specifically potassium (K), and silica the melt-induced agglomeration may start before the ash encounters the sand particles [Scala, 2018]. Certain kinds of biomass, especially herbaceous biomass such as straw, could lead to extensive agglomeration, as the fuel itself has the necessary elements to create alkali-silicate melts [Gatternig and Karl, 2015]. When biomass rich in silica and alkali metals is used the melt-induced agglomeration mechanism occurs much more quickly than the coating-induced agglomeration mechanism [Morris et al., 2018] [Kaknics et al., 2015]. Woody biomass tends to be the preferred biomass resource for fluidised bed applications as it has lower quantities of alkali metals and therefore a lower tendency for agglomeration to occur [Morris et al., 2018].

Coating-induced Agglomeration

The coating process consists of enriched layers of alkali and earth alkaline metals that interact with the silicon in the bed particles [Kaknics et al., 2015]. These layers are continuously growing due to the formation of sticky alkali silicates of low melting temperatures [Morris et al., 2018]. Despite the large variety of fuels, the formation of two or three layers of coating on the bed particles is a recurrent phenomenon in the coating induced agglomeration mechanism [Morris et al., 2018]. When K-lean ash fuels are used the particles show a two-layer system, with an inner layer rich in Ca-silicate compounds, the outer being a highly porous coating layer resembling the composition of the fuel ash [Morris et al., 2018] [Gatternig and Karl, 2015]. In contrast, K-rich ash fuels show an additional innermost layer rich in silicates and K, giving an indication of the migration of the reactive compounds to the silica grain interface by solid-state diffusion [Scala, 2018] [Gatternig and Karl, 2015]. Figure 2-10 shows the schematic process of coated-induced agglomeration mechanism.

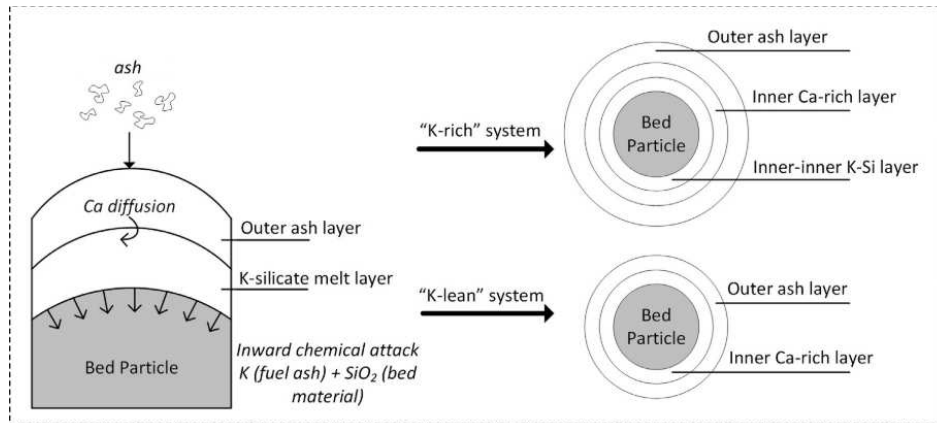


Figure 2-10: Coating-induced agglomeration mechanism in a system with a SiO_2 -based bed material [Morris et al., 2018].

At high temperatures, the layers agglomerate upon contact or collision. The agglomerates may be further strengthened by sintering, leading to the fusion of adjacent particles creating larger agglomerates with hardened structures [Morris et al., 2018] [Mettanant et al., 2009]. At these fluidisation conditions, the larger agglomerates can no longer stay in a fluidised state, leading

to defluidisation of the bed and collapse of the process. Figure 2-11 shows the schematic progression of bed agglomeration in fluidised beds.

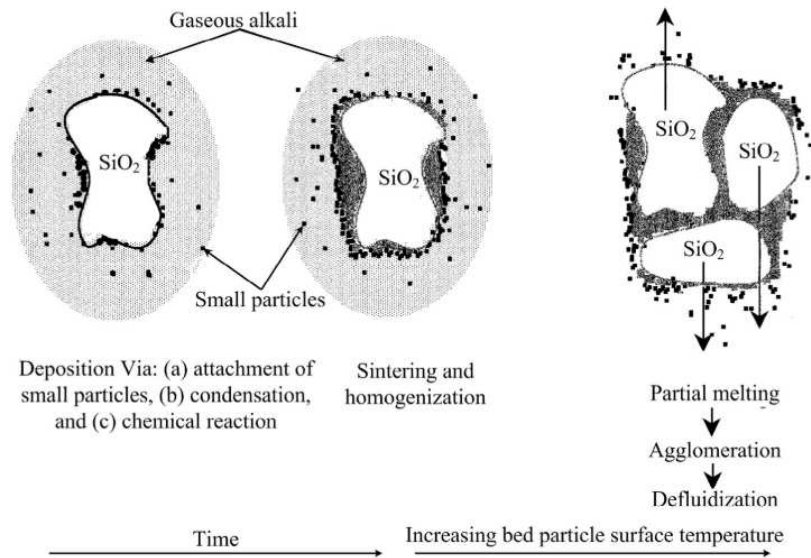


Figure 2-11: Progression of bed agglomeration mechanisms in fluidised beds (adapted from [Niu et al., 2016a]).

The existence of larger agglomerates in the bed with increased size may disturb the fluidisation behaviour of the bed. It could lead to an uneven distribution of temperature, hot spots, and segregation [Bartels et al., 2008]. In addition, both coating-induced and melt-induced agglomeration could be enhanced by sintering leading to even larger agglomerates with increased or strengthened bonds, worsening the agglomeration of the bed [Morris et al., 2018].

2.7.2 Agglomeration Tendency Determination and Detection Methods

The detection of agglomeration is a key factor in the thermochemical conversion of solid fuels in fluidised beds. Several detection methods for agglomeration have been proposed based on fuel ash measurements before processing and the analysis of parameters during the process [Morris et al., 2018] [Bartels et al., 2008]. These methods have been classified into two main groups, processes ex-situ and on-line [Scala, 2018].

The processes ex-situ are based on the fuel ash characterisation and behaviour prediction before the use of the fuel in the fluidised bed. These processes are divided into experimental methods (i.e. simultaneous dilatometry - electrical conductance measurements, standard ash fusion test, and dilatometry or thermal mechanical analysis (TMA)) and theoretical/empirical methods (i.e. thermochemical predictions and indices) [Morris et al., 2018]. These methods are performed outside the fluidised bed and comprise the fuel ash characterisation to assess the likely agglomeration tendency [Scala, 2018]. Although the prediction of agglomeration based on these methods has not shown a high accuracy level [Bartels et al., 2008], they are an inexpensive alternative to characterise the behaviour of fuels under processing conditions, providing useful preliminary information to assess agglomeration tendency.

Online methods use several parameters such as pressure, temperature, and detection of gas phase alkali components to determine agglomeration tendency [Bartels et al., 2008]. In fluidised beds, the measurements of pressure, and temperature at different locations in the reactors are considered the simplest available approach [Scala, 2018]. Changes in these two parameters give a real-time indication of the hydrodynamics in the case of pressure and level of mixing by the differences in the temperature profile across the fluidised bed [Scala, 2018]. Nevertheless, the drop in pressure in the bed could hide the presence of small-scale disturbances due to the measuring of the bed as a whole unit [Morris et al., 2018]. As for temperature measurements, due to the high level of mixing, the detection and identification of located temperatures peaks have been a challenging issue in the agglomeration prediction during fluidised beds operation [Morris et al., 2018]. The location of temperature measurements positions plays a crucial role in terms of the significance of the measurement according to the processing conditions.

Extensive research efforts have been made to increase the accuracy of agglomeration prediction methods in fluidised beds. Ex-situ methods provide

preliminary information that can be useful as an initial inexpensive measure to validate the use of fuels in later tests in fluidised beds. The use of online methods considering both process parameters (i.e. temperature and pressure) has shown acceptable results to some extent [Scala, 2018]. Nevertheless, the detection of changes in the bed under fluidisation conditions based on these parameters has been significant upon defluidisation conditions, when chances to make changes to the operational parameters are reduced [Scala, 2018]. Recent trends aiming to increase the use of pure biomass in fluidised beds or in co-processing with coal for heat and power production make the agglomeration challenge more relevant. In fact, the development of counteractions to reduce the risk of agglomeration phenomenon is necessary due to differences between the fuels and higher alkali metals content in biomass.

2.7.3 Agglomeration Counteractions Strategies

Among the different methods for counteracting agglomeration could be distinguished pre-processing of the fuel, operational actions and use of additives or alternative bed materials [Scala, 2018] [Dahlquist, 2013] [Silvennoinen and Hedman, 2013]. Despite the lower ash content of most biomass resources compared to coal, the higher alkali metals content in biomass, specifically potassium, represents a challenge in terms of agglomeration tendency [Wang et al., 2017c] [Vassilev et al., 2015].

In the pre-processing of fuels, the leaching of water-soluble compounds in biomass prior to use has shown good results to reduce ash related technical challenges [Kerienè et al., 2016] [Vassilev et al., 2013] [Gogebakan et al., 2009] [Vamvuka et al., 2008]. Nevertheless, a complete removal of the troublesome elements is not possible [Narayan et al., 2016] and leaching facilities at large scale may raise additional environmental concerns linked to the fate of K-, Cl-, Na-, S- and P-bearing compounds and other hazardous trace elements [Vassilev et al., 2015] or lead to a drastic increase in the operational costs [Scala, 2018].

Among the operational actions, reducing the temperature process and increasing gas flow have shown successful results in preventing agglomeration [Scala, 2018]. These two measures are the simplest and most influential ways to avoid or delay the agglomeration of the bed [Bartels et al., 2008]. Nevertheless, any modification in temperature and gas flow are not the desired action to take and only considered as emergency measures due to the massive impact on the process hydrodynamics, elutriation rate, pollutants emissions and combustion performance [Morris et al., 2018] [Bartels et al., 2008]. Another operational action implemented in fluidised beds is the close control of the bed particle size by the periodic partial replacement of the bed material with fresh sand [Scala, 2018]. Nevertheless, the partial replacement of the bed material implies higher operational costs.

The use of additives or alternative bed materials aims to provide alternative reactions to alkali metals and to avoid the formation of low-melting point silicates by changing the ash composition. Several studies have focused on the use of additives or alternative bed materials to minimise or eliminate the agglomeration in fluidised beds [Morris et al., 2018]. Furthermore, the presence of higher-melting compounds has been reported as beneficial to prevent other ash related issues in boilers such as fouling and slagging [Vassilev et al., 2015]. As several materials could be technically suitable for this purpose, the cost of the additive or alternative bed material is a primary factor to consider for the application at industrial scale [Bartels et al., 2008]. Additional challenges are related to the effect on emissions and the cost of used bed material handling [Bartels et al., 2008].

The presence of silicon during the combustion in fluidised beds, either in the fuel ash or in the bed material, has a massive influence on the portion of potassium released to the gas phase and fixed on the surface of the bed particles [Bartels et al., 2008]. During combustion, potassium tends to be released in gaseous phase as KOH and K_2SO_4 [Niu et al., 2016a] or it can be released as KCl if chlorine is present in the fuel [Hupa, 2012] [Shao et al., 2011], due to the capacity of chlorine to facilitate the mobility of several inorganic compounds, in particular potassium [Nuamah et al., 2012a] [Shao

et al., 2010]. This phenomenon has a significant influence on the combustion of biomass because potassium is the most abundant source of alkali metals in most of the biomass fuels and the possibility to form low melting alkali silicates with low melting temperatures [Wang et al., 2017c].

In terms of changing the ash composition, co-combustion of coal and biomass may be considered an initial measure due to the possibility to change the ash composition and further reduction of volatile alkali species [Morris et al., 2018]. The Al-bearing compounds in the coal ash could shift the alkali silicates formation in favour of alkali-aluminum silicates, which have much higher melting temperatures [Niu et al., 2016a] [Selvakumaran et al., 2014] [Bartels et al., 2008]. Furthermore, due to the higher sulphur content in coal ash compared to biomass, the release of potassium as KCl may be reduced in favour of K_2SO_4 , which is less harmful [Khan et al., 2009] [Leckner, 2007]. As for additives, several materials such as kaolin, bauxite, dolomite, limestone have been tested with a reported potential to reduce the agglomeration tendency. As regards to alternative bed materials, dolomite, magnesite, ferric oxide, alumina, feldspar and aluminum rich materials have been tested [Dahlquist, 2013]. In the following sections further details about the use of additives and alternative bed materials in fluidised beds combustion are reviewed.

Additives

The use of additives is a crucial research area to minimise the effect of agglomeration phenomenon in the thermochemical processing of solid fuels. A broad range of materials have been used as additives, these are mainly grouped into four categories: (1) aluminium-silicates based additives, (2) sulphur based additives, (3) calcium based additives, and (4) phosphorus based additives [Wang et al., 2017c] [Wang et al., 2016b] [Fournel et al., 2015] [Dahlquist, 2013]. Among these additives, those including aluminium and magnesium silicates along with alkaline earth carbonates and oxides have shown good results [Scala, 2018] [Niu et al., 2016a]. In fact, the aluminium-silicates based additives are the preferred choice reported in the

literature [Niu et al., 2016b][Shao et al., 2012a]. Nevertheless, the capacity of additives to reduce ash related issues is heavily influenced by the content of troublesome elements in the fuels and reactive components in the additives along with process parameters and combustion technology [Wang et al., 2012a].

Several approaches have been tested to introduce the additives into the processing systems. The additives could be blended with the fuel in the pre-processing preparations of the fuel such as densification, mixed with the fuel as it is transported by a conveyor, or added into the combustion systems as powders or solutions via installed spraying systems [Niu et al., 2016a] [Fournel et al., 2015] [Wang et al., 2012a]. Based on the reported results three main mechanisms for additives to decrease the ash-related issues have been identified: (1) enhancing ash melting temperatures by altering or diluting the ash composition with refractory elements (i.e., Si, Al, and Ca); (2) binding and converting low-melting species into less troublesome compounds with high melting temperatures; and (3) reducing concentrations of problematic ash species (i.e. KCl) in the combustion system by means of physical adsorption [Wang et al., 2017c] [Niu et al., 2016a].

The work of [Wang et al., 2016b] investigated the ash sintering of rye straw and the effects of calcite, kaolin and Ca-sludge as an additive to biomass ratio of 4 wt%. The results showed calcite to be more effective to mitigate sintering of the rye straw ash. It was attributed to the extensive formation of high temperature melting K-Ca-silicates and K-Ca-phosphates. Upon kaolin addition, a significant increase in the melting temperatures was observed, due to the shift from low temperature melting K-silicates to high temperature melting K-Al-silicates. Ca-sludge was shown to be the less efficient additive in this study, which was mainly attributed to the reduced formation of high temperature melting K-Ca-silicates and K-Ca-phosphates.

[Wang et al., 2014] investigated the ash sintering behaviour of barley straw ash and the capacity of kaolin and zeolite 24A to capture KCl vapours. The results from thermogravimetric experiments showed a decrease in the over-

all *KCl* capturing efficiencies of the two additives to the extent the heating time and temperature process increase. It was mainly attributed to the reduction of surface areas and chemically active compounds of the two additives with increasing temperature and heating time. Nevertheless, better performance was reported when kaolin was used. As for the ash sintering, X-Ray Diffraction (XRD), and scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) tests revealed severe melting of the barley straw ash due to formation and fusion of low temperature melting potassium silicates. Both additives showed the capability to reduce the ash sintering due to the formation of high melting temperature aluminium silicates.

[Wang et al., 2012b] used kaolin and calcite as an additive to biomass ratio of 4 wt% to study the sintering behaviour of ashes from raw barley straw and husk in a pellet burner. Compared to barley straw ash, the barley husk ash showed a higher sintering tendency, with severe melting during combustion. Nevertheless, both additives increased the ash melting temperature of both fuels by the formation of higher temperature melting compounds. Kaolin showed to promote the formation of alkali aluminium silicates compounds for both fuels. Upon additives use the ash sintering tendency was significantly decreased.

In experiments to optimise briquette fuel performance, [Wang et al., 2017c] investigated the influence on phosphorus-based additives ($NH_4H_2PO_4$ and $Ca(H_2PO_4)_2$) on potassium fixation and ash melting characteristics during the combustion of briquettes from maize straws and cotton stalks in a muffle furnace. The results showed the improved potassium fixation at different levels with better results for $NH_4H_2PO_4$ and increased ash fusion temperatures when both additives were used. Moreover, additional experiments showed an increase of ash fusibility temperatures in the range of 55 - 277 °C, it was mainly attributed to the presence of high melting point K-Ca-phosphates found in further XRD tests.

[Selvakumaran et al., 2014] investigated the effect of silica, calcium and alumina at 5-10 wt% on ash sintering and agglomeration tendency of six Indian

lignite samples, one southern hemisphere bituminous coal and anthracite in a 125 MWe CFB. The results showed a reduction in agglomeration tendency with a change in the ash sintering patterns to a lower or higher temperature with calcium-based and silica-based additives, respectively. In contrast, alumina showed no influence on the sintering patterns for the fuels studied.

[Shao et al., 2012b] performed co-combustion experiments of lignite and peat blends in a bubbling fluidised bed combustor. The experiments focused on the effect of blending ratio and the addition of sulphur on ash and chlorine deposition. The addition of sulphur showed a decreasing tendency of chlorine deposition via sulfation. Nevertheless, the ash deposition rate showed reduced values for lignite combustion, whereas for peat combustion there was an increasing trend.

In co-combustion experiments of a high ash and sulphur content lignite with olive residue, hazelnut shell, and cotton residue in a bubbling fluidised bed, [Gogebakan et al., 2009] used the ash obtained previously from the combustion of the same lignite in the same test rig as bed material and limestone as an additive. The research focused on ash deposition characteristics. The results revealed low deposition rates with high concentrations of *Si*, *Ca*, *S*, *Fe*, and *Al* in the deposit samples. Calcium sulphate and potassium sulphate were detected as major and minor components of the deposits, respectively. High sulphur and aluminium silicates content of lignite resulted in the formation of alkali sulphates instead of the troublesome alkali silicates.

In closing, the use of additives represents a positive effect in terms of reduction of ash sintering and agglomeration issues. Additives have shown to be successful in shifting the formation of alkali silicates with low melting temperatures to compounds with higher melting temperatures. Among the materials commonly used as additives, those containing aluminium silicates such as kaolin, have shown better performance to reduce the ash-related issues. It represents an additional benefit from co-combustion of coal and biomass as kaolinite and aluminium silicates are abundantly present in the ash of most of coal [Shao et al., 2012a]. It offers alternatives to dilute the

alkali metals from biomass ash, while fixing them into high melting temperatures compounds [Scala, 2018].

In general, the selection of the most optimal additive should regard the ash composition of the fuel, operational parameters and process technology. Moreover, close attention should be paid to the cost and mechanical stress resistance of the additive along with the handling of used bed material and any other environmental challenge. Therefore, it is necessary to continue the research efforts to find additives that effectively could prevent the ash sintering and agglomeration challenge. It may offer better alternatives to the unsolved technical challenges such as loss of additive mass and reactivity during the processing of solid fuels.

Alternative Bed Materials

Another approach to the reduction of the agglomeration phenomenon is to change the bed material from the most used silica sand to alternative materials with little or no silica. Among the materials tested, those consisting of Al-, Mg-, Ca-bearing compounds or their mixtures have shown good results [Scala, 2018]. Despite the benefits to reduce the agglomeration tendency, in some cases the use of alternatives bed materials has shown contradictory effects in terms of the release of chlorine, potassium and influencing the obtained emissions.

In fluidised bed combustion experiments, [Ji et al., 2017] studied the ash behaviour, the release of K and Cl and emissions of NO_x and SO_2 obtained during reed black liquor combustion using a calcium-based zeolite and limestone as bed materials. The results showed that higher temperatures promote the K release for both bed materials. Nevertheless, calcium-based zeolite led to lower overall K release due to the formation of aluminium-alkali silicates. As for the release of Cl , higher temperatures facilitated its release when the calcium-based zeolite was used, whilst limestone showed contradictory Cl release patterns. NO_x emissions were increased either with calcium-based zeolite or limestone, with higher values for limestone. It was

attributed to the conversion of fuel N to NO_x under CaO catalysis. In terms of SO_2 emissions, calcium-based zeolite showed a slight increase, whereas limestone showed a relevant reduction.

In fluidised bed gasification experiments, [Recari et al., 2017] used two waste derived fuels (SRFs) with silica sand, dolomite and olivine as bed materials. The effect of experimental conditions on gasification performance, and tar production was investigated. Additionally, levels of polycyclic aromatic hydrocarbons (PAHs) and minor contaminants (HCl , H_2S , HCN , and NH_3) in the obtained gas were considered. Dolomite showed higher catalytic activity than olivine in terms of tar and minor contaminants reduction whilst olivine showed higher performance to reduce light PAHs and nitrogenous compounds (HCN and NH_3) in the producer gas.

In experiments to investigate the combustion performance and emissions in a fluidised bed using alumina, limestone, and dolomite as bed materials, [Ninduangdee and Kuprianov, 2016] and [Ninduangdee and Kuprianov, 2015b] used high alkali empty fruit bunch and palm kernel shells, respectively. The results showed high combustion efficiency values, and acceptable CO and NO emissions at 40-60 % excess air (depending on the bed material). No agglomeration was observed during the experiments. Nevertheless, the alumina bed particles showed a coating layer rich in K , Ca , Si and Mg , this kind of coating layer was not observed in the limestone or dolomite bed particles. Moreover, the capacity of alumina to decrease the agglomeration tendency diminished gradually. Limestone and dolomite required the addition of fresh material to keep the same bed height. It was attributed to the bed particles carry-over due to the calcination and breakage.

[Chaivatamaset and Tia, 2015] studied the bed agglomeration behaviour during the combustion of eucalyptus bark in a BFB with silica sand and alumina as bed materials. This study focused on the influence of operating conditions and bed materials on the bed agglomeration tendency. In addition, further analysis was carried out to elucidate the behaviour of fuel inorganic elements and the governing mechanism of the agglomeration. When silica

sand was used, the bed agglomeration was mainly attributed to the formation of potassium silicate compounds as a liquid phase during the combustion due to the chemical reaction between the bed particles and the released ash constituents. Furthermore, the increase of the bed temperature, sand particle size and the decrease of air velocity were reported as defluidisation promoter. In conclusion, alumina was reported as successful to prevent the bed agglomeration since it was inactive in the formation of viscous molten substances during combustion.

In [Shao et al., 2012b], [Shao et al., 2012a], [Shao et al., 2011] and [Shao et al., 2010] extensive research was reported about co-combustion of lignite, peat, and woody biomass blends in a BFB reactor with olivine as bed material. The experiments focused on the influence of operational parameters on the ash deposition tendencies. The results from the co-combustion tests of woody biomass and lignite suggested strong interactions of chemical compositions in blended fuels. A more severe ash deposition tendency was observed insofar as the alkali, alkaline earth metals and halogen elements (*Cl* and *Br*) content increased. In addition, the moisture content was reported as a positive factor to hinder the ash deposition of the individual fuels and blends tested. As for combustion and co-combustion of lignite coal and chlorine-rich peat, the chlorine content played a key role in the ash deposition tendency. Nevertheless, the addition of sulphur was reported as effective to decrease the ash deposition for lignite combustion, inversely, the ash deposition rate was slightly increased after sulphur addition for peat fuel combustion.

In combustion experiments in a fluidised bed, [Kaknics et al., 2015] used miscanthus with three different bed materials namely silica sand, raw and calcined olivine, and dolomite as an additive to investigate the ash agglomeration, effect of atmosphere and the influence of biomass harvest time. The physical adhesion was reported as the main mechanism when silica sand was used. Olivine and calcined olivine showed a thin layer containing Ca-silicate or K-Mg-silicates according to the harvest time, suggesting a significant effect on potassium and calcium concentration in the fuel in terms of the difference

in harvest time. In addition, no difference in the mechanism of interaction between the ash and bed particles upon the oxidising and reducing atmosphere was reported.

As shown above, the selection of an alternative bed material should be tailored to the requirements of the process considering the fuel ash composition and operational conditions. In the broad body of reported research results, there is no agreement about the most effective material to decrease the agglomeration tendency in fluidised beds. In fact, the use of a specific additive or bed material to decrease agglomeration could have a negative effect on other aspects leading to additional issues. Furthermore, other factors such as cost, availability and attrition tendency along with waste bed material handling or even effects on the combustion efficiency should be considered to determine its technical feasibility. Therefore, additional efforts to obtain data will help to address these research gaps and contribute to find additives and alternative bed materials to substitute the traditional silica sand. Recently, a novel approach based on the use of oxygen carriers [Thunman et al., 2013], and brought from the chemical looping combustion concept was demonstrated in the combustion of solid fuels in a fluidised bed, it could represent additional benefits in terms of combustion efficiency and reduced emissions.

Oxygen Carrier Aided Combustion (OCAC)

The efficient processing of solid fuels depends to a large extent on the combustion efficiency and stability of the process. These two factors are hugely influenced by the contact of oxygen and fuel during the process [Wang et al., 2017b]. The better the contact between the oxygen and fuel the lower the excess air required to achieve high-efficiency levels. Among other benefits, better oxygen and fuel contact could lead to even temperatures during the process reducing the likelihood of hot spots and the risk of agglomeration along with the benefits of less emissions of NO_x , SO_2 , CO and lower levels of unburnt carbon in the ash [Hughes et al., 2017], [Rydén et al., 2016] [Thunman et al., 2013].

Recently, a new approach, called oxygen carrier aided combustion (OCAC), has focused on improving the fluidised bed combustion using reactive materials [Thunman et al., 2013]. It could improve the contact between oxygen and fuel based on the partial or total replacement of the bed material by the use of solid oxygen carrier materials. In oxygen-lean areas, the oxygen carrier material may provide the required oxygen for processing instead of the oxygen from the air [Rydén et al., 2016]. Originally used in Chemical-Looping Combustion (CLC) for CO_2 capture with a reduced cost for gas separation, the oxygen carrier may be reduced and oxidised through redox reactions acting as an oxygen buffer that absorbs oxygen in oxygen-rich areas of the reactor and supplies oxygen to oxygen-lean areas, enhancing the overall oxygen fuel contact [Thunman et al., 2013].

There is a broad range of materials that may be used as an oxygen carrier. Commonly, the oxygen carrier used in CLC for combustion of solid fuels are manufactured from metals oxides such as NiO , Fe_2O_3 , Mn_3O_4 or CuO due to better resistance to mechanical stress and long operational time with high reaction activity, key desired features in the process [Thunman et al., 2013]. Nevertheless, the use of oxygen carriers does not diminish concerns about the ash issues during processing. Indeed, partial replacement of up to 30 % on a daily basis of the used bed material to keep under control the particles size of the bed is a common practice in industrial applications, which raises concerns about the feasibility of this approach [Rydén et al., 2016]. Therefore, the research efforts are focused on low-cost natural minerals with sufficient reactivity, hardly need of pre-processing and adequate fluidisation properties [Wang et al., 2017b].

Most of the attention has been on natural occurring Fe- or Mn-bearing minerals due to their availability and low cost. In combustion experiments in a 12 MWth circulating fluidised bed with air staging and reduced excess air by [Thunman et al., 2013], a Fe-, Ti-bearing mineral called ilmenite ($FeTiO_3$) was used as an additive up to 40 wt% in a silica sand bed with woody biomass as fuel. The results showed a decrease in CO and NO_x emissions of 80 %

and 30 %, respectively. These reductions were attributed to the addition of ilmenite to the bed. In addition, it was reported a reduction in the accumulation of deposits on the heat surfaces in comparison with the operation with pure silica sand.

[Hughes et al., 2017] investigated the use of ilmenite as an additive and alternative bed material to improve the combustion performance and sulphur capture in a 50 kWth pilot-scale fluidised bed combustor at atmospheric and pressurised conditions under oxy-fuel atmosphere using two Canadian coals with under bed fuel and sorbent injection. The results showed a CO reduction of up to 30 % and 13 % according to the coal used. The CO reduction was reported to be more prominent at low oxygen concentration in the flue gas. In addition, no agglomeration was reported during the experiments. Nevertheless, an increase in the NO_x emissions was reported and mainly attributed to the quicker reaction rates of oxygen from the air than that from the oxygen carrier. Moreover, loss of bed particles due to the attrition in the bed was observed.

Studies using manganese oxides have shown similar results. In combustion experiments with calcined manganese ore as an additive and alternative bed material in a 12 MWth circulating fluidised bed, [Rydén et al., 2016] used wood chips to investigate the combustion efficiency and the need of excess air. The results revealed improvements in the fuel conversion, especially in the dense bottom bed. Nevertheless, the use of the alternative bed material did not always reduce the emissions, with even higher values when the bed was entirely manganese ore. Indeed, NO emissions were always higher when manganese ore was added to the bed compared to the bed of pure silica sand.

In comparative combustion experiments of wood char in a small fluidised bed reactor made of quartz (870 mm in length and inner diameter of 22 mm), [Wang et al., 2017b] studied the combustion performance and NO emissions at different air to fuel ratios with four oxygen carriers (ilmenite, manganese ore and two by-product oxides from steel production), quartz

sand was used as the reference case. The results showed an improvement in combustion efficiency with reduced CO emissions. It was possible to decrease the excess air and, thereby, lower the NO emissions keeping the same level of CO emissions. The increase in combustion efficiency was attributed to the reactivity of the oxygen carriers with CO . Although manganese ore showed higher performance than the other oxygen carriers, it agglomerated at early stages of processing.

Few researchers have addressed the analysis of alkali metals capture by oxygen carriers. In extensive research on woody biomass combustion, [Corcoran et al., 2014] studied the physical and chemical changes in ilmenite under combustion conditions. The results revealed the segregation of iron to the surface and the enrichment of titanium in the core of the particles along with the inward migration of K into the particles. In addition, it was reported a calcium-rich double layer on the particle, surrounding the iron layer and the formation of KTi_8O_{16} as a consequence of the diffusion of potassium. In further combustion experiments, [Corcoran et al., 2018b] found that insofar as the time of exposure increases, potassium migrated into the particle core with a Ca-bearing layer coating the particles along with the inward migration of Ca into the particles for longer times of exposure. More recently, [Corcoran et al., 2018a] investigated the mechanical stability of two different occurring ores (sand and rock) of ilmenite during long-term exposure. The results revealed ilmenite from sand to be more consistent in its mechanical stability over time.

2.8 Summary

The evidence presented in this chapter suggests that there are still unsolved challenges about the processing of solid fuels in pure or in co-processing schemes. Despite the use of several biomass resources, mainly woody materials have shown to be effective to increase the reactivity of coal in co-processing with additional benefits in terms of emissions reduction. Nevertheless, the ash related issues have hampered the increase of the biomass ratio in the blends. Several additional concerns have been raised about the

implications of the extensive use of woody materials in terms of resources and land use. Based on that, the use of herbaceous biomass has lured more attention in recent years, but here again, the ash related issues play a crucial role to assess the feasibility of the process, with an even stronger likelihood of ash related issues due to higher alkali metals content and other troublesome elements than in woody materials.

Chapter 3

Experimental Methods

This chapter describes and discusses the implemented methods in this research. Based on the problem statement and research motivation explained in the Introduction (see Chapter 1), an experimental approach has been adopted. It consists of three different studies conducted to answer the research questions, thus:

- Thermogravimetric (TGA) studies - Chapter 4
- Ash fusibility temperatures (AFT) studies - Chapter 5
- Fluidised bed combustion (FBC) experiments - Chapter 6

Each of these three studies comprises a number of sections which cover the work plan for this research; explaining the analytical techniques, apparatus, and experimental parameters. Furthermore, descriptions of advantages, limitations and approach implemented to minimise error sources are included in following sections.

3.1 Material Selection and Characterisation

3.1.1 Fuel Samples Preparation

According to the as received conditions and final use of samples specific preparations were required. Table 3-1 describes the fuels used in this research, their source and the studies in which they were used.

Table 3-1: Overview of fuel samples and their use in this research

Resource	Source	Use
Bituminous coal (BC)	Obtained from British Sugar Company in the UK	TGA studies Chapter 4
Coffee Husk (CH)	Obtained from a coffee farm located at 1615 m above sea level in Ragonvalia - Colombia	
Spent coffee grounds (SCG) - Sample I	Obtained from the beverage of coffee beans of a Colombian commercial brand	
Wood (WP)	Obtained from pellets commercial product - Brites from Balcas Ltd.	
Bituminous coal (BC)	Obtained from British Sugar Company in the UK	AFT studies Chapter 5
Wheat straw (STW)	Obtained from commercial pellets product - Agripellets Ltd.	FBC experiments Chapter 6
Spent coffee grounds (SCG) - Sample II	Collected from a coffee shop at Jubilee Campus of University of Nottingham, UK	

TGA - Thermogravimetric analysis

AFT - Ash fusibility temperatures

FBC - Fluidised bed combustion

The bituminous coal (BC) used in this research consisted of 150 kg supplied in a particle size range of 20 - 30 mm and washed, which means submitted to a cleaning process to reduce the content of stones and impurities. Two different particles size samples of BC were prepared. It required the initial reduction of the particles size by crushing of the coal lumps in a Retsch jaw crusher BB 400 XL, along with further sieving in a Russell sieve shaker to obtain lumps in a size range of 12 - 20 mm for FBC experiments and sieving by vibrating screens in an electromagnetic shaker to obtain a particle size $< 212 \mu\text{m}$ for TGA studies.

As for the biomass, commercial wood pellets (WP) and wheat straw pellets (STW) along with coffee husk (CH) samples were milled using a Retsch ultracentrifugal mill ZM 100 then sieved by vibrating screens in an electromagnetic shaker to a particle size $< 212 \mu\text{m}$ for TGA studies. As for spent coffee grounds (SCG), two different sources were used due to the limited

availability of the initial resource. Therefore, the material corresponding to the sample I was sieved by vibrating screens in an electromagnetic shaker to a particle size $< 212 \mu\text{m}$ to perform TGA studies. Additionally, 100 kg of SCG corresponding to sample II were collected from a coffee shop at Jubilee Campus of the University of Nottingham in Nottingham, UK to perform AFT studies and FBC experiments. Due to as received moisture content higher than 60 wt% in sample II, it was required the previous moisture reduction by natural air drying during 72 hours at room temperature and additional 2 hours drying at 110°C in a Gallenkamp hotbox oven to reach 15 wt% moisture content, which is suggested in the literature as optimum moisture content for most of biomass for pellets manufacturing [Whittaker and Shield, 2017] [Nunes et al., 2014]. Then, a fraction of 2 kg of SCG (sample II) was sieved by vibrating screens in an electromagnetic shaker to a particle size $< 212 \mu\text{m}$ to obtain the ash to perform AFT studies and the remaining fraction used to manufacture pellets.

The blends of BC and biomass samples for TGA studies were prepared at three different biomass ratios of 10, 30 and 50 wt%. It was performed by weighing the respective amount of each component on top of each other in a plastic container and then submitted to vibrating mixing in an electromagnetic shaker for 5 minutes. This method of mixing was found to be adequate by testing the repeatability of the measurements. Sample mass loss through the mixing process was negligible.

Spent Coffee Grounds (SCG) Pellets Manufacturing

Pellets of 6 mm diameter and approximately 25 mm length from SCG were made using a KL120B pellet machine. Due to the limited capacity of the hopper in the pellet machine, the manufacturing of the SCG pellets was made in batches. It contributed to avoid the clogging of the pellet machine and facilitated the quality assessment of the pellets. Batches of 5 kg of SCG (15 wt% moisture content) were used during the manufacturing process. Figure 3-1 shows the pellets machine and top view of the hopper.

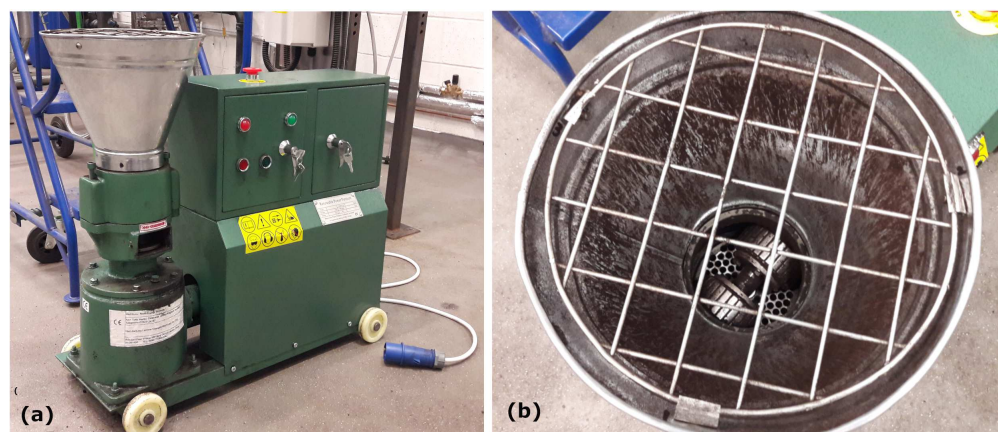


Figure 3-1: KL120B pellet machine, (a) general arrangement, and (b) top view of the hopper after SCG processing

It is worth noting that no binder was added to the SCG for the pellets manufacturing process. It was mainly due to the high lignin content of SCG of up to 40 wt% [Jeguirim et al., 2014b] [Mussatto et al., 2011]. Lignin is one of the traditional organic binders used in biomass densification [Hu et al., 2015a]. Indeed, a strong positive relationship between pellet durability and lignin content has been reported [Whittaker and Shield, 2017]. Furthermore, high lignin content in SCG is acknowledged as a promoter of its higher fixed carbon fraction because lignin is a more stable component than hemicellulose and cellulose found in biomass [Jeguirim et al., 2014b].

Pellets manufacturing consisted of an initial trial and error process to determine the adequate conditions. An initial batch was pelletised by passing the material several times through the pellet machine until the final product showed optimum consistency. Then, the pellets were cooled down for 2 hours at room temperature to allow the expel of remaining moisture and store in a vacuum bag. This process was repeated for every SCG batch until 40 kg of SCG pellets with satisfactory characteristics were obtained. Furthermore, manual mixing of the total amount of SCG pellets was performed to reach homogeneity of the sample. Suitability of manufactured SCG pellets was confirmed by additional tests in the feeding system of the fluidised bed reactor to assess the integrity of the pellets and reduced presence of fines

after passing through the screw feeder. No additional analysis was made to the SCG pellets. Figure 3-2 shows the SCG pellets process from as received to the final pellets.



Figure 3-2: SCG pellets manufacturing progression, (a) as received (moisture content > 60 wt%), (b) moisture content $\sim$ 15 wt%, and (c) manufactured SCG pellets.

3.1.2 Fuel Ash Samples Preparation

A fraction of the samples of BC and STW prepared for the TGA studies, and SCG (sample II) at a particle size $< 212 \mu\text{m}$ were ashed to perform the fuels ash characterisation and ash fusibility temperatures studies correspondingly. In studies about the effect of three ash preparation methods of combustion of coal and biomass blends, [Jing et al., 2016] reported the lowest modifications of sintering temperatures of the samples when a muffle furnace was used. In this research, ashing was carried out in a Carbolite CFW 1200 furnace according to BS/EN/ISO 18122:2015 and BS/ISO 1171:2010, respectively. The main difference lies in the lower temperature to prepare biomass ash samples than that for coal to minimise the evolution of high potassium content in biomass [Deng et al., 2013].

Biomass samples were heated to 250°C at $4.5^\circ\text{C}/\text{min}$ and kept for 60 min to allow the volatiles to leave the test portion before ignition. Then, the temperature was raised evenly to 550°C over a period of 30 min at $10^\circ\text{C}/\text{min}$ and kept at this level for 4 hours. BC was heated to 500°C at $10^\circ\text{C}/\text{min}$ and kept for 30 min. Thereafter, the furnace temperature raised to 815°C and kept for 4 hours to ensure that the organics were burnt adequately. Finally all ash samples were stored in glass containers to perform the corresponding ash characterisation.

The ash samples of BC, STW, and SCG (sample II) were ground and sieved to less than 75 μm in an agate mortar and store in glass containers (see Figure 3-3). Then, blends of BC ash with each biomass ash sample (STW and SCG) at 40, 60 and 80 wt% were prepared. All the blends were submitted to vibrating mixing in an electromagnetic shaker until they reached uniformity and kept in sealed glass containers. This method to prepare the ash blends based on mixing the ash from pure fuels instead of ashing the blended fuels has shown to be better to replicate the ash behaviour in a large scale combustor [Xing et al., 2016a].



Figure 3-3: Sieved ash samples of wheat straw (left), spent coffee grounds (middle) according to BS/EN/ISO 18122:2015 and bituminous coal (right) according to BS/ISO 1171:2010.

3.1.3 Fuels Characterisation

Elemental, Proximate Analysis and Heating Value

Fuels characterisation was based on the proximate and elemental analysis along with heating value determination. All the characterisation experiments were performed at least twice to ensure repeatability, the average and standard deviations of all the runs are given in Appendix A. Initially, the elemental analysis was performed using a LECO 628 analyser (see Figure 3-4a), in which the weight percent of carbon, hydrogen, and nitrogen in samples can be detected simultaneously. Sulphur content was determined using an independent LECO sulphur add-on module (see Figure 3-4b). The determi-

nation of the weight percent of oxygen was calculated by difference. The high heating value (HHV) of the samples were measured in an IKA C5000 Bomb Calorimeter (see Figure 3-4c). Table 3-2 shows the results of the proximate and ultimate analyses, as well as the heating values of the fuels used in this research.

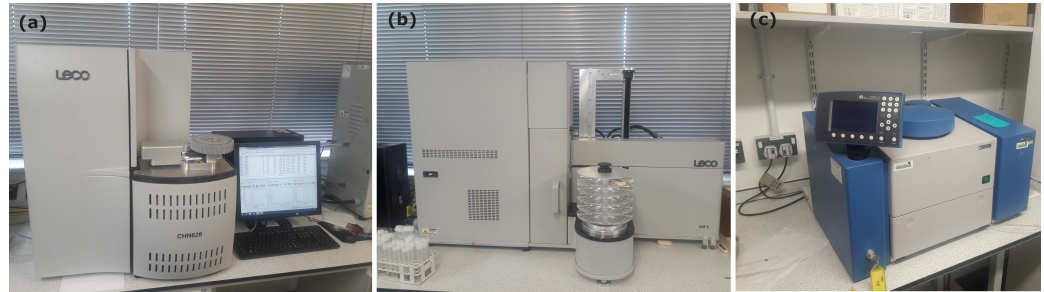


Figure 3-4: Analytical equipment used for fuels characterisation, (a) LECO 628 analyser, (b) LECO sulphur add-on module 628-S, and (c) IKA C5000 Bomb Calorimeter.

Table 3-2: Ultimate and proximate analysis, and high heating value of bituminous coal (BC), wood pellets (WP), spent coffee grounds (SCG), wheat straw (STW), and coffee husk (CH).

	Ultimate analysis					Proximate analysis							Heating value
Fuels	% C	% H	% O*	% N	% S	Ash (%)	Moisture (%)	VM (%)	FC (%)	VM/FC ratio	H/C ratio	O/C ratio	HHV (MJ/kg)
BC	70.94	5.28	20.86	1.68	1.23	7.76	2.83	37.48	51.93	0.72	0.07	0.29	31.69
WP	46.84	6.22	46.47	0.28	0.19	0.89	7.06	81.71	10.34	7.90	0.13	0.99	19.14
SCG **	49.43	8.34	40.99	1.06	0.18	1.89	9.16	77.35	11.60	6.67	0.17	0.83	23.02
SCG ⁺⁺	52.36	7.12	38.17	2.23	0.12	1.11	6.46	77.16	15.28	5.05	0.14	0.73	22.30
STW	40.88	5.96	51.87	0.71	0.58	5.92	4.96	72.52	16.59	4.37	0.15	1.27	17.41
CH	45.67	6.12	47.58	0.49	0.14	1.51	6.94	80.40	11.15	7.21	0.13	1.04	18.46

*, calculated by difference

**, SCG - sample I

⁺⁺, SCG sample II

VM, Volatile matter

FC, Fixed carbon

HHV, High heating value

According to the results in Table 3-2, the chemical composition of biomass materials in this study are in the same range of values than those reported

in others studies [Lu et al., 2017] [Zellagui et al., 2016] [Cai et al., 2016] [Cruz and Crnkovic, 2016] [Rakthong et al., 2015] [Kok and Özgür, 2013] [Limousy et al., 2013] [Moon et al., 2013] [Deng et al., 2013] [Slopiecka et al., 2011]. The main differences between biomass and coal are in the lower heating values and higher moisture content for biomass. Among biomass considered, SCG showed a higher heating value due to the higher carbon and hydrogen content. Regarding ultimate analysis, the main differences are on higher contents of carbon, nitrogen, and sulphur for coal and higher content of oxygen for biomass. The higher oxygen concentration of biomass has been reported to imply higher reactivity in comparison with coal [Zhou et al., 2015] [Buratti et al., 2015].

As for nitrogen content, biomass resources commonly show lower values than coal, like those for CH, STW, and WP, which represent one of the benefits of biomass use in terms of reduced NO_x emissions. Nevertheless, SCG (sample II) used in this study showed higher nitrogen content than coal, similar nitrogen content in SCG was reported by [Wei et al., 2018] [Byul et al., 2017] [Wei et al., 2016] [Jeguirim et al., 2016] [Li et al., 2014] [Li et al., 2014] [Limousy et al., 2013]. It may have a significant influence on the use of spent coffee grounds as a potential fuel.

Furthermore, among the biomass fuels tested, SCG showed low VM/FC and O/C ratios. It has been attributed to higher lignin content in SCG. Previous studies have reported lignin contents in SCG up to 40 wt% [Jeguirim et al., 2016] [Jeguirim et al., 2014b]. These parameters have been reported as relevant to promote easier ignition [Zhou et al., 2015] [Jeguirim et al., 2014a], which could have a beneficial effect on the thermochemical decomposition behaviour.

Fuel Ash Chemical Composition

Fuel ash chemical composition was based on X-ray fluorescence (XRF) technique, which is a non-destructive method to determine the elemental com-

position of materials. It is considered to have high accuracy level for elemental determination in the ash [Zhu et al., 2018b]. XRF for ash analysis is commonly reported in the literature as a relatively rapid and convenient method [Ma et al., 2017] [Xing et al., 2016b]. This technique is based on the wavelength-dispersive spectroscopic principle, which is made possible based on the behaviour of atoms when submitted to radiation. It produces the release of energy in the form of characteristic fluorescent X-rays due to the displacement of electrons from their atomic orbital positions. Each element in a sample generates a set of characteristic fluorescent X-rays that is unique for that specific element. In this research, the ash chemical composition of fuels was determined by XRF tests using an Epsilon 3 XL high-performance bench-top spectrometer system to establish the percentage of each element present in the previously prepared ash samples according to BS EN ISO 18122:2015 and BS-ISO 1171: 2010, respectively. Table 3-3 shows the results of ash chemical composition by XRF tests of the fuels used in this research.

Table 3-3: Ash composition of bituminous coal (BC), wood pellets (WP), spent coffee grounds (SCG), wheat straw (STW), and coffee husk (CH), expressed as oxides.

Fuels	Ash composition (wt%)												
	SiO_2	P_2O_5	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	Cr_2O_3	MnO_2	Cl
BC	43.21	0.27	11.84	35.41	4.03	0.83	0.18	0.90	2.28	0.96	0.04	0.05	0.00
WP	3.33	6.10	2.82	1.46	52.53	6.54	0.29	18.10	6.27	0.07	0.16	2.22	0.09
SCG**	0.00	18.26	0.56	0.00	12.76	20.41	0.00	34.83	12.78	0.01	0.00	0.29	0.10
SCG ⁺⁺	0.00	18.40	0.52	0.00	13.57	21.91	0.00	38.20	6.84	0.00	0.00	0.34	0.20
STW	64.69	2.82	0.42	0.55	8.05	3.33	0.00	16.18	2.29	0.01	0.01	0.04	1.60
CH	10.94	4.03	17.30	2.92	27.67	6.97	0.00	22.42	5.07	0.22	1.92	0.16	0.38

** , SCG - sample I

⁺⁺ , SCG sample II

The determination of ash composition is a factor of particular interest in the thermochemical processing of fuels. The results presented in Table 3-3 show that all the fuels contain varying amounts of inorganic matter. The main chemical components detected in BC in descending order were silicates, aluminium, and iron oxides (SiO_2 , Al_2O_3 , and Fe_2O_3), counting for

more than 90 % of total ash. The results from biomass samples are in good agreement with results commonly reported for biomass ash composition with SiO_2 , K_2O , CaO , and MgO as the major ash components [Zhu et al., 2018b] [Vassilev et al., 2013] [Hupa, 2012]. As for by-products from the coffee crop, the main chemical components detected in CH in descending order were CaO , K_2O , Fe_2O_3 , and SiO_2 , counting for more than 78 % of total ash. The main chemical components detected in SCG in descending order were K_2O , MgO , P_2O_5 , and CaO , counting for more than 92 % of total ash. Negligible content of SiO_2 was detected in SCG. Similar results have been reported in the literature by [Wei et al., 2018] [Li et al., 2014] [Limousy et al., 2013].

The by-products from coffee crop used in this study showed a significant content of alkali metals, specifically K_2O , corresponding to 38.20 wt% (SCG) and 22.42 wt% (CH). These values were higher than the content of K_2O in STW, 16.18 wt%. The alkali metals have been reported as promoters of minerals catalytic effect in previous studies [Jeguirim et al., 2014a]. Nevertheless, STW also showed a relevant content of SiO_2 counting for more than 64 wt% of the ash. The presence of SiO_2 and K_2O in fuel ash has been reported as a promoter of extensive ash agglomeration, as the fuel itself has the necessary material to create alkali-silicate melts triggering the melt-induced agglomeration mechanism (see section 2.7.1). As for WP, the largest contributors to ash were CaO and K_2O , counting for more than 70 % of total ash, with a reduced content of SiO_2 . As for STW, the main chemical components detected in descending order were SiO_2 , K_2O , and CaO , counting for more than 88 % of total ash.

Furthermore, basic oxides such as CaO and K_2O can reduce the ash fusibility temperatures (AFT) [Ma et al., 2017] [Lu et al., 2017]. Indeed, it is a common practice in the industry, the use of fluxing agents such as CaO to reduce AFT of coal ash [Ma et al., 2017] [Liu et al., 2013a]. Nevertheless, the addition of low proportions of CaO has been reported to initially decrease the AFT values and then followed an increase when CaO proportion increases to an excessive level [Li et al., 2017a] [Folgueras et al., 2015] [Liu et al., 2013a] [Deng et al., 2013].

3.2 Thermogravimetric Analysis (TGA) Studies

This section describes the experimental techniques, equipment, and operating parameters implemented in the TGA Studies. Thermogravimetric analysis (TGA) technique is part of a broad group of thermoanalytical methods in which a property of a specific material is under study [Gallacher, 1998]. Despite TGA technique works at different conditions compared to real scenarios, it could be considered an easy and useful approach for the characterisation of thermochemical behaviour of materials [Vamvuka and Sfakiotakis, 2011]. In fact, TGA is the most common technique used for studying the thermal behaviour of materials.

In the literature, there are many examples of TGA studies which analyse the thermal behaviour of different materials e.g. polymers, food, fuels, explosives, etc. [Brown and Gallagher, 2008]. This analysis measures the weight loss of a material as a function of increasing temperature, or isothermally as a function of time, in a controlled atmosphere. The atmosphere (e.g. inert, reducing and oxidising) can be changed during the measurement as well as sample ratios and heating rates in a comparable way to real case scenarios [Brown and Gallagher, 2008] [Hatakeyama and Liu, 1998]. TGA can be used to characterise any material that exhibits a weight change and to detect phase changes due to decomposition, oxidation, or dehydration. This information helps to identify the percent weight change and correlate chemical structure, processing, and end-use performance. Recently, TGA has made significant contributions to the study of renewable energy resources, specifically regarding their suitability for energetic use [Hill, 2012].

Previous research on co-combustion of coal and biomass blends using TGA have been mainly focused on the interactions between the fuels in the blends and the study of synergistic effects. Most of the studies have investigated the thermal behaviour of fuel blends under inert and oxidising, and more recently under oxy-fuel conditions. Extensive research has been performed on commercial biomass fuels, which are available on the market as densified products (e.g. pellets or briquettes), such as wood, wheat straw, and

miscanthus [Zhou et al., 2016] [Vhathvarothai et al., 2014] [Moon et al., 2013]. Other studies have used different types of biomass such as bamboo, soybean stalk sawdust, peanut shell, rice husk char, torrefied beetroot and switchgrass [Yan et al., 2016] [Toptas et al., 2015] [Sarkar et al., 2014] [Zhou et al., 2014] [Liu et al., 2013b]. Non-traditional biomass including cellulosic ethanol residue, sewage sludge, municipal solid waste and laying hens manure in co-combustion with coal have been studied as well [Junga et al., 2017] [Buratti et al., 2015] [Magdziarz and Wilk, 2013] [Muthuraman et al., 2010].

3.2.1 Apparatus

Thermogravimetric Analyser

TGA experiments were performed using a thermogravimetric analyser, Q series TGA Q500, manufactured by TA Instruments (see Figure 3-5). It is used in conjunction with a TA Instruments thermal analysis controller and associated software, to make up a thermal analysis system.

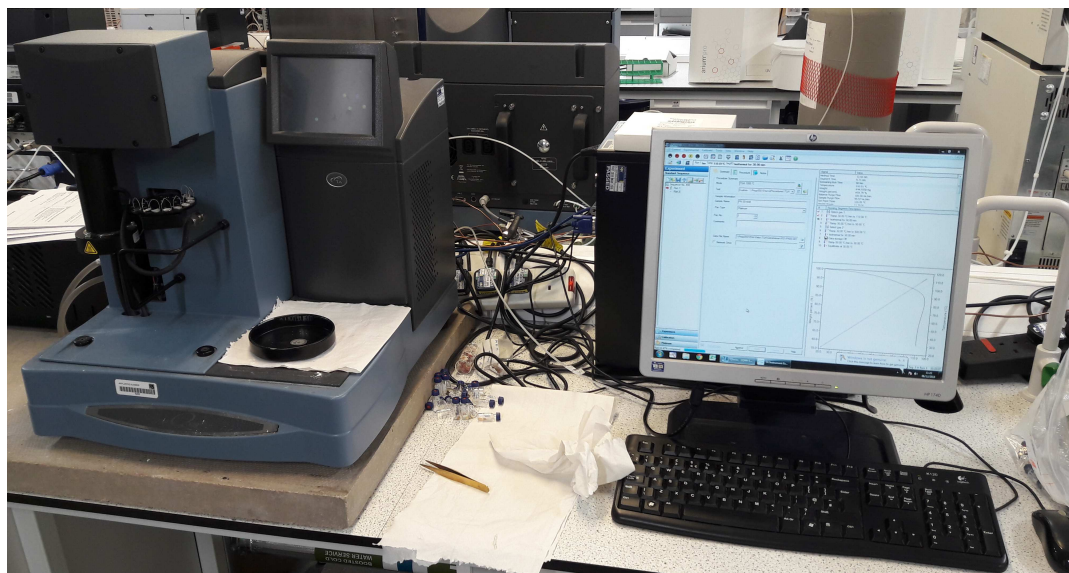


Figure 3-5: Thermogravimetric Analyser - TGA Q500 set-up.

After previous preparation of samples, a cleaning process of the platinum pans before every run was carried out. It consisted of gently removing of any residue with acetone along with a stream of water, and then heating under

a butane flame. Brass tweezers were always used to manipulate the pans to avoid any cross-contamination. After tare procedure to set the baseline weight, specific amounts of the samples were loaded in the pans and an experimental program set accordingly. Figure 3-6 presents the key components in the thermogravimetric analyser such as balance, furnace, and thermocouple as well as the autosampler tray and pans.

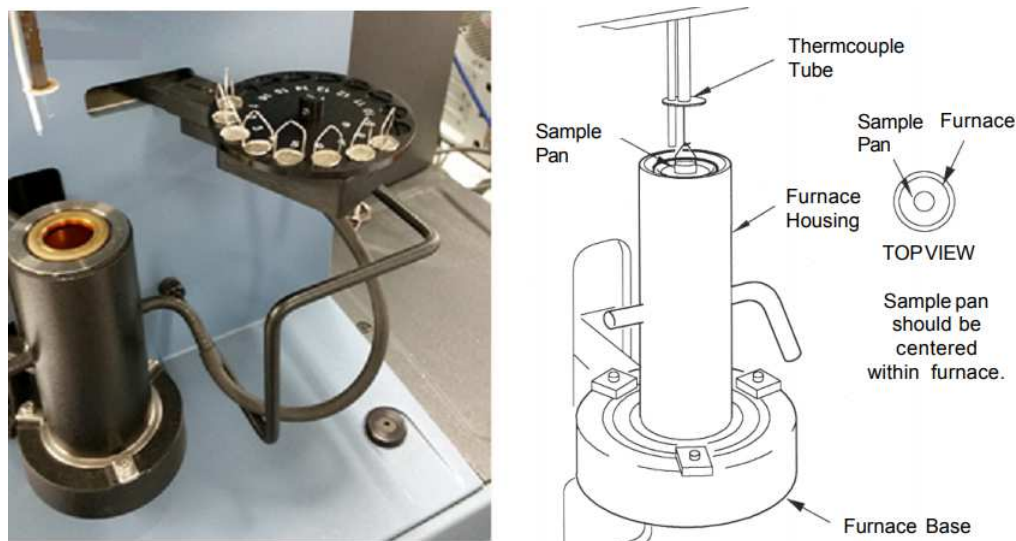


Figure 3-6: Autosampler with platinum crucibles and the furnace of thermogravimetric analyser - TGA Q500.

The balance in TGA Q500 equipment operates on a null-balance principle, which means that in this equipment 2 photodiodes and currents are used to meter the movement of the balance from the null position, the current is proportional to the weight change during the experiments. One of the main limitations linked to the thermogravimetric technique is the overlapping of weight losses due to complex thermal behaviour of samples. Nevertheless, slower heating and reduced size samples can decrease the effect of this limitation and increase the results resolution. In this study, the thermogravimetric technique was used to determine the proximate analysis of samples and to perform dynamic thermogravimetric tests of samples to characterise the thermal behaviour of pure fuels and their blends. Further explanation about the operating parameters and experimental considerations for these tests are included in the following section.

3.2.2 TGA Experiments for Proximate Analysis

The TGA technique is considered a useful method for determining various physical properties of fuels namely moisture, volatile matter, fixed carbon, and ash content. Moisture and volatile matter can be determined by the controlled heating upon inert conditions. Thereafter the switch of the atmosphere to oxidising conditions (air) allows the ash content determination in the sample. The difference between the remaining solid fraction (ash) and the remaining fraction after the devolatilisation takes place corresponds to the fixed carbon. This approach for the proximate analysis have shown high agreement with the ASTM values [Czajka, 2018] [Jeguirim et al., 2014a] [El may et al., 2012] [Munir et al., 2009] [Mayoral et al., 2001].

In this research each sample (10 ± 0.5 mg) was heated in a nitrogen atmosphere with a constant flow of 50 ml/min from room temperature to 110 °C at 10 °C/min and kept isothermal at the temperature for 10 min to ensure complete removal of moisture. Then, the sample was heated further to 900 °C at a heating rate of 20 °C/min and kept isothermal at the temperature for 30 min to ensure a complete stabilisation of the sample. Then, the air was supplied and the sample kept isothermal at the temperature for 60 min to ensure a complete stabilisation of the sample. As an example, Figure 3-7 shows a typical weight loss and heating profile with corresponding fractions considered in the proximate analysis of spent coffee grounds used in this research. The results of proximate analysis of fuels considered in TGA studies, and AFT studies and FBC experiments are included in Table 3-2.

3.2.3 Devolatilisation and Combustion Experiments

Devolatilisation and combustion experiments were performed using a TGA Q500 with circular platinum crucibles with 2 mm height and 5 mm diameter. A sample mass of 10 ± 0.5 mg was used for each test. It was evenly distributed in the crucible to avoid the effects of side reactions or diffusion phenomena limitations i.e. heat and mass transfer during thermal process-

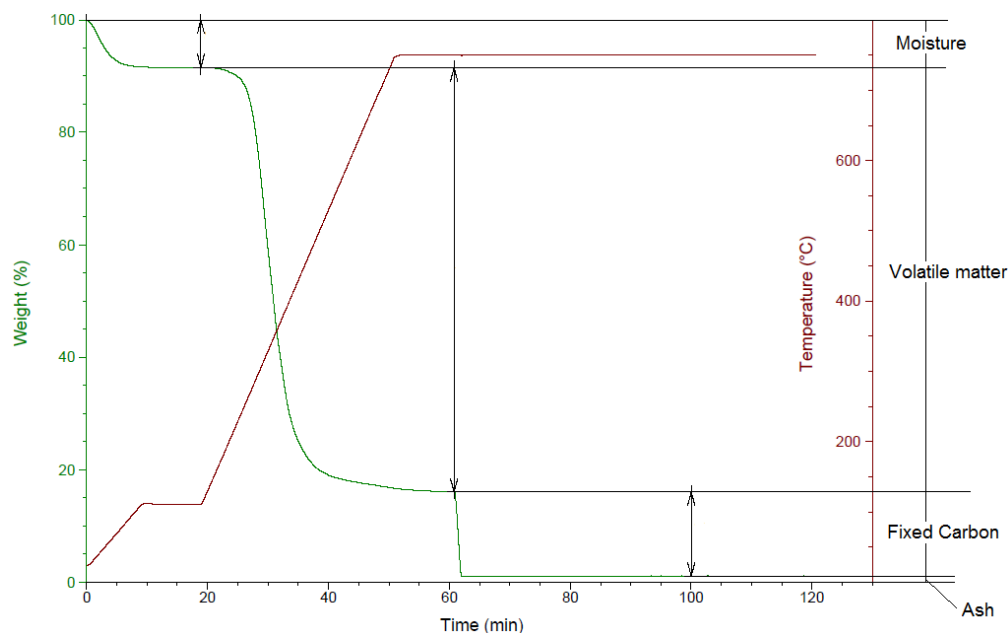


Figure 3-7: Weight loss of spent coffee grounds - Proximate analysis.

ing. In addition, the experiments were carried out at least twice to ensure repeatability, a third sample was used if results differed more than 5 %.

During devolatilisation experiments, the sample was heated in a nitrogen atmosphere with a constant flow of 50 ml/min from ambient temperature to 110 °C at 10 °C/min. It was kept isothermal at the temperature for 10 min to ensure complete removal of moisture, then heated further to 950 °C at 20 °C/min and kept isothermal at the temperature for 30 min to ensure a complete stabilisation of the sample. Combustion experiments were performed in air with a constant flow rate of 50 ml/min, with the same procedure for complete removal of moisture, then the sample was heated from 110 to 950 °C and kept isothermal at the temperature for 30 min to ensure a complete stabilisation of the sample. Additional experiments at different heating rates were carried out to confirm the findings about synergistic effects during thermal decomposition of the blends. Further results and discussion about TGA studies in this research are explained in detail in Chapter 4.

3.3 Ash Fusibility Temperatures (AFT) Studies

This section describes the experimental techniques, equipment, and operating parameters implemented in the AFT Studies. Although there are some limitations, the AFT test is a broadly used method to characterise ash fuels behaviour [Yan et al., 2017] [Ma et al., 2017] [Niu et al., 2016a] [Vassilev et al., 2014]. It has shown to be adequate to predict the ash behaviour from sintering/shrinkage to melting by the determination of four temperatures, namely initial defomation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) [Wang et al., 2017a] [Li et al., 2017b] [Niu et al., 2016a] [Vassilev et al., 2014] [Vassilev et al., 2013].

3.3.1 Apparatus

Ash Fusibility Furnace

Ash fusibility experiments were performed using an ash fusibility furnace, CAF G5, manufactured by Carbolite. It is an instrument whose operational principle relies on the controlled heating up of ash samples in a furnace to study their ash fusibility behaviour under specific reducing or oxidising conditions. It is used in conjunction with a high-resolution camera with capabilities to take thermal images to track changes in the samples. Figure 3-8 shows the ash fusibility furnace set-up used in this research.

After previous preparation of samples, a loading process consisting of the positioning of the samples on the sample carrier inside the work tube must be performed before every run. Figure 3-9 shows the steps of samples loading along with a sample image from the thermal camera during operation.

Once the samples were loaded the furnace door was closed to start the heating up process. The ash fusibility furnace used in this research was constructed to use H_2 and CO_2 test gases with CO_2 as purge gas (compatible with BS ISO 540 : 2008) wit an adjustable starting temperature from 815°C.

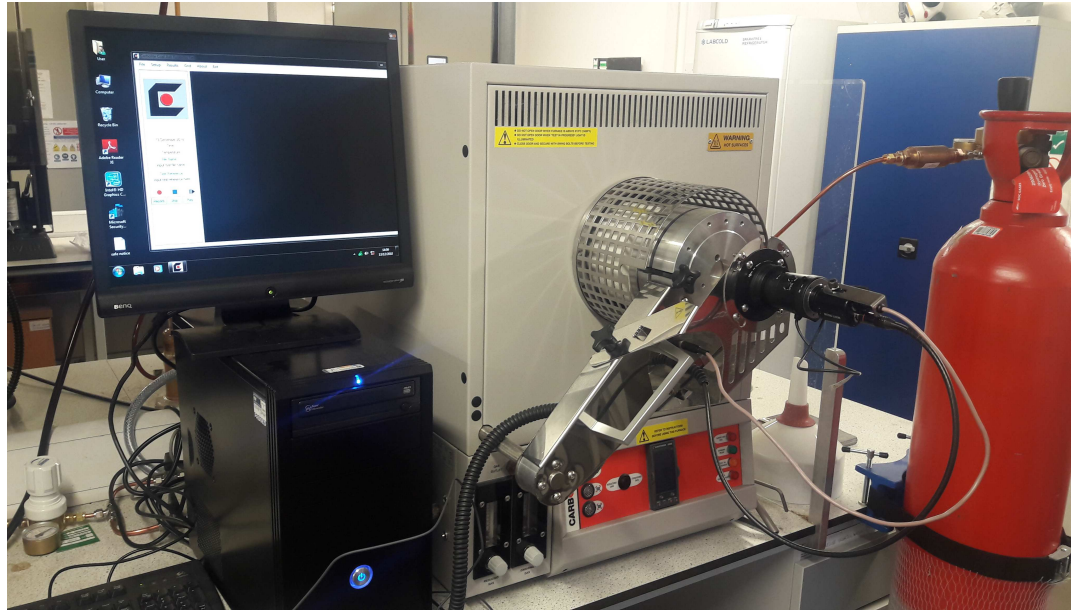


Figure 3-8: Ash fusibility furnace - Carbolitem, CAF G5.

One of the main limitations linked to the ash fusibility test technique is the different conditions in AFT test in comparison with a real operation. Moreover, one of the major flaws in the ash fusion test is the reliance on visual observation instead of an objective physical measurement. In this study, ash fusibility temperatures technique was used to characterise the thermal behaviour of pure fuel ashes and their blends by the ash fusibility temperatures determination. Further explanation about the operating parameters and experimental considerations for these tests are included in the following sections.

3.3.2 Test Samples Preparation

There are two conventional test shapes for AFT analysis namely pyramidal and cylindrical ash pellets. Both ash pellets may be made manually by mixing a certain amount of ash with dextrin to act as a binder. Then, the mixture is placed in the mold and pressed to allow the pellet to be formed. Nevertheless, it has been reported that dextrin can result in the formation of voids at low temperature whilst it decomposes [Pang et al., 2013]. Furthermore, it has been established that if sufficient pressure is used pellets can be prepared without the need of any binder [Pang et al., 2013].

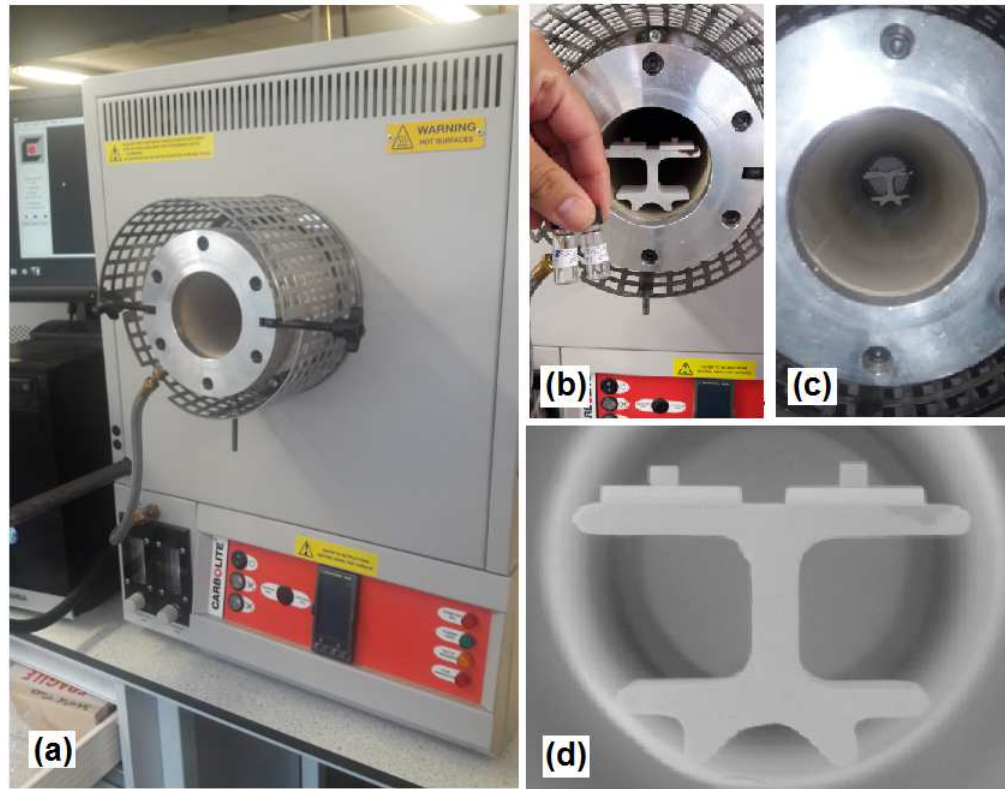


Figure 3-9: Loading of samples in the ash fusibility furnace, (a) working tube open, (b) initial position of sample carrier for loading samples, (c) final position of sample carrier and (d) image from thermal camera.

In this study, cylindrical pellets of ash samples and their blends were prepared with samples of 100 mg in a 5 mm evacuable die set manufactured by Specac, using an Instron 3369 tensometer system to produce consistent ash pellets. The same compression profile was applied to every sample to secure highly reproducible pieces with 5 mm diameter under a maximum compression pressure of 5000 psi and a holding time of 60 seconds. Figure 3-10 describes the procedure followed to prepare the cylindrical ash pellets. Further details about the ash blends and later ash pellets preparations are included in the AFT studies in section 5.2 in Chapter 5.

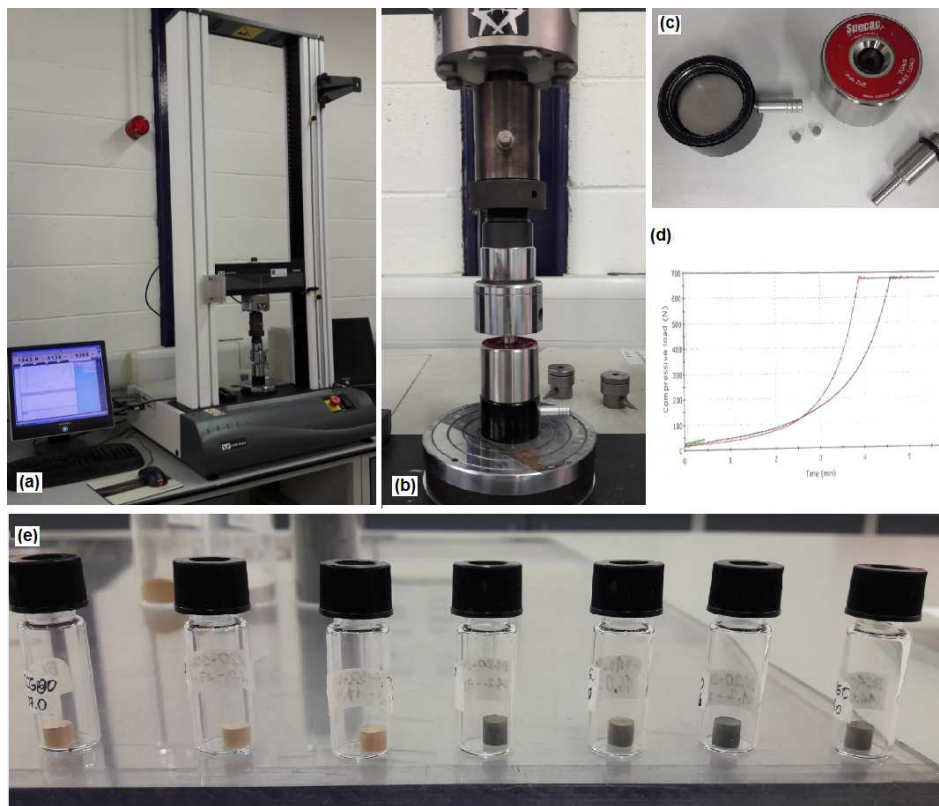


Figure 3-10: Description of cylindrical ash pellets preparations, (a) Instron 3369 tensometer system, (b) mounted die set in the compression section, (c) die set, (d) typical compression profile, and (e) sample of prepared cylindrical ash pellets ready for AFT studies.

3.3.3 AFT Measurements

Ash fusibility temperatures (AFT) measurements were performed according to BS ISO 540:2008 Hard coal and coke - Determination of ash fusibility. The ash pellets were heated at 7 °C/min to 1580 °C under oxidising conditions (CO_2) at 1 l/min. During the heating process, the shape change of the pellets was detected by a thermal camera and recorded every 5 °C. The experiments were carried out at least twice to verify repeatability, a third sample was used if results differed more than 5 %. Based on recorded images, four characteristic temperatures were determined according to the changes in the cylinders: deformational temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT). Figure 3-11 shows the characteristic shapes of the cylindrical test piece and corresponding temperatures.

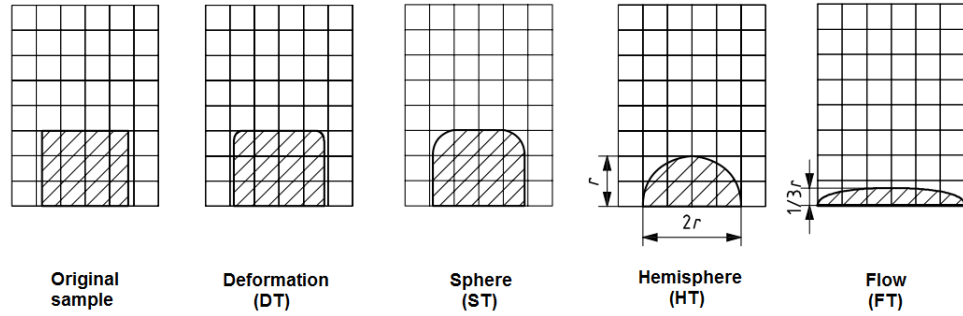


Figure 3-11: Characteristic shapes of the cylindrical test piece (BS ISO 540:2008).

The analysis of the recorded images to determine the fusion temperatures was carried out by manual method through the CAF test software, which allows the placing of a numbered grid over the sample under study in the image. Figure 3-12 shows the typical placing of the grid over the ash sample to analyse changes in the shape in AFT experiments. The same analysis was repeated for each other sample in the image to obtain the characteristic temperatures.

Furthermore, to improve the image analysis a vector-based image processing application was devised in MATLABTM (R2018b) software for this research. It allowed tracking the changes in the sample shape framing the region of interest in the image with an improved possibility to zoom-in by the implementation of a finer grid. In addition, it facilitated to track and compare changes in several samples in the same image. Figure 3-13 shows the improvements in the tracking of changes in the sample by framing the region of interest and zoomed-in sample image.

As a result, the tracking of changes in the samples was enhanced in comparison to the by default method provided by the CAF test software. Furthermore, higher accuracy was achieved by decreasing the difference in observed temperatures for ash pellets from the same sample under study.

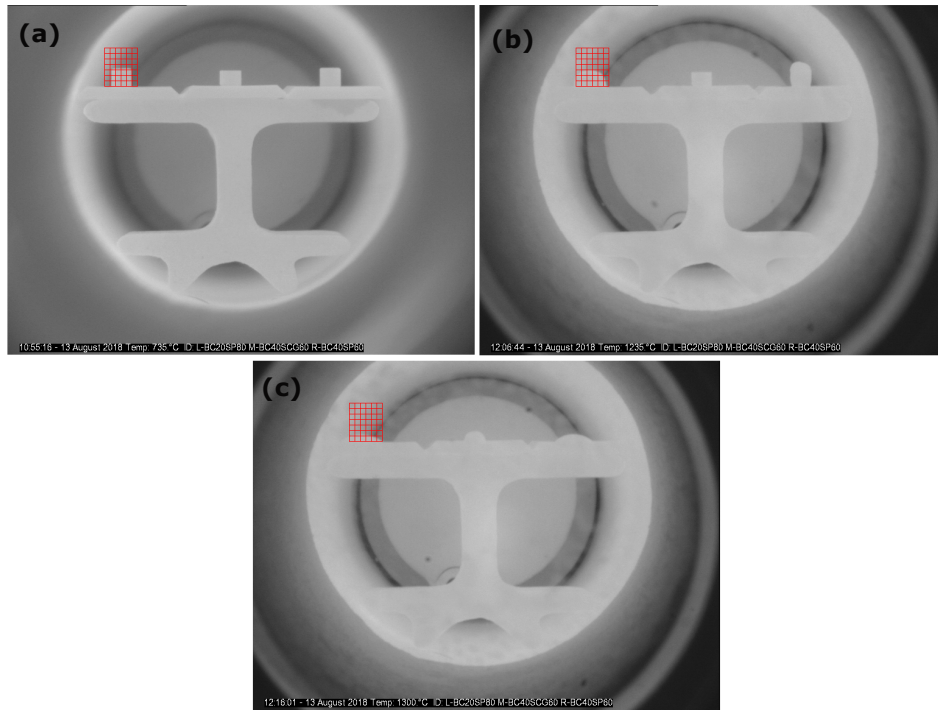


Figure 3-12: Typical placing of the grid over the ash sample by CAF test software to perform AFT analysis, (a) at 735 °C, (b) at 1235 °C, and (c) at 1300 °C

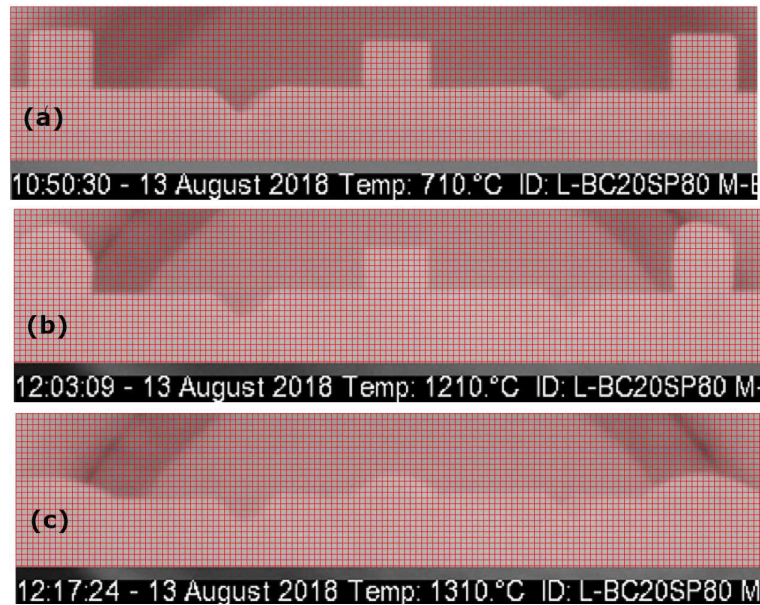


Figure 3-13: Placing of the grid over the sample by the vector-based image processing application to perform AFT analysis, (a) at 710 °C, (b) at 1210 °C, and (c) at 1310 °C

3.4 Fluidised Bed Combustion (FBC) Experiments

The fluidised bed technology represents an improvement in combustion sector due to the increased efficiency and reduced emissions. This technology allows the use of a wide range of different fuels with a broader range of characteristics. Furthermore, enhanced mixing in fluidised beds leads to higher heat transfer rates and increased combustion efficiency compared to conventional stoker or pulverised coal combustion technologies. Additionally, lower operating temperature in the reactor allows the reductions of NO_x emissions. Following sections describe the experimental techniques, equipment, and operating parameters implemented in the FBC experiments in this research.

3.4.1 Description of the Experimental Set-up

All the experiments were carried out in the existing 30 kWth bubbling fluidised bed (BFB) combustor of the Low Carbon Energy and Resource Technologies Research Group of the University of Nottingham. Further details about the design and commissioning of the BFB combustor can be found in [Afilaka, 2015]. It is capable of burning a wide range of fuels, and of reproducing the typical process conditions and gas compositions of commercial FBC systems with similar capacity. It consists of a BFB reactor, gas-solid cyclone, fuel feeding system, fluidising fan, flue gas sampling and analyser (see Appendix F), and data-logging system. The schematic diagram of the experimental set-up along with a real photo are illustrated in Figure 3-14.

The BFB reactor is made of a 6 inches 40S (wall thickness of 7.11 mm) high-grade stainless steel pipe (ASTM A-312) with 154 mm internal diameter and a height of 2000 mm. It is divided into three sections namely plenum chamber, fluidised bed and freeboard with corresponding heights of 200, 750 and 1050 mm, respectively. The fuel feeding point is located in the freeboard section at a height of 1200 mm from the bottom of the BFB reactor. The flue gas and fine particles outlet point is located in the centreline of the freeboard section at a height of 1880 mm from the bottom of the BFB reactor. Between

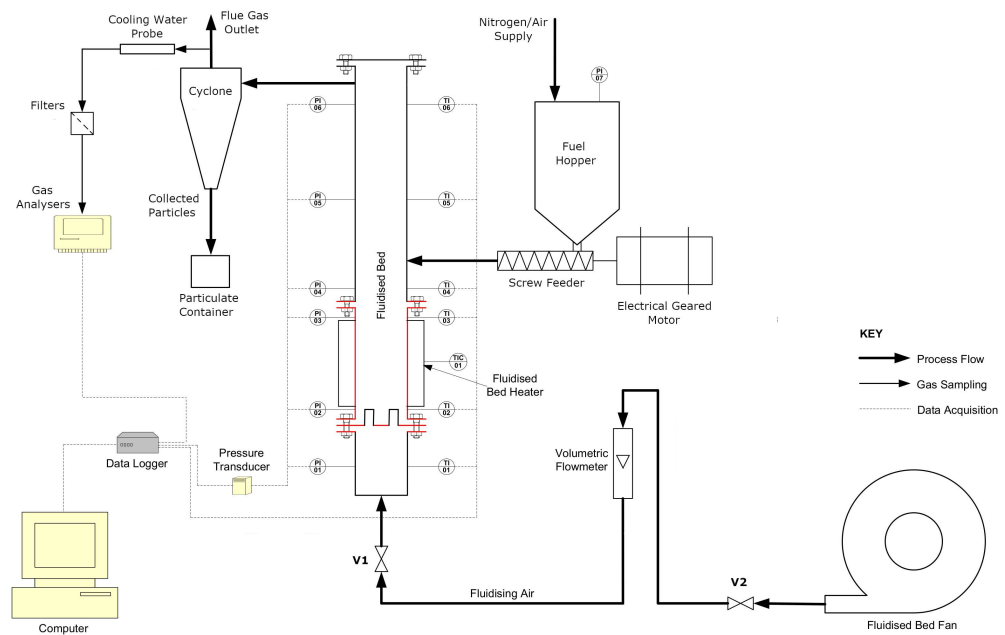


Figure 3-14: Schematic diagram (top) and photo of pilot-scale (bottom) BFB combustor.

the fluidised bed and freeboard sections is located the air distribution plate, which consists of an arrangement of four nozzles. Figure 3-15 shows the schematic disposition of the BFB reactor and the distribution plate.

The BFB reactor is equipped with electrical heating to start-up the process. It consists of two semi cylindrical Watlow ceramic fibre electrical heaters (VS108A18T-0001R), with 203 mm internal diameter by 457 mm long, electrical rating of 240V - 3900 W (total power rating of 7800W) and a maximum operating temperature of 982°C to provide the require temperature before the onset of fuel feeding. A pressure transducer was used to measure the differential pressure across the dense phase of the BFB reactor. Six K-type thermocouples were mounted across the reactor length (100, 300, 900, 1130, 1450 and 1770 mm from the bottom of BFB reactor).

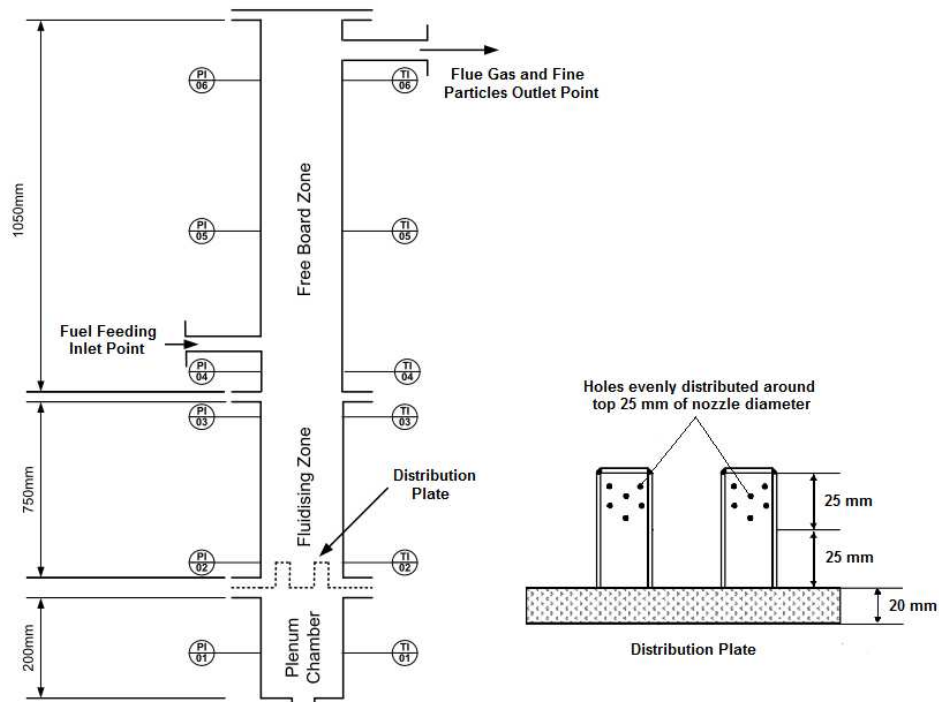


Figure 3-15: Schematic diagram of the BFB reactor and distribution plate (Not to scale)(adapted from [Afilaka, 2015]).

The fuel feeding system consists of a cylindrical hopper of 254 mm internal diameter and a height of 500 mm, along with a screw feeder powered by a

SEW-EURODRIVE helical geared motor (model R67 DRE80M4/TF) which is controlled by an Allen - Bradley IP20 variable speed drive (model PowerFlex 4 AC Drive) to regulate the fuel feed rate. The hopper has a separate nitrogen supply line to create an inert environment and provide back-pressure to prevent hot gas flow into the feed line and fuel hopper from the BFB reactor.

During the experiments the fluidising air is supplied by a 2900 rpm centrifugal fan (model BM 841) manufactured by Fans and Blowers Ltd. The fan is controlled by a Weg technology variable speed drive (model CFM-11). The fan and variable frequency drive operations are controlled remotely using the Super Drive G2 software supplied by Weg. The connection between the fluidising fan and BFB reactor was made by a 50 mm outer diameter flexible stainless steel pipe to the plenum chamber at the bottom of the BFB reactor. In addition, as an operational indicator during the combustion experiments, the volumetric flow rate of fluidising air supply was monitored by a low pressure variable area volumetric air flowmeter (see Figure 3-16a) with a measure range from 120 to 1100 LPM at 20°C, manufactured by Cache Instrumentation Ltd. to provide an estimate measurement of air flow rate supplied into the BFB reactor.

An external cyclone at the exit of the BFB reactor was used to capture in a particulate container (see Figure 3-16d) the fine particles entrained by the flue gas effluent. The flue gas was permanently sampled (0.5 l/min) via the sampling probe located at the top of the cyclone before its release to the atmosphere. The flue gas sample was cooled down and filtered by an in-house designed gas cooling and cleaning system (see Figure 3-16c). Afterwards, it was conditioned by a Horiba technology gas sampler (model VS-3000), which was connected to a regularly calibrated Horiba technology gas analyser (model VA-3000) with a repeatability of ± 0.5 % on a full scale range (FSR) to analyse the NO_x composition in the flue gas and a regularly calibrated ABB technology gas analyser (model EL 3020) with a repeatability of ≤ 0.5 % on a FSR to analyse the O_2 , CO_2 and CO composition in the flue gas stream (see Figure 3-16b).

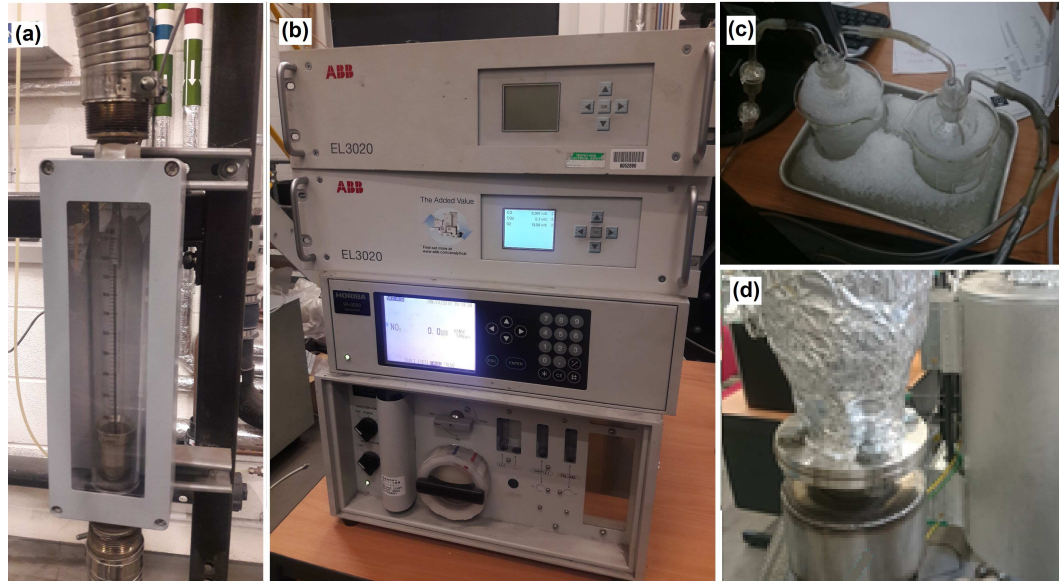


Figure 3-16: Auxiliary components of BFB reactor, (a) variable area volumetric air flowmeter, (b) gas analysers, (c) gas cooling and cleaning system, and (d) particulate container.

The signals from the thermocouples in the BFB reactor, the pressure transducer, and gas composition from the analysers were continuously monitored using a DT80 DataTaker five-channel logger (model DT80 series 2), which was connected to a DataTaker Technology twenty-channel expansion module (CEM20) each with an accuracy of $\pm 0.01\%$ on a full scale span (FSS). For the entire duration of the experiments, readings were taken every 10 seconds using a workstation equipped with a custom-designed data logging software supplied by DataTaker.

3.4.2 Bed Materials and Additives Characterisation

The experiments in the BFB combustor used silica sand as bed material for the reference case. Specifically, the Garside 14/25 sand was chosen to be used as the bed material for the operation of the BFB combustor, due to its availability and usage in several UK industrial BFB combustor systems. The ilmenite used in the experiments was supplied by Titania A/S (Norway). In addition, kaolin and bauxite were used as additives for comparison purpose due to their broad use in the industry to reduce the agglomeration phenomenon. All the materials were used as received. The physical and

chemical analysis of the materials supplied by the manufacturers are shown in Table 3-4.

Table 3-4: Physical and chemical analysis of bed materials and additives

	Material Property		Garside 14/25 (silica sand)	Ilmenite	Bauxite	Molochite 16/30 (kaolin)
Physical properties	Size range (mm)		0.6 to 1.18	0.6 - 0.8	0.7 to 1.1	0.7 to 1.0
	Grain shape		Sub angular to rounded	Angular	Angular	Angular
	Colour		Yellowish brown	Dark grayish-black	Buff and grey	White
	Specific gravity		2.65	3.70	3.0	2.70
Chemical properties	Name	Compound	Weight (%)			
	Silica	<i>SiO₂</i>	96.67	27.68	12.1	54.0
	Alumina	<i>Al₂O₃</i>	0.33	10.32	80.8	42.0
	Titanium	<i>TiO₂</i>	0.03	25.74	2.70	0.07
	Iron	<i>Fe₂O₃</i>	2.4	22.56	3.82	1.30
	Magnesium	<i>MgO</i>	<0.01	6.97	-	0.30
	Calcium	<i>CaO</i>	0.01	3.81	2.5 - 3	0.07
	Sodium	<i>Na₂O</i>	0.03	1.57	2.5 - 3	-
	Potassium	<i>K₂O</i>	0.01	0.53	2.5 - 3	2.0
	Phosphate	<i>P₂O₅</i>	<0.01	0.13	0.15	-
	Manganese	<i>MnO₂</i>	<0.005	0.20	-	-
	Chromium	<i>Cr₂O₃</i>	0.02	0.08	<0.05	-

The particle size distribution of bed materials used (Garside 14/25 sand and ilmenite) was analysed using a standard test method according to ASTM D6913/D6913M-17 (see Appendix C). Moreover, it is worth noting that the particle size of the materials used in this research was restricted to be < 1 mm according to the selection of working parameters for the experiments in the BFB combustor. It corresponds to group B in Geldart classification (see Appendix E), which is characterised by the fact that bubbles appear as soon as the superficial gas velocity exceeds the minimum fluidisation velocity (U_{mf}) [Basu, 2006] [Gibilaro, 2001]. The size of the bubble increases as the bubble rises and there is no maximum bubble size. The bed collapses immediately when the gas flow is terminated [Valverde, 2015] [Scala, 2013].

3.4.3 Hydrodynamic Parameters

Fluidisation Velocities

The phenomenon of fluidisation in gas-solid systems is characterised by the operation at which solid particles are in suspension state in a gas. This suspension state originates from the counterbalance of frictional forces between particles and gas, and the weight of the particles [Lackner et al., 2010]. To establish the appropriate fluidisation regime for any given application, it is required to calculate the minimum fluidisation velocity (U_{mf}) and the terminal velocity (U_t) of the bed particles [Scala, 2013] [Yang, 2003]. The U_{mf} is the superficial fluid velocity at which the fluid drag force balances the gravity acting on the bed [Scala, 2013]. At any value below U_{mf} , a packed bed of solid particles remains fixed. At U_{mf} , the bed is considered to be an incipiently fluidised bed or a bed at minimum fluidisation [Basu, 2006] [Kunii and Levenspiel, 1991]. With an increase in flow rate beyond minimum fluidisation, large instabilities with bubbling and channeling of gas are observed, in which gas bubbles coalesce and grow as they rise [GIDASPOW, 1994]. At higher flow rates, agitation becomes more violent and the movement of solids becomes more vigorous [Kunii and Levenspiel, 1991]. It is worth noting that the bed does not expand much beyond its volume at minimum fluidisation.

As for the terminal velocity, it is the minimum velocity of the pneumatic transport of the particles. If the gas velocity approaches the terminal velocity of some of the particles, then such particles can be elutriated, or carried completely out of the system in the exit gas [Scala, 2013]. When the terminal velocity is exceeded the upper surface of the bed disappears, entrainment becomes appreciable with a turbulent motion of solid clusters and voids of gas of various sizes and shapes instead of bubbles. Any further increase in gas velocity will carry out the particles with the gas leading to pneumatic transport of solids [Kunii and Levenspiel, 1991].

Minimum Fluidisation Velocity. A widely employed approach to estimate the minimum fluidisation velocity U_{mf} is by simplification of the Ergun equa-

tion for the packed bed. The force balance at the minimum fluidisation is given by:

$$[\text{weight of solid particles}] - [\text{buoyancy acting on particles}] = [\text{pressure drop of fluid across the bed}] \times [\text{bed cross-sectional area}]$$

At the point of minimum fluidisation, the pressure drop is enough to support the weight of the particles and can be expressed as [Basu, 2006] [Yang, 2003]

$$(1 - \varepsilon_{mf})(\rho_p - \rho_f)gL_f A_t = \Delta P A_t \quad (3-1)$$

Where A_t is the bed cross section, g gravity acceleration, L_f bed height, ΔP the pressure drop due to fluid flow measured between bed bottom and top (positive for upward flow), ρ_f density of fluid, ρ_p apparent density of solid and ε_{mf} void fraction of bed.

For the pressure drop, it could be obtained from the equation for calculating the minimum fluidisation velocity, including both the kinetic energy term and the viscous term from the following Ergun correlation [Scala, 2013]:

$$\frac{\Delta P}{L} = 150 \frac{(1 - \varepsilon_{mf})^2}{\varepsilon_{mf}^3} \frac{\mu u_0}{\phi^2 d_p^2} + 1.75 \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}^3} \frac{\rho_f u_0^2}{\phi d_p} \quad (3-2)$$

where d_p , u_0 , ϕ and μ are mean particle diameter, superficial fluid velocity, sphericity of a particle and viscosity of fluid, respectively. Moreover, based on experimental data, [Wen and Yu, 1966] suggested a simplified form of the Ergun equation by assuming the following:

$$\frac{1 - \varepsilon_{mf}}{\phi^2 \varepsilon_{mf}^3} \cong 11 \quad \text{and} \quad \frac{1}{\phi \varepsilon_{mf}^3} \cong 14 \quad (3-3)$$

Considering that:

$$Re_{mf} = \frac{d_p \mu_{mf} \rho_f}{\mu} \quad (3-4)$$

Additionally, by substituting values from equation 3-3 into Ergun correlation as shown in equation 3-2 and then substituting it into the pressure drop equation at minimum fluidisation as shown in equation 3-1, in a simplified form, the Ergun equation, in terms of Reynolds number and Archimedes number, can be reduced to:

$$Re_{mf} = [C_1^2 + C_2 Ar]^{1/2} - C_1 \quad (3-5)$$

where Ar is the Archimedes number [Scala, 2013].

$$Ar = \frac{d_p^3 \rho_f (\rho_p - \rho_f)}{\mu} \quad (3-6)$$

There are many sets of values suggested for the constants C_1 and C_2 based on different databases used for correlation [Yang, 2003]. Nevertheless, for the particles size of bed materials used in this research the corresponding form of the simplified Ergun equation is:

$$Re_{mf} = [33.7^2 + 0.0408 Ar]^{1/2} - 33.7 \quad (3-7)$$

Rearranging 3-4, the minimum fluidisation velocity U_{mf} equation is:

$$U_{mf} = \left[\frac{\mu_{mf}}{d_p \rho_f} \right] Re_{mf} \quad (3-8)$$

For the purpose of this work, the parameters for the fluidising velocity calculation are as follows: $T_{amb} = 20^\circ C$, $\mu_{amb} = 1.81 \times 10^{-5} \text{ kg/ms}$, $\rho_{g,amb} = 1.204 \text{ kg/m}^3$, $\rho_s = 2650 \text{ kg/m}^3$ (silica sand) and $\rho_s = 3700 \text{ kg/m}^3$ (ilmenite), $d_s = 0.8 \text{ mm}$ (silica sand), and $d_s = 0.67 \text{ mm}$ (ilmenite), and $g = 9.81 \text{ m/s}^2$.

Terminal Velocity. The terminal velocity (U_t) in a bubbling fluidised bed is the maximum allowable velocity for operation. At this velocity some of the particles can be elutriated, or carried completely out of the system in the exit gas [Scala, 2013]. A fluidised bed consists of polydispersive mixtures of solids, in which the terminal velocity of the smallest particle may be just equal to or even less than the minimum fluidisation velocity of the largest particle. Therefore, the particle size distribution of the bed plays a key role in

the stability of fluidisation. An increase in the size of the solids particles brings about not only a significant increase of U_{mf} and U_t but also a narrowness of the range of gas velocity for which a stable fluidisation may be maintained [Lackner et al., 2010]. In this research the terminal velocity was determined according to [Basu, 2006] as follows:

$$Ar = \frac{3}{4} C_D \left[\frac{d_p U_t \rho_g}{\mu} \right]^2 \quad (3-9)$$

Equation 3-9 reduces to the following forms for different values of the drag coefficient:

$$\frac{d_p U_t \rho_g}{\mu} = \frac{Ar}{18} \quad \text{Stokes law, } Re < 0.4 \quad (3-10)$$

$$\frac{d_p U_t \rho_g}{\mu} = \left[\frac{Ar}{7.5} \right]^{0.666} \quad \text{Intermediate law, } 0.4 < Re < 500 \quad (3-11)$$

$$\frac{d_p U_t \rho_g}{\mu} = \left[\frac{Ar}{0.33} \right]^{0.5} \quad \text{Newton's law, } Re > 500 \quad (3-12)$$

In general terms, to reduce the carryover of fines in fluidised bed the operating superficial velocity must be in the range between the minimum fluidisation velocity and the terminal velocity, $U_{mf} < U < U_t$.

Validation of Fluidising Velocity. The calculated values of minimum fluidisation velocities using equations 3-1 to 3-12 are 0.42 m/s and 0.43 m/s at 20 °C, and 0.23 m/s and 0.22 m/s at 900 °C for Garside 14/25 and ilmenite, respectively. In practice, BFB combustors operate at gas velocities several times higher than U_{mf} [Lackner et al., 2010]. Indeed, the superficial gas velocity commonly used in BFB combustors corresponds to 8 - 10 times U_{mf} [Oka, 2004]. In this research the operating superficial velocity was predetermined to be eight times bigger than U_{mf} . It gives a superficial velocity at 900 °C for Garside 14/25 and ilmenite of 1.85 m/s and 1.76 m/s, respectively. According to [Loo and Koppejan, 2008], a bubbling fluidised regime with reduced erosion rates is achieved and sustained by an operating superficial velocity in the range of 1.0 - 2.0 m/s.

Additional experimental validation of the minimum fluidisation velocity were performed by means of a prototype of the BFB reactor with similar dimensions, made of clear polycarbonate material. These cold fluidisation tests allowed to measure the volumetric flow rate of the air supplied and corresponding U_{mf} . Furthermore, it enabled visual observation and assessment of fluidisation quality at operating superficial velocity (see Figure 3-17). It was made by filling up the prototype to 20 cm of bed material and setting a gas velocity higher than U_{mf} , which was gradually decreased until defluidisation of the bed occurred. This method has been reported as appropriate for determining U_{mf} due to the lack of structural formation effects of the bed that could arise if the gas velocity is increased from a fixed bed condition, resulting in inaccurate U_{mf} values [Scala, 2013]. Furthermore, a sample of the fuel blend was added from the top of the prototype to replicate the operating condition and evaluate mixing level. No segregation of fuel was observed. In addition, the expanded bed height was observed to be approximately constant under operation with both bed materials.

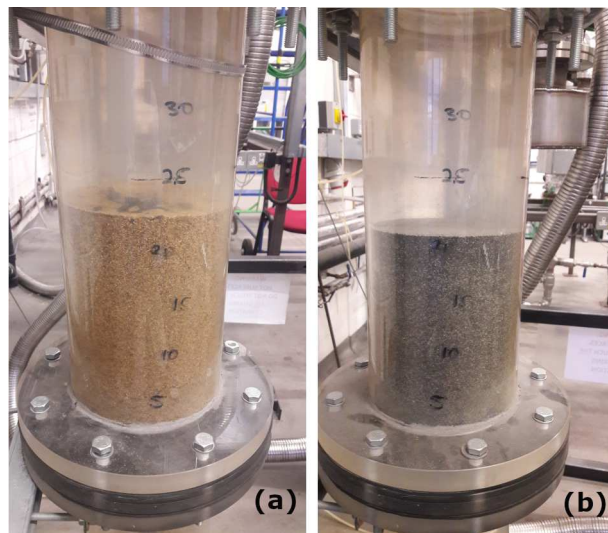


Figure 3-17: Cold fluidisation test in the BFB prototype,(a) Garside 14/25 (b) Ilmenite.

Vigorous fluidisation with high mixing level was observed. Furthermore, the addition of the blend sample did not show any change in the fluidisa-

tion quality. These preliminary tests suggested good quality fluidisation for both bed materials without any indication of segregation between coal and biomass pellets in the blend. Therefore, similar conditions can be expected during the experiments at operating temperature (i.e. 900 °C) in the BFB combustor.

3.4.4 Experimental Combustion and Sampling Procedure

The combustion of coal and biomass blends was performed at a bed temperature of 900 °C $\pm$ 20 °C in the BFB combustor at atmospheric pressure. The procedure implemented during the combustion process consisted of four stages namely pre start-up preparation, start-up, fuel combustion, and shut-down.

Pre Start-up Preparation

The pre-start preparation for each experiment consisted of two procedures of preparation and loading of bed material and fuel, respectively. Afterwards, a checking process of suitable operability of auxiliary components was performed. These activities were carried out the previous day to each run.

Bed Material. The operational principle of the combustion experiments in the BFB reactor in terms of the bed height corresponded to a shallow bed, which is characterised by a height-to-length ratio far below one and a length-to-width ratio of at least 5 [Pécora and Parise, 2006]. Among others advantages, shallow beds show small bed pressure drop and reduce power consumption in fluidising air [Parise, 2006] [Brzic et al., 2005]. The static bed height for all the experiments was set to 20 cm, corresponding to a bed inventory of 6 kg and 8.37 kg of Garside 14/25 sand and ilmenite, respectively. When kaolin, bauxite or ilmenite were used as additives, 10 wt% of the Garside 14/25 sand used as bed material was substituted by the corresponding additive. The bed material for each experiment was poured into the BFB reactor through the flange located at the top of the reactor.

Fuel Blends Preparation. Fuels prepared according to the procedure described in 3.1.1 were measured, manually blended and poured into the fuel hopper which has a holding capacity of up to 15 kg. The fuel blends corresponded to bituminous coal (BC) blended with biomass pellets of wheat straw (STW) and wood (WP) at 15 and 40 wt%. As for spent coffee grounds pellets (SCG) manufactured in this research, only the blend with 40 wt% was considered due to limited availability of the resource. All the amounts were measured using a Kern and Shon GMBH weighing scale (model: ECB 20K20) with a readability and repeatability of 20 g. Figure 3-18 shows some of the pure fuels and the blends used in this research.



Figure 3-18: Selected samples of pure fuels and blends used in the BFB combustion experiments, (a) bituminous coal (BC), (b) commercial wheat straw pellets (STW), (c) in-house manufactured spent coffee ground pellets (SCG), (d) BC blended with STW at 40 wt%, (e) BC blended with STW at 15 wt%, and (f) BC blended with SCG at 40 wt%.

Fuel Feeding System Calibration. The calibration of the fuel feeder system was performed by setting a program of different speeds of the feeder screw using the variable speed drive connected to the geared motor. A plastic bucket was placed on a weighing scale where conveyed fuel was collected and weighted constantly over a fixed period of time. A detailed description of feeding system calibration experiments is shown in Appendix B. Figure 3-19 shows the calibration results for all the fuels used in the combustion experiments in the BFB combustor.

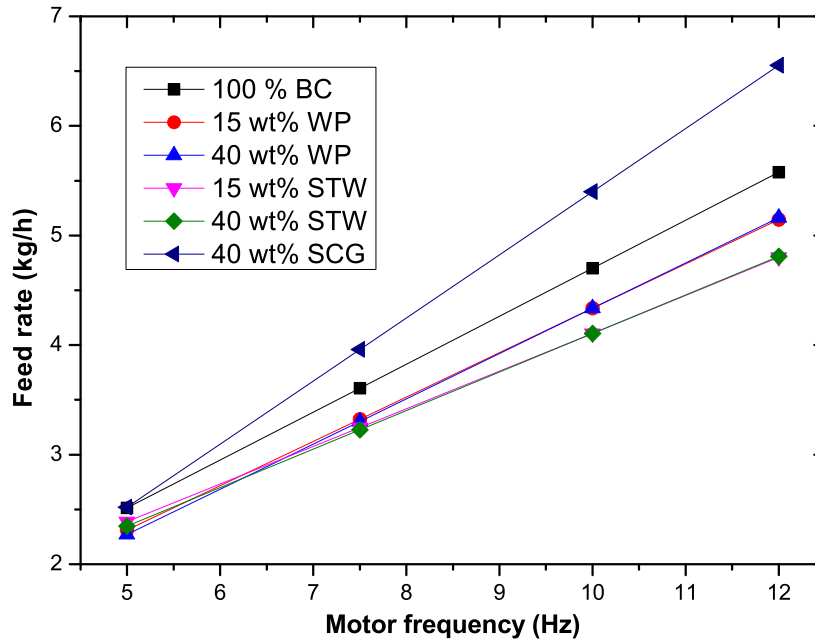


Figure 3-19: Feeding calibration results using bituminous coal (BC), commercial wheat straw pellets (STW) blended at 15 wt% and 40 wt%, commercial wood pellets (WP) blended at 15 wt% and 40 wt%, and in-house manufactured spent coffee ground pellets (SCG) blended at 40 wt%.

Start-up

The activities carried out at the beginning of each experiment in the BFB reactor started with the flow of cooling water to the flue gas sample probe, monitoring and collection of temperatures and pressure drop, and the initiation of bed heater and fan control by the main switch in the control panel. The heating rate was set to 400 °C/hour with a set-point of 850 °C. The temperature limit controller was set to 890 °C which is 40°C above the set-point of the heating controller. Then, the on button for the BFB reactor heater control system was pressed to start the heating cycle for the corresponding run.

After 20 minutes of heaters operation, the fluidising fan was turned on and ramped up to a speed of 2700 rpm using the Super Drive G2 software installed in the workstation. The manual ball valve (V1, see Figure 3-14 top) located at the bottom of the BFB reactor was opened and regulated to a fluidising air flow rate of 200 litres/minute (room temperature and pressure -

RTP) measured using the variable area flowmeter. It was allowed to operate at this condition for other 20 minutes after which the fluidising air flow rate was further increased by 60 litres/minute to 260 litres/minute at a time interval of 40 minutes from the beginning of the heating cycle.

This procedure was repeated at 60, 80, 100, and 120 minutes from the beginning of the heating cycle. Correspondingly, the fluidising air flow rate was increased by 60 litres/minute each time to 320, 380, 440 and 500 litres/minute at each time interval accordingly. After 120 minutes (2 hours) of continuous operation from the beginning of the heating cycle, with the corresponding fluidising air flow rate of 500 litres/minute, the system was further allowed to continue operating at this condition until the bed temperature reached 600 °C. This normally takes between 150 and 200 minutes from the beginning of the heating cycle.

Fuel Combustion

After the bed temperature in the BFB reactor reached 600 °C, the fuel feeding into the BFB reactor was initiated. The feeder inverter frequency for each fuel blend was set accordingly to the results from the screw feeder calibration program (detailed information is included in Appendix B). Immediately the fuel started entering the BFB reactor, the temperature measured across the five thermocouples in the BFB reactor started to increase and detected in the workstation. The bed temperature was left to continue increasing at this condition until operating bed temperature of 900 °C. Afterwards, the fluidising air flow rate into the BFB reactor was increased to 640 litres/minute using V1 (see Figure 3-14 top). The BFB reactor was left to continue operating at this condition and stabilise to the operating bed temperature. Steady-state was reached once the operating bed temperature was steady within 900 ± 20 °C margin. In addition, the fuel feed rate was adjusted to maintain stable operation at the operating temperature.

Furthermore, the temperatures and pressure were continually monitored online (every 10 seconds) by the DT80 series data logger. It served to deter-

mine the state of fuel combustion and make adjustments. Similarly, flue gas composition (O_2 , CO_2 , CO , and NO_x) was monitored by using the flue gas sampling probe cooled with water and connected to the in-house gas cooling and conditioning system to remove particulates and moisture before entering into the gas analysers (see Appendix F). All the signals were displayed on the flue gas composition charts on the BFB reactor workstation.

Shutdown

After approximately 5 hours of steady fuel combustion, the run was considered successful and fuel feeding was stopped to start the cooling down of the BFB reactor. This process consisted of turning off the feeder inverter, keeping the same fluidising air flow rate for 45 minutes more. Afterwards, the fan speed was reduced to 1500 rpm and kept at this condition until the BFB reactor bed temperature dropped below 200 °C. Then, the fluidising fan, air supply to the hopper, and flow of cooling water to the sampling probe were stopped.

3.4.5 Used Bed Material and Ash Characterisation

After completing each combustion experiment additional subsequent actions were carried out the day after each run. It was mainly to obtain samples of the used bed material, ash in the particulate container, and determination of the fuel consumption. The used bed material was visually inspected for signs of sintering or agglomeration, samples were obtained by opening the flange located at the top of the BFB reactor. Found agglomerates were labelled and stored prior to be analysed by SEM-EDX and XRF techniques. The ash samples were collected to determine unburnt carbon in ash according to ASTM D7348 Standard Test Method for Loss on Ignition (LOI) of Solid Combustion Residues. The remaining fuel in the hopper was measured to estimate the fuel consumption and perform the determination of gaseous emissions (CO_2 , CO , and NO_x) on an energy basis by the analysis of collected data from the gas analysers. After getting previously described samples, new fuel was loaded to the hooper to perform a second run with the same bed mate-

rial. After completing the second run the plenum section of the BFB reactor was disassembled to unload the used bed material and new bed material was loaded to start preparations for the next experiment.

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)

The scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) is a well-established and accepted technique used in the analysis of surfaces. It is considered a relatively rapid, inexpensive, and basically a non-destructive method. It allows the visual observation of an area of interest producing high-resolution imaging of surfaces with better resolution of normal optical microscopy. Among other application in different fields, this technique is broadly used to study morphology, sintering or agglomeration in the thermochemical processing of solid fuels. SEM images provide a great deal of information about the area being inspected. Simultaneously, EDX can be used to obtain quantitative chemical analysis information. These techniques have been used in several studies to explain sintering and agglomeration of bed particles during coal or biomass thermochemical processing [Scala, 2018] [Morris et al., 2018] [Vassilev et al., 2015].

The SEM working principle is based on the use of an electron gun, which emits electrons that get accelerated by an applied voltage. These electrons are a highly-focused, scanning (primary) electron beam. As a result of the primary electron interactions with the surface a variety of signals including low energy secondary electrons (SE), backscattered electrons (BSE) and X-rays that carry different information is generated [Spliethoff, 2010]. These signals are collected depending on the detector on the equipment and then are measured, and the values are mapped as variations in brightness on the image display. The intensity of SE gives topographic information useful to construct an image of the sample surface. The intensity of BSE can be correlated to the atomic number of the elements within the sampling volume giving some qualitative elemental information. The analysis of characteristic X-rays (EDX analysis) emitted from the sample gives more quantitative

elemental information, which allows conclusions about the distribution of different chemical elements within the sample. Therefore, SEM-EDX may provide a better understanding of the elements and interactions causing agglomeration and sintering formation.

In this research the SEM-EDX analysis was carried out using a SEM Quanta 600 equipped with EDX Genesis 4000i X-ray analyser. Elements included in the EDX analysis were typically K, Na, Ca, Mg, Fe, Al, Si, P, S and Cl after C and O contributions from the sample holder were removed. A backscattered electron (BSE) detector, accelerated voltage 20 kV operated under high vacuum was used to gain information on the spatial resolution of elements. The interactive oxides mode method was used for quantification of materials under SEM-EDX. The spectra working distance was 13 mm.

Samples Preparation and Method. The agglomerates samples were prepared through the encasing of samples in an epoxy-based resin. The resin blocks were subjected to polishing with a decreasing polishing particle size until a sufficient area of the sample was cut and the surface was smooth. Then all the samples were subjected to carbon coating prior the analysis. The preparation process took about two days on average to complete from start to finish.

Chapter 4

Thermogravimetric Analysis of Blends of By-products From Coffee Crop with a Bituminous Coal

By-products from coffee crops are an attractive source of biomass energy as they are renewable, abundantly available and do not compete with food crops. They have potential to substitute the fossil fuels to meet the ever-increasing world energy demand. This chapter investigates the thermal decomposition of blends of by-products (spent coffee ground (SCG), coffee husk (CH)) of coffee crops at 10, 30 and 50 wt %, with a bituminous coal (BC) to address their usefulness for energetic applications. For comparison purposes, blends of wood pellets (WP) and BC at the same mass ratios are also considered. Dynamic thermogravimetric analyses (TGA) were performed to assess thermal behaviour and fuel interactions in the blends during decomposition by the additive model along with devolatilisation (Dv), ignition (Di) and combustion indices (S).

4.1 Introduction

Co-combustion, which consists in the inclusion of biomass in the coal combustion process, has arisen as an interesting alternative. Among other advantages, co-combustion in comparison with exclusive coal use could reduce

GHG emissions and lower costs of adapting existing dedicated coal facilities than the building of new dedicated biomass systems without any need for permanent biomass supply because the plant could burn coal if biomass is not available [Dai et al., 2008] [Nuamah et al., 2012a] [Sahu et al., 2014]. Nevertheless, the use of two different fuels imposes many challenges due to their potential interactions during combustion and the effects on combustion efficiency and plant operations. These challenges are mainly due to the difference between the fuels in terms of chemical and physical properties, particularly the devolatilisation behaviour, char reactivity, and ash characteristics [Hupa, 2012] [IRENA, 2013].

Among the multiple biomass resources available for energy generation, agro-industrial residues can be a viable alternative to the traditionally used woody materials. In this sense, the coffee crop is a relevant industrial sector in about 80 countries, and one of the most popular beverages and the second largest traded commodity after petroleum [Mata et al., 2018] [Murthy and Madhava Naidu, 2012]. Global coffee production increased by almost 17 % between 2000 - 2012 [Campos-Vega et al., 2015]. Despite its known relevance, environmental impact resulted from the by-products of the coffee industry has increased drastically, mainly due to the high growth rates of this industrial sector in recent years. By-products from coffee crop represent about 80 % of the total coffee cherry (fruit) weight [Campos-Vega et al., 2015] [Esquivel and Jiménez, 2012]. Several studies have been performed to use these residues from coffee processing [Campos-Vega et al., 2015]. Up to now, most progress has been achieved in their use for industrial purposes such as animal feeding industry and recently for energy products including biodiesel, bioethanol or other compounds [Esquivel and Jiménez, 2012] [Mussatto et al., 2011].

Traditionally, spent coffee grounds and coffee husk have been partially used as fuel in boilers of the same industry for either heat or power generation. Nevertheless, the formation and emission of particulate matter when these residues are used in combustion processes should be considered due to the effect on air quality [Mussatto et al., 2011]. These by-products have potential to be used in blends with coal in the combustion process for emissions

reductions, due to its higher heating value compared with other biomass resources and available amount. Nevertheless, there is limited information in the literature about the thermal behaviour of these materials under co-combustion conditions.

Thermogravimetric analysis (TGA) is the most common technique used for studying the thermal behaviour of materials. In the literature, there are many examples of TGA studies which analyse the thermal behaviour of different materials e.g. polymers, food, fuels, explosives, etc. [Brown and Gallagher, 2008]. In this kind of analysis, the weight loss of a material is measured as a function of temperature and the gaseous reaction environment, such as inert, reducing and oxidising which can be used and changed during the measurement [Brown and Gallagher, 2008] [Hatakeyama and Liu, 1998]. Recently, TGA has made significant contributions to the study of renewable energy resources, specifically regarding their suitability for energetic use [Hill, 2012].

Previous investigations on co-combustion of coal and biomass blends using TGA have been mainly focused on the interactions between the fuels in the blends and the assessment of likely synergistic effects under inert and oxidising, and more recently under oxy-fuel conditions. In many of these studies, biomass fuels which are available on the market as densified products i.e. pellets or briquettes, such as wood, wheat straw, and miscanthus have been used [Zhou et al., 2016] [Vhathvarothai et al., 2014] [Moon et al., 2013]. There have also been some investigations considering other kinds of biomass in co-combustion experiments along with coal such as bamboo, soybean stalk sawdust, peanut shell, rice husk char, torrefied biomass beetroot and switchgrass [Yan et al., 2016] [Toptas et al., 2015] [Sarkar et al., 2014] [Zhou et al., 2014] [Liu et al., 2013b]. Other non-traditional biomass materials that have been used in the studies of co-combustion with coal include cellulosic ethanol residue, sewage sludge, municipal solid waste and laying hens manure [Junga et al., 2017] [Buratti et al., 2015] [Magdziarz and Wilk, 2013] [Muthuraman et al., 2010]. However, few TGA investigations can be found from the literature focusing on the use of the by-products from the coffee crops in pure or in blends with other materials.

Most of the studies about by-products from the coffee crops have been mainly focused on the use of residues from the roasting process in pure or in blends with other biomass materials. TGA was used in the kinetic modelling of thermal degradation of pure samples of coffee wastes and fireboard furniture production waste under inert conditions [Becidan et al., 2007]. The thermal behaviour of pure samples and blends of coffee waste, wood, demolition wood and glossy paper was characterised by TGA studies under inert and oxidising conditions [Skreiberg et al., 2011]. Kinetic and thermal behaviour of pure coffee husk, oil palm residues, corn cobs and peanut shells were characterised by TGA under inert conditions [Jeguirim et al., 2014a]. In studies conducted under inert conditions to evaluate the thermal behaviour of coffee husk and rice husk blends, it was reported the improvement of thermal degradation of the blends and reduced residual mass [Mhilu, 2014]. Coffee residues from soluble coffee industry were studied and compared with other traditional biomass materials under inert conditions by TGA and later study of pure coffee waste performance under reducing conditions in a laboratory two-stage quartz fixed bed in terms of obtained volatile fractions [Chaiklangmuang et al., 2015].

Studies about SCG or SCG-coal blends are particularly scarce. TGA of single biomass materials and their blends were conducted to characterise devolatilisation kinetics and combustion characteristics of SCG and sawdust to produce pellets for energy production [Jeguirim et al., 2014b]. In experiments under inert conditions using SCG, the effect of the heating rate was studied in terms of thermal behaviour and elemental composition of the obtained fractions [Li et al., 2014]. SCG was used in experiments under inert conditions conducted to investigate the influence of CO_2 in the devolatilisation process as a guideline for the utilisation of CO_2 in SCG gasification [Cho et al., 2015]. TGA tests of anthracite blended with SCG under oxy-fuel and air conditions were performed to study the influence of oxygen content at different blending ratios to characterise their thermal behaviour [Wei et al., 2016]. TGA analyses were performed to investigate the energetic potential

of pure SCG and blended with CH at 5 wt%, additional combustion experiments in a domestic combustor to assess the combustion performance of the materials were performed [Jeguirim et al., 2016].

The evidence presented in this section suggests that more attention is required for the thermal characterisation of by-products from the coffee crops in blends with bituminous coal, which is one of the most used fuels for electricity generation [Agency for Natural Resources and Energy, 2017]. Moreover, no comparison of the effect of biomass ratio with either SCG or CH in blends with BC about thermal decomposition characteristics and combustion performance in comparison to broadly used biomass such as wood pellets have been reported. This chapter investigates the thermal decomposition of blends of by-products (spent coffee ground (SCG) and coffee husk (CH)) of coffee crops at 10, 30 and 50 wt%, with bituminous coal (BC) under inert and oxidising conditions (N_2 and Air) by TGA to address their usefulness for energetic applications. For comparison purpose, blends of wood pellets (WP) and BC at the same mass ratio are also considered. The results can contribute to understand the behaviour of these blends under inert and oxidising conditions establishing their potential use with relevant information for the design and optimisation of thermochemical conversion systems at bigger scales.

4.2 Devolatilisation and Combustion Experiments

Devolatilisation and combustion experiments were performed using a thermogravimetric analyser (TGA Q500) with circular platinum crucibles with 2 mm height and 5 mm diameter. A sample mass of 10 ± 0.5 mg was used for each test and evenly distributed in the crucible to avoid the effects of side reactions or diffusion phenomena limitations i.e. heat and mass transfer during thermal processing. In addition, the experiments were carried out at least twice to ensure repeatability, a third sample was used if results differed more than 5 %. During devolatilisation experiments, the sample was heated in a nitrogen atmosphere with a constant flow of 50 ml/min from ambient temperature to 110 °C at 10 °C/min. It was kept isothermal at the temperature for 10 min to ensure complete removal of moisture, then heater further

to 950 °C at 20 °C/min and kept isothermal at the temperature for 30 min to ensure a complete stabilisation of the sample. Combustion experiments were performed in air with a constant flow rate of 50 ml/min, with the same procedure for complete removal of moisture, then the sample was heated from 110 to 950 °C and kept isothermal at the temperature for 30 min to ensure complete stabilisation of the sample. Additional experiments were carried out to investigate the effect of heating rate on the thermal behaviour of the blends.

4.3 Results and Discussion

Devolatilisation and combustion characteristics, such as ignition temperature, peak temperature, and burnout temperature were studied by TGA tests to figure out how thermal decomposition of BC was affected by blending with different types of carbonaceous materials at 10, 30 and 50 wt%. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were created by Universal analysis 2000 software. Both TG and DTG curves were smoothed to simplify comparison between different curves by adjacent-averaging technique considering 50 points of window.

4.3.1 Thermal Degradation Under Inert Atmosphere

Single Materials Characterisation

Devolatilisation experiments of SCG, CH, WP, and BC were performed separately with their decomposition and reaction rates shown in Figure 4-1. The conversion curves show the typical profile for biomass materials and coal in agreement with similar results obtained for other authors [Yan et al., 2016] [Vhathvarothai et al., 2014] [Moon et al., 2013] [Slopiecka et al., 2011] [Munir et al., 2009]. Coal has many kinds of bonds, which in comparison with those in biomass materials are more stable. Therefore, its decomposition takes place at higher temperature with low weight loss due to relatively high content of fixed carbon [Jeong et al., 2015] [Song et al., 2014] [Munther et al., 2010]. Similarly, the reduced content of volatile matter in coal is reflected in slower reaction rates and higher amount of char obtained.

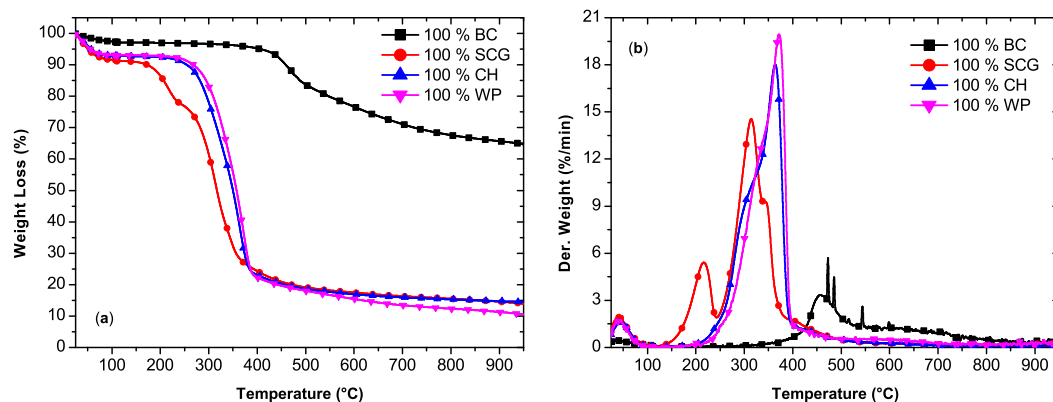


Figure 4-1: TG (a) and DTG (b) curves for bituminous coal (BC), spent coffee grounds (SCG), coffee husk (CH) and wood pellets (WP) performed under inert atmosphere (N_2) at 20 °C/min.

In the thermal decomposition of biomass three stages can be identified: moisture and light volatiles release, main devolatilisation corresponding to cellulose and hemicellulose thermal degradation and later continuous slight decomposition corresponding mainly to lignin degradation and char formation [Jeguirim et al., 2016] [Niu et al., 2016b].

The first stage, corresponding to moisture and light volatiles release occurred in the range of 25 - 130 °C for all materials. The second stage, main devolatilisation, comprises the most of the weight loss, where volatiles were decomposed and released from the biomass, contributing approximately to mass loss of the total weight of the samples as follows: WP (89.66 wt%) > SCG (86.17 wt%) > CH (85.54 wt%) > BC (35 wt%), (see Figure 4-1a). The initial decomposition temperature was found as follows: BC (417 °C) > WP (244 °C) > CH (234 °C) > SCG (167 °C). These variations in initial degradation temperatures of biomass have been related to the difference in the elemental and chemical composition of the samples [Munir et al., 2009]. Interestingly, SCG showed the lowest initial devolatilisation temperature. It can be attributed to the thermal decomposition of lipids, which can reach up to 15 wt% in raw SCG [Vardon et al., 2013]. These compounds are known to rapidly breakdown during pyrolysis into bio-oil organics [Mata et al., 2018].

The order of maximum rate of weight losses (wt%/min) and corresponding peak temperatures (°C) were found as follows; WP = 19.94 > CH = 18.0 > SCG = 14.54 > BC = 3.35 and BC = 457 > WP = 372 > CH = 364 > SCG = 314. The average degradation rates (wt%/min) observed in this zone were WP = 5.58, CH = 5.52, SCG = 4.68 and BC = 0.9. The final temperatures of the main devolatilisation stage were BC (530 °C), WP (390 °C), CH (390 °C) and SCG (380 °C).

TG and DTG curves for SCG show a clear difference during devolatilisation stage compared to the other fuels. Indeed, in the DTG curve two different peaks with a clear separation can be observed. The first DTG peak occurred at 219 °C with a maximum mass loss rate of 5.4 wt%/min, it is attributed to hemicellulose decomposition, the second DTG peak occurred at 314 °C with a maximum mass loss rate of 14.4 wt%/min, it is attributed to cellulose decomposition. This separation has been reported to be related to the cellulose-to-hemicellulose ratio. Low cellulose-to-hemicellulose ratio produces a clear separation of the hemicellulose peak [Jin et al., 2013] [Słowiecka et al., 2011]. As for WP and CH samples, the hemicellulose peak is visible only as a shoulder, meaning that hemicellulose decomposition overlaps with that of cellulose. From this analysis it can be inferred that the global maximum decomposition rate in DTG curve is also enhanced by the decomposition of lignin, similar conclusions have been reported previously [Gašparović et al., 2012].

Furthermore, the TG and DTG curves in Figure 4-1 show a similar devolatilisation behaviour between CH and WP but different from SCG. This could be due to comparatively lower volatile matter (VM) and higher fixed carbon (FC) content in SCG, as the ratio of VM to FC for the samples of CH and WP ranges from 7.21 to 7.90, whereas for SCG this value is 6.67. Similarly, the oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios from SCG, CH, and WP are bigger than those from BC. High H/C and O/C ratios have been reported as generators of massive amounts of H and OH radicals which could act as hydrogen donors, promoting the decomposition of the aromatic compounds in the coal during thermal degradation [Song et al., 2014].

Blends Materials Characterisation Under Inert Atmosphere

The devolatilisation experiments of blends of spent coffee ground (SCG), coffee husk (CH) and wood pellets (WP) at 10, 30 and 50 wt%, with a bituminous coal (BC) were performed under an inert atmosphere, the TG and DTG curves of the blends are depicted in Figure 4-2. To elucidate the influence of blending ratio the curves for the pure materials were included.

From the comparison of single materials with the blends in Figure 4-2, it can be seen that in the thermal decomposition of two materials together there is a clear contribution from the decomposition behaviours of the pure materials. TG curves show how the final mass after the devolatilisation of the blends samples decreased to the extent the biomass ratio increases. At 90/10 wt%, this value varies as follows: BC-CH (60.44 wt%) > BC-SCG (59.04 wt%) > BC-WP (58.15 wt%). At 70/30 wt%, this value varies as follows: BC-CH (51.09 wt%) > BC-SCG (49.63 wt%) > BC-WP (49.41 wt%). At 50/50 wt%, this value varies as follows: BC-SCG (39.29 wt%) > BC-CH (38.48 wt%) > BC-WP (30.07 wt%). Nevertheless, The results reveal that the final residual mass obtained after devolatilisation could not be predicted by a linear correlation of the ratios of pure fuels in the blends.

Regarding DTG curves in Figure 4-2, all the blends showed two characteristics peaks linked to decomposition of volatile matter in biomass and coal. In the case of SCG, there is a third peak which appears at an early temperature and takes more relevance as the biomass ratio increases. This peak is related to the high hemicellulose content in SCG and its decomposition. CH and WP curves showed this peak as a shoulder on the main peak. To the extent the biomass ratio increases the initial devolatilisation temperature (T_{in}) of the blend decreases, it is mainly due to the low devolatilisation temperature of the biomass samples [Yan et al., 2016]. In addition, the intensity of the main DTG peak increases as the biomass ratio increases in the blend. The temperature of the main peak (T_{max}) values shows a small range of variation as reported in other studies [Wu et al., 2016]. Nevertheless, For SCG and CH, this temperature shows a higher value for the mass ratio of 90/10 wt%.

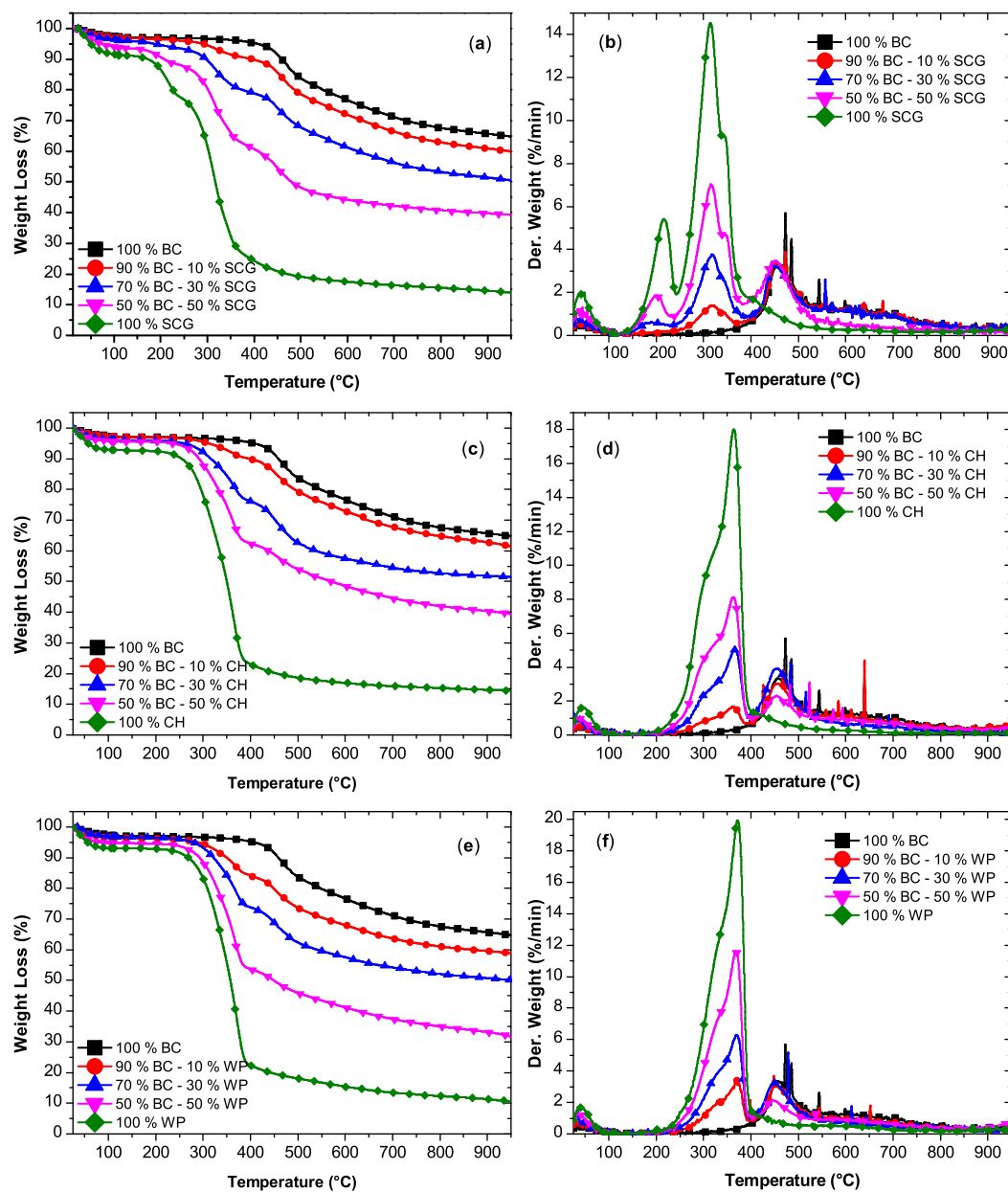


Figure 4-2: Comparison of TG and DTG curves of bituminous coal (BC) blended with spent coffee grounds (SCG) (a, b), coffee husk (CH) (c, d) and wood pellets (WP) (e, f) under inert atmosphere (N_2) at 20 °C/min.

It is an indication of the volatile matter released from BC as the main driver of the devolatilisation at that biomass ratio.

Interaction of Coal and Biomass Under Inert Atmosphere

To establish the interaction between coal and biomass in addition to its extent, the comparison based on the additive model has been broadly reported in the literature [Liu et al., 2018a] [Wu et al., 2016] [Aboyade et al., 2013] [Vamvuka and Sfakiotakis, 2011]. It assumes there is no interaction between two materials during co-processing when there is no difference between the experimental and calculated final mass values [Xu et al., 2019] [Wu et al., 2016] [Jeong et al., 2015] [Song et al., 2014]. It has been reported that the occurrence of a positive synergistic effect in the devolatilisation of blends promotes the release of more volatiles in coal processing than the sum of that released from devolatilisation of each material individually [Wu et al., 2019] [Satyam Naidu et al., 2016]. Among others, the inorganic matter in the biomass and higher H/C ratios in biomass have been identified as a promoter of the interactions between the materials in the blend [Aboyade et al., 2013]. In this study, calculated values are obtained by weighted average with the sum of the values from single materials in proportion to the blended biomass ratios for TG and DTG curves, thus:

$$W_{calculated} = X_C W_C + X_B W_B \quad (4-1)$$

Where X_C and X_B correspond to coal and biomass ratios, respectively. W_C and W_B correspond to the measured experimental value of the single materials in the blend, coal, and biomass, respectively. The results of experimental and calculated TG and DTG values for the blends of coal and each biomass considered in this study under inert atmosphere are shown in Figure 4-3.

As for BC-SCG blends (see Figure 4-3a, b), the experimental weight loss curve at 50/50 wt% does not show a relevant difference with calculated values until 430 °C, from this temperature, there is an increasing trend with a maximum difference at 536 °C with later decreasing trend showing a positive synergistic effect during devolatilisation of the blend. The addition of

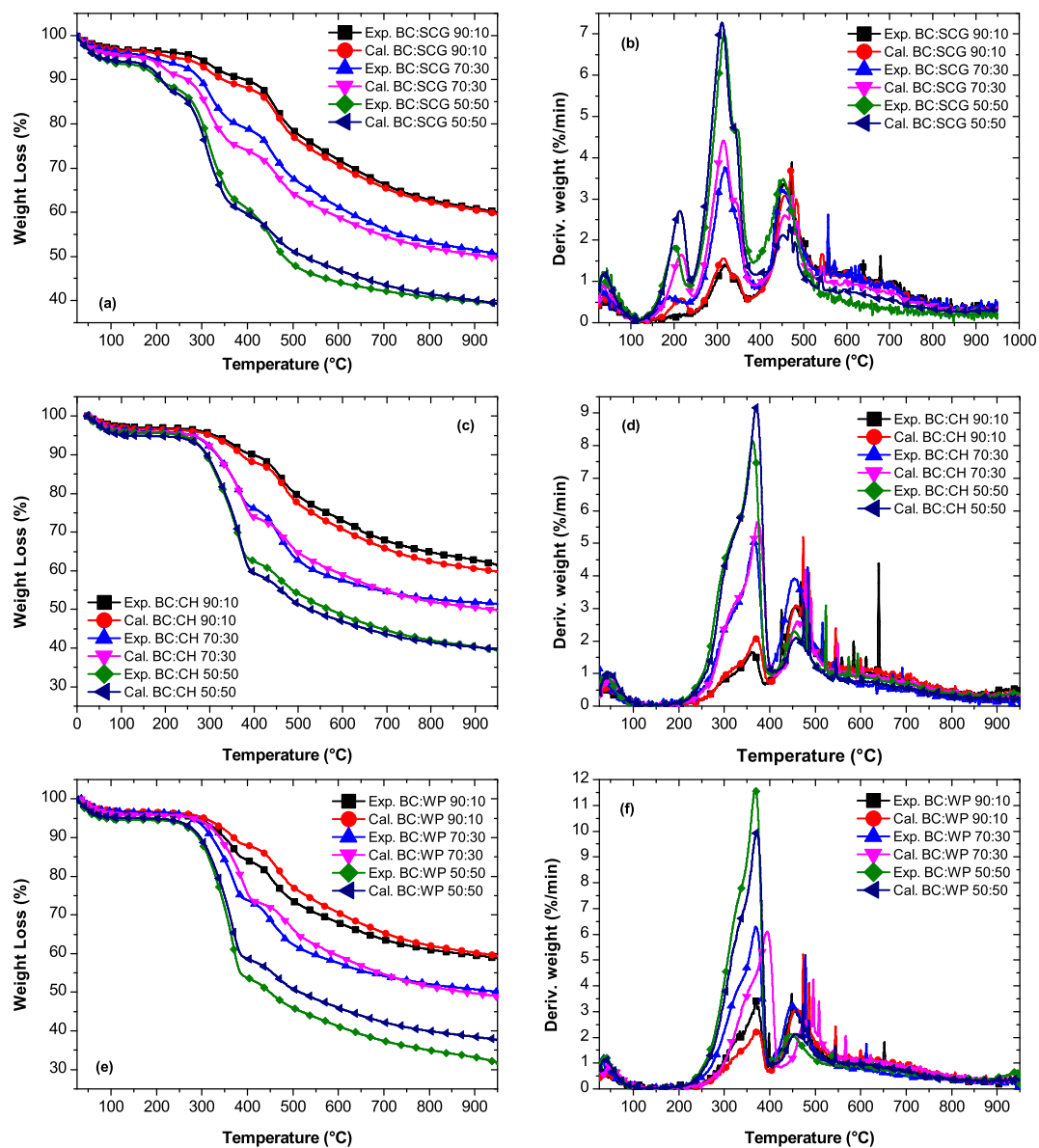


Figure 4-3: Comparison of experimental (Exp.) and calculated (Cal.) values of TG and DTG curves of bituminous coal (BC) with spent coffee grounds (SCG) (a, b), coffee husk (CH) (c, d) and wood pellets (WP) (e, f) under inert atmosphere (N_2) at 20 °C/min.

SCG at 10 and 30 wt% ratios decelerated the BC decomposition, resulting in a negative synergistic effects due to more residual char in comparison with calculated values.

Regarding BC-CH blends (see Figure 4-3c, d), the experimental weight loss curve at 70/30 wt% shows higher decomposition values than calculated values in the range between 445 - 725 °C, with a maximum difference at 518 °C with the later decreasing trend showing a positive synergistic effect during devolatilisation of the blend. The addition of CH at 10 and 50 wt% ratios decelerated the BC decomposition, resulting in negative synergistic effects due to more residual char in comparison with calculated values.

As for BC-WP blends (see Figure 4-3e,f), the experimental weight loss curves show higher decomposition values than in calculated curve for all the blends with a decreasing trend after maximum differences at 425 °C and 480 °C for 90/10 wt% and 70/30 wt%, respectively. The weight loss for the experimental curve for 50/50 wt % shows a constantly increasing trend of higher decomposition values in comparison with the calculated curve at temperatures higher than 362 °C, it may be attributed to a positive synergistic effect during devolatilisation of the blend.

These results confirm the interaction of the materials in the blend leading to positive and negative synergistic effect when by-products from coffee crop are blended with bituminous coal. The difference between experimental and calculated values in TG and DTG curves increases gradually as the spent coffee ground (SCG) and wood pellets (WP) ratios increase, leading to higher rates of weight loss. In previous studies of co-pyrolysis of fuels, these interactions have been attributed to free radical reaction (such as H transfer) or due to the catalytic action of metal ions in raw material [Xu et al., 2019].

In contrast, coffee husk (CH) showed an opposite trend insofar as the blending ratio increased, resulting in more residual char. It may be attributed to the prevalence of the recombination reaction at higher blending ratios, leading to higher tars production and lower total carbon conversion at high

blending ratios, whereas the degradation reaction is favoured when the blending ratio is lower. Similar results were reported in experiments using different coal ranks blended with pine sawdust [Song et al., 2014] [Park et al., 2010]. As for the shift between Exp. and Cal. curves for BC:WP 70:30 (see Figure 4-3f), similar trends were reported during experiments using blends of coal gauge and pine sawdust varying oxygen concentration and the heating rate. It was explained by the occurrence of thermal effects due to the preference of biomass combustion instead of coal [Zhang et al., 2016].

Devolatilisation Index

The devolatilisation index (D_v) was used to quantify the performance of volatile matter released from the pure materials and their blends. It is considered that larger values of (D_v) correlate with higher release of volatile matter [Xu et al., 2019] [Liu et al., 2018a] [Wu et al., 2016] [Liu et al., 2013b], it is defined as follows:

$$D_v = \frac{DTG_{max}}{T_{in} T_{max} \Delta T_{1/2}} \quad (4-2)$$

Where DTG_{max} is the maximum weight loss rate, T_{in} is the initial devolatilisation temperature, specifically the corresponding temperature at a mass loss of 1 wt%/min and T_{max} is the maximum weight loss temperature. $\Delta T_{1/2}$ is the temperature interval when the value of $DTG/DTG_{max} = 1/2$ between the descending and rising part of the DTG peak. All these values can be obtained from TG and DTG curves (see Figure 4-2). The results of thermal decomposition characteristics for single materials and their blends under inert atmosphere (N_2) are presented in Table 4-1.

As for single materials, Table 4-1 shows that D_v for BC is 2.08, which agrees with similar values reported in the literature [Wu et al., 2016]. The D_v values for biomass materials are as follows: SCG (39.28) > WP (31.98) > CH (26.64), showing the difference in the performance of devolatilisation for biomass compared to coal. It can be attributed to the higher volatile matter and higher H/C and O/C molar ratios in biomass compared to coal (see Table 3-2).

Table 4-1: Thermal decomposition characteristics for single materials and their blends under inert atmosphere (N_2) at 20 °C/min.

Fuels	T_{in} (°C)	$\Delta T_{1/2}$ (°C)	Peak temp. T_{max} (°C)	Max. rate of weight loss DTG_{max} (wt% min ⁻¹)	Devolatilisation Index $D_v(10^{-7} \text{ wt\% min}^{-1} \text{ } ^\circ\text{C}^{-3})$
Bituminous coal (BC)	417	84.62	456.72	3.35	2.08
BC-SCG 90/10	297	74.45	447.85	3.34	3.37
BC-SCG 70/30	267	69.72	316.54	3.77	6.40
BC-SCG 50/50	175	72.56	315.47	7.03	17.55
Spent coffee grounds (SCG)	167	70.54	314.23	14.54	39.28
BC-CH 90/10	322	91.97	456.37	3.05	2.26
BC-CH 70/30	247	75.92	364.84	5.01	7.32
BC-CH 50/50	253	85.08	362.37	8.13	10.42
Coffee Husk (CH)	234	79.35	363.78	18.00	26.65
BC-WP 90/10	296	64.90	369.54	3.43	4.83
BC-WP 70/30	275	69.55	368.62	6.30	8.94
BC-WP 50/50	257	67.70	368.36	11.64	18.16
Wood Pellets (WP)	244	68.81	371.84	19.94	31.98

As for the blends, it has been reported that the amount of volatile matter released from coal could be increased by adding hydrogen donors from other organic resources [Park et al., 2010]. In this study, the D_v values from blends of BC-CH showed a reduced trend compared to those from BC-SCG and BC-WP. Despite the difference in D_v values for the pure materials, BC-SCG and BC-WP blends showed slightly different values between them. It could be an indication of the devolatilisation of blends in this study is mainly dominated by the bituminous coal (BC). It agrees with previous findings reported in the literature, in which during thermal decomposition experiments of blended fuels was stated that the one having the lower reactivity will determine the overall rate of reaction and the residence time of the fuels in the reactor [Satyam Naidu et al., 2016]. Nevertheless, to the extent that the biomass ratio was increased D_v value increased for all blends, indicating that biomass addition foster volatile matter release.

Furthermore, to the extent that the biomass mass ratio increases the maximum weight loss temperature (T_{max}) of the blends shifts to lower values. It has been reported as an indication of synergistic effect during devolatilisation of coal and biomass blends [Xu et al., 2019] [Song et al., 2014] [Vhathvarothai et al., 2014]. These results reveal that the addition of SCG, WP, and CH to BC thermal degradation improves the release of volatile matter from the blends.

4.3.2 Thermal Degradation Under Oxidising Atmosphere

Single Materials Characterisation

Combustion experiments of BC blended with SCG, CH and WP were performed separately with their decomposition and reaction rates shown in Figure 4-4. The conversion curves show the typical profile for biomass and coal in agreement with similar results obtained for other authors [Wei et al., 2016] [Cai et al., 2016] [Liu et al., 2016] [Buratti et al., 2015] [Vhathvarothai et al., 2014] [Kok and Özgür, 2013]. As mentioned before, coal has many kinds of bonds, which in comparison with those in biomass materials are more stable. Therefore, there is a relevant difference in the thermal behaviour of the samples. Coal decomposition takes place at a higher temperature with low weight loss due to relatively reduced volatile matter content and high content of fixed carbon, which is reflected in slower reaction rates [Jeong et al., 2015] [Song et al., 2014] [Munther et al., 2010].

The trends under oxidising conditions showed higher decomposition rates compared to those under inert conditions. It was attributed to the different range of reactions promoted by the presence of oxygen and the thermal decomposition of the remaining char from the devolatilisation. As for biomass thermal decomposition three main stages can be identified: moisture and light volatiles release, main release of volatiles and their ignition (cellulose and hemicellulose thermal degradation) along with lignin degradation leading to char formation, and the last stage which corresponds to the char oxidation.

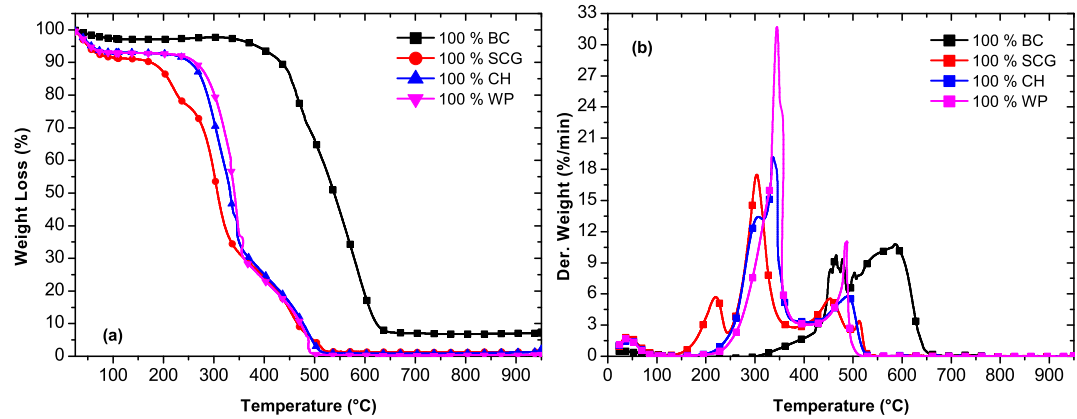


Figure 4-4: TG (a) and DTG (b) curves for bituminous coal (BC), spent coffee grounds (SCG), coffee husk (CH) and wood pellets (WP) performed under oxidising atmosphere (Air).

The first stage corresponding to moisture and light volatiles release ranges from 25 - 130 °C for all materials. The second stage occurred at temperatures between 169 - 363 °C, depending on the fuel. After the thermochemical decomposition, the residual mass of the samples corresponding ash was BC (7.45 wt%) > CH (2.13 wt%) > SCG (1.31 wt%) > WP (0.65 wt%). The ignition temperature (T_i), defined as the temperature at which the combustion rate increased to 1 wt%/min at the start of the main combustion process was as follows: BC (363 °C) > WP (243 °C) > CH (233 °C) > SCG (169 °C). SCG showed the lowest ignition temperature. It is attributed to the breakdown of the lipids in SCG at an early stage of processing. No relevant difference was observed between the initial devolatilisation and ignition temperatures under inert and oxidising atmosphere, respectively. The burnout temperature (T_b), defined as the temperature at which the combustion rate decreased to 1 wt%/min at the end of the main combustion process was as follows: BC (641 °C) > SCG (522 °C) > CH (515 °C) > WP (499 °C).

The maximum rate of weight loss (wt%/min) during the main combustion process was higher than the weight loss rates under inert conditions as follows: WP (32.73) > CH (19.29) > SCG (17.63) > BC (10.89). The more intense peaks represent the oxidative devolatilisation region of the process, in this region the rate of weight loss was quick enough to reach its maximum

at a lower corresponding peak temperature in comparison with the values from inert conditions $BC (465\text{ }^{\circ}C) > WP (345\text{ }^{\circ}C) > CH (338\text{ }^{\circ}C) > SCG (304\text{ }^{\circ}C)$. The average degradation rates (wt%/min) observed in this zone were $WP = 7.08$, $CH = 6.43$, $SCG = 5.63$ and $BC = 0.65$.

A clear separation between the first two peaks during devolatilisation stage for SCG was evident (see Figure 4-4b). In this case, the first peak occurred at $220\text{ }^{\circ}C$ with a maximum rate loss of $5.80\text{ wt\%/min}$, the second DTG peak occurred at $304\text{ }^{\circ}C$ with a maximum rate loss of $17.63\text{ wt\%/min}$. These two peaks and the separation between them have been related to the low cellulose-to-hemicellulose ratio [Jin et al., 2013] [Slopiecka et al., 2011]. As for WP and CH, the hemicellulose peak is visible only as a shoulder, meaning that hemicellulose decomposition overlaps with cellulose decomposition. In addition, a 4th peak occurring at $518\text{ }^{\circ}C$ during the third stage of decomposition of SCG was observed, and confirmed by additional experiments at lower heating rates to discard any effect of the heating rate (see Figure 4-5). This peak has been attributed to the decomposition of the lignin in SCG and not readily char influenced by mineral content for different biomass materials [Jeguirim et al., 2014b] [Li et al., 2014]. From this analysis can be inferred that the global maximum decomposition rate in DTG curve is also enhanced by the decomposition of lignin, similar findings have been reported in the literature [Gašparović et al., 2012].

Blends Materials Characterisation

The TG and DTG curves of combustion of BC blended with SCG, CH and WP at 10, 30 and 50 wt% at $20\text{ }^{\circ}C/\text{min}$ are depicted in Figure 4-6. To the extent that the biomass ratio increases in the blends, the curves shift gradually from BC to the biomass material, respectively. In DTG curves can be observed two main regions. The first one characterised by the hemicellulose and cellulose decomposition from the biomass in the blend. The second region is wider mainly due to the release of volatile matter in coal along with the char combustion, which burns slowly over the whole temperature range.

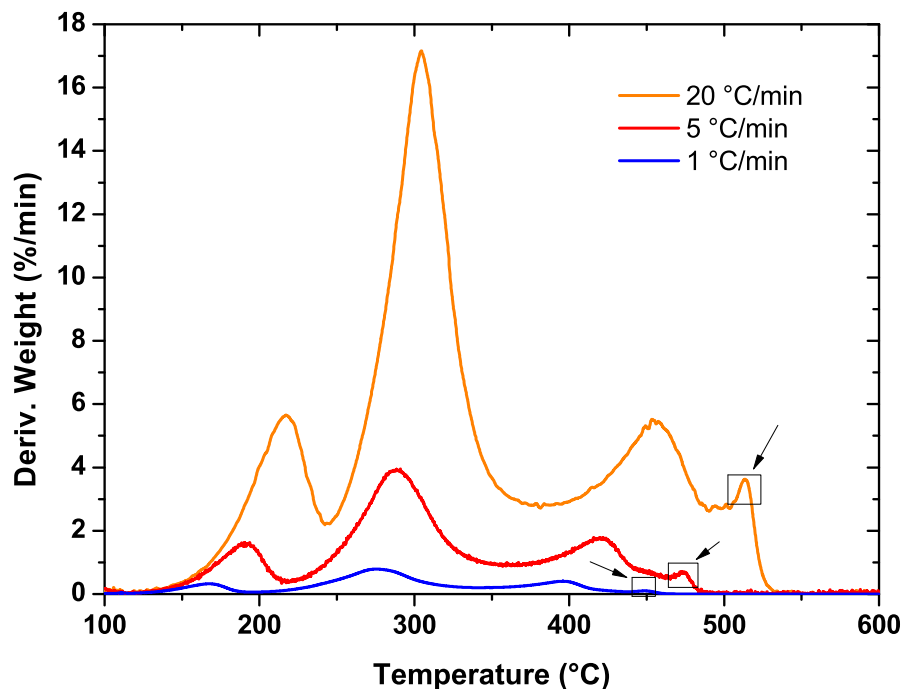


Figure 4-5: Confirmation of existence of 4th peak in DTG curves of spent coffee grounds (SCG) at different heating rates.

The analysis of the maximum rate of weight loss reveals that for all the BC-SCG blends the maximum decomposition rate shows up in the second region of the main combustion process (see Figure 4-6b). Among BC-SCG blends, the blend corresponding to 70/30 wt% showed the highest value of the maximum rate loss corresponding to 13.63 wt%/min at 465 °C. As for BC-CH blends, the blend at 50/50 wt% showed the highest value of the maximum rate of weight loss corresponding to 12.02 wt%/min at 335 °C, it was located in the first region of the main combustion process. BC-CH blend ratios of 30 and 10 wt% showed the maximum rate of weight loss peak of the blends in the second region corresponding to the main combustion process (see Figure 4-6d). As for BC-WP blends, the highest value of the maximum rate of weight loss was 18.04 wt%/min, which occurred at 341 °C for the blend at 50/50 wt%. BC-WP blend ratios of 10 and 30 wt% showed the maximum rate of weight loss peak of the blends in the first and second region, respectively (see Figure 4-6f).

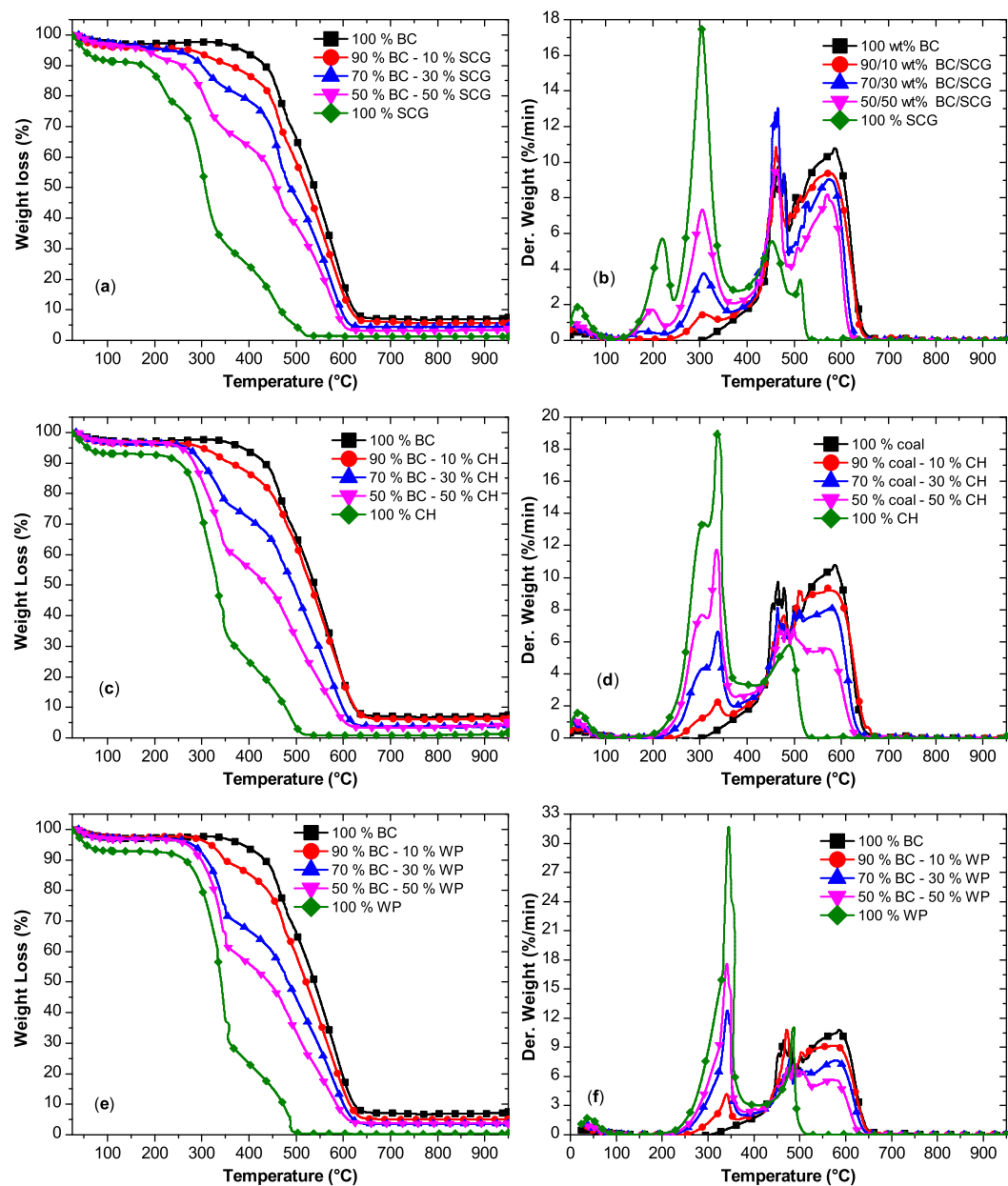


Figure 4-6: Comparison of TG and DTG curves of bituminous coal (BC) blended with spent coffee grounds (SCG) (a, b), coffee husk (CH) (c, d) and wood pellets (WP) (e, f) under oxidising atmosphere (Air) at 20 °C/min.

Furthermore, in Figure 4-7 can be observed that the BC-WP blends show a sustained trend to the increase of the maximum rate of weight loss to the extent the biomass ratio is increased while reducing the peak temperature. For BC-CH at 90/10 and 70/30 wt%, and for BC-SCG at 50/50 wt% is evident a decrease in the maximum rate of weight loss in comparison with values obtained from the pure materials in the blends (see Figure 4-7a) and an increase in the correspondent temperature for the BC-CH blends. It has been linked to lowering of reactivity due to the interactions of the materials in the blend [Toptas et al., 2015] [Munir et al., 2009] [Toptas et al., 2015].

For all the blends, it is evident the dominance of the second region (char combustion) at low biomass ratios. Nevertheless, it has been reported that the char yield and its oxidation rate do not depend on the composition of the single materials exclusively but also on the interaction of the particles involved and oxygen availability [Wei et al., 2016] [Zhang et al., 2016]. In general, such findings have a massive relevance to establishing the proper biomass ratio for co-combustion schemes due to the importance of the time required for char oxidation to achieve high-efficiency levels during combustion. It has been broadly reported as one of the most relevant aspects of the design and operation of reactors [Sarkar et al., 2014] [Vhathvarothai et al., 2014] [Vamvuka and Sfakiotakis, 2011].

Figure 4-8 shows the combustion parameters of the single materials and their blends, calculated from TG and DTG curves. It can be seen that to the extent that the biomass ratio increases, the ignition and burnout temperatures of the blends decrease, due to the higher reactivity of biomass (see Figure 4-6). Specifically, the reduction in the ignition temperature (see Figure 4-8a) could be attributed to the higher volatile matter content in the blends as the biomass ratio is increased, which promotes the ignition and complete combustion of the blend. It is expected that the blending of high volatile content materials with coal always lowers the ignition temperature [Buratti et al., 2015]. It could be a relevant factor for high-rank coal combustion due to its low volatile matter and relatively high ash content, which could be improved by the addition of biomass.

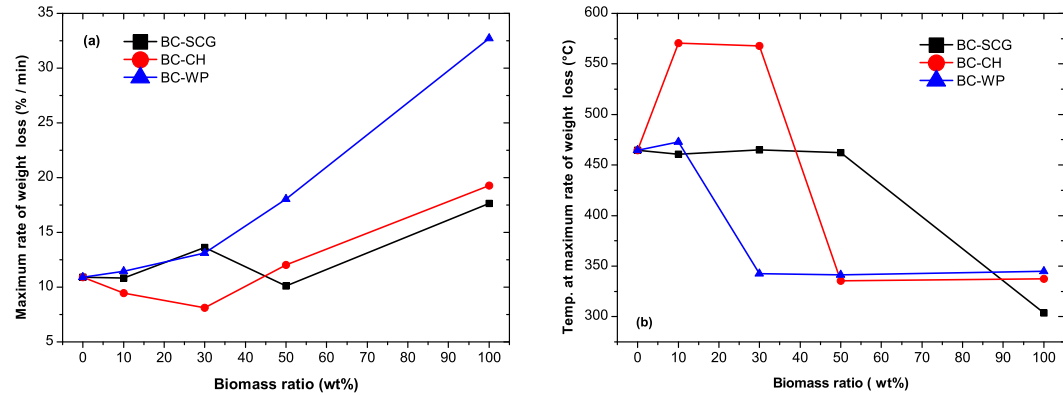


Figure 4-7: Maximum rate of weight loss (a) and temperature at maximum rate of weight loss (b) for the blends of bituminous coal (BC) with spent coffee grounds (SCG), coffee husk (CH) and wood pellets (WP) performed under oxidising atmosphere (Air) at 20 °C/min.

Similarly, in Figure 4-8a is evident a relevant reduction in the ignition temperature for BC-SCG at 50/50 wt% in comparison with the blends from the other biomass materials. It is attributed to the earlier start of the mass loss due to the low cellulose-to-hemicellulose ratio in SCG, which could lead to reduced values of the ignition temperature. In co-combustion schemes, the volatile matter released from the biomass materials releases enough energy to reduce the ignition temperature of the coal in the blend. Nevertheless, it has been reported that ignition temperature depends on some other factors such as the availability of oxygen and particle heating rate [Muthuraman et al., 2010].

As for the burnout temperature of the blends, trends in Figure 4-8b show a clear reduction to the extent the biomass ratio increases. It is an indication of the improvement of BC combustion as a consequence of the inclusion of SCG, CH or WP. In general, the inclusion of high reactive materials such as biomass could lead to reductions in the burnout temperature of the blends. Similar trends have been reported by other authors for co-combustion of coal and biomass [Muthuraman et al., 2010]. Furthermore, the lower the burnout temperature the less the time required for fuels to burn out, reducing the difficulty of the fuel to burn and minimising unburnt carbon losses [Buratti et al., 2015] [Toptas et al., 2015].

Additionally, Figure 4-8b shows that for BC-CH at 90/10 wt% the burnout temperature is slightly increased to a higher value compared to pure BC. A similar trend has been attributed to oxygen availability, inhibition of coal ash in the complete combustion of the biomass and temperature profiles in processing reactor, due to the independent burning of the materials in the blend [Yan et al., 2016]. The increase of biomass blending ratios and the quicker burning rates of biomass could lead to the reduction of oxygen availability for coal and reduce the incremental effect of improvement in the burnout [Muthuraman et al., 2010].

Furthermore, the decrease of the burnout temperature has been reported to be influenced by the mineral matter content in the fuels. Specifically, the influence of alkali metals and alkali earth metals on burnout temperature has been reported in the order of $K > Na > Ca$ [Yan et al., 2016]. [Wei et al., 2016], reported a significant reduction of the ignition and burnout temperature in co-combustion experiments of anthracite and spent coffee grounds blends to investigate the effect of oxygen availability, biomass ratio and heating rate. It could be an indication of the fundamental role of oxygen availability and the heating rate when co-combustion of coal and biomass is performed.

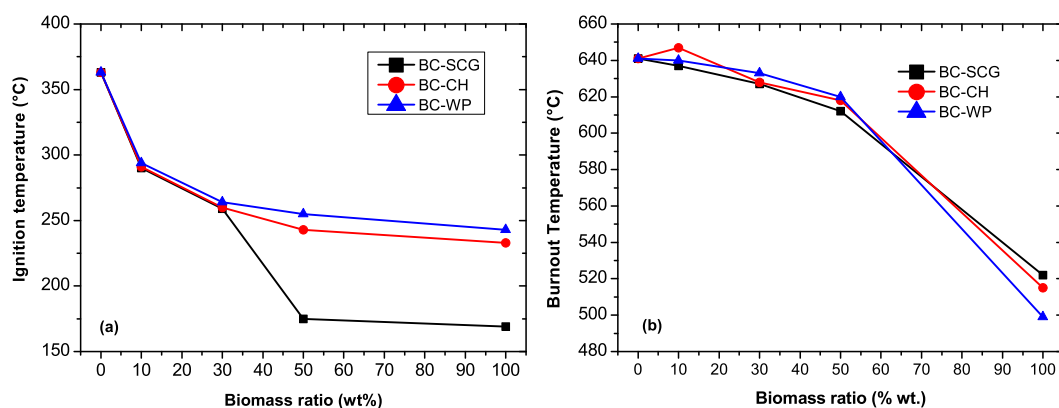


Figure 4-8: Ignition temperature (a) and burnout temperature (b) of bituminous coal (BC) blended with spent coffee grounds (SCG), coffee husk (CH) and wood pellets (WP) (e, f) under oxidising atmosphere (Air) at 20 °C/min.

The reduction in either the ignition or burnout temperatures in the co-combustion experiments in this study is not proportional to the biomass ratio in the blend, which elucidates the complexity of thermal degradation of blends due to the various factors involved. Similar findings were reported in TGA studies of co-combustion of sub-bituminous coal blended with cellulosic ethanol residue (CER) [Buratti et al., 2015]. In co-combustion experiments of three coal samples and wood pellets, a non-linear decrease of ignition and burnout temperatures was reported and attributed to the high volatile matter content in the biomass and its devolatilisation [Moon et al., 2013]. Likewise, in co-combustion experiments of bituminous coal (BC), rice husk (RH), pine sawdust (PS) by [Wang et al., 2016a], it was reported the non-linear reduction of the ignition and burnout temperature. It could be inferred that combustion characteristics cannot be predicted by an additive behaviour. Similar findings have been reported by [Wang et al., 2016a] [Buratti et al., 2015] [Vhathvarothai et al., 2014] [Muthuraman et al., 2010] [Munir et al., 2009].

Ignition and Combustion Indices

As with the thermal degradation under inert atmosphere in section 4.3.1, in this study two different indices were used to quantify the combustion performance. These are the ignition index (D_i), which refers to how quick or slow the fuel is ignited and combustion index (S), which refers to comprehensive characteristics of combustion. These indices have been broadly used to characterise the combustion behaviour of different fuels [Cong et al., 2019] [Liu et al., 2018c] [Cai et al., 2016] [Liu et al., 2013b] [Vamvuka and Sfakiotakis, 2011] [Wang et al., 2011] [Wei et al., 2016].

$$D_i = \frac{DTG_{max}}{T_i T_{peak}} \quad (4-3)$$

$$S = \frac{DTG_{max} DTG_{avg}}{T_i^2 T_b} \quad (4-4)$$

Where DTG_{max} is the maximum weight loss rate, T_i is the ignition temperature, T_{peak} is the maximum weight loss temperature, T_b is the burnout

temperature and DTG_{avg} is the average weight loss rate between the ignition and burnout temperature, which is calculated thus:

$$D_{avg} = \frac{\alpha_{T_b} - \alpha_{T_i}}{\left(\frac{T_i - T_b}{\beta}\right)} \quad (4-5)$$

Where α_{T_b} and α_{T_i} are the fractions of material degraded at the burnout and ignition temperature, respectively, and β is the heating rate. All these values can be obtained from DTG curves (see Figure 4-6) and are presented in Table 4-2.

Table 4-2: Thermal decomposition characteristics for single materials and their blends under oxidising atmosphere (Air) at 20 °C/min.

Fuels	T _i (°C)	T _b (°C)	Peak temp. T _{max} (°C)	Max. rate of weight loss DTG _{max} (wt% min ⁻¹)	Ignition index D _i (10 ⁻⁶ wt% °C ⁻²)	Combustion index S (10 ⁻⁷ wt% min ⁻² °C ⁻³)
Bituminous coal (BC)	363	641	465	10.89	64.57	8.23
BC-SCG 90/10	290	637	460	10.83	81.06	10.23
BC-SCG 70/30	259	627	465	13.63	112.30	16.06
BC-SCG 50/50	175	612	462	10.11	124.97	22.65
Spent coffee grounds (SCG)	169	522	304	17.63	343.75	59.48
BC-CH 90/10	291	647	571	9.44	56.84	8.58
BC-CH 70/30	260	628	568	8.13	55.07	9.49
BC-CH 50/50	243	618	335	12.02	147.56	16.16
Coffee Husk (CH)	233	515	338	19.29	245.27	44.42
BC-WP 90/10	294	640	473	11.44	82.30	10.90
BC-WP 70/30	264	633	342	13.12	145.07	14.85
BC-WP 50/50	255	620	341	18.04	207.33	22.49
Wood Pellets (WP)	243	490	345	32.73	390.31	79.02

Regarding single materials, Table 4-2 shows that D_i for bituminous coal BC is 64.57. For biomass materials D_i values are as follows: WP (390.31) > SCG (343.75) > CH (245.27). It reveals the prevalent difference in the quality of ignition for biomass over coal. It can be attributed to the higher volatile matter content in biomass (see Table 3-2). As for the blends, it has been reported in previous studies that the ignition of coal could be improved by adding biomass [Sarkar et al., 2014] [Vamvuka and Sfakiotakis, 2011]

[Vhathvarothai et al., 2014]. It is evident for all the blends in comparison with pure coal. Moreover, in this study the order of ignition index (D_i) values is as follows: BC-WP > BC-SCG > BC-CH. To the extent higher values of ignition index (D_i) are achieved better ignition performance in the blend is obtained [Wang et al., 2011]. The lower values for BC-CH blends are mainly attributed to their lower maximum rate of weight loss and higher maximum weight loss temperature (see Figure 4-7).

As regards the combustion index (S), Table 4-2 shows that this value for BC is 8.23. For biomass materials S values are as follows: WP (79.02) > SCG (59.48) > CH (44.42). It could be observed the prevalent difference in the quality of comprehensive combustion for biomass over coal. It can be concluded that WP and SCG are the most reactive materials, whereas CH the less reactive, among the biomass fuels considered in this study. Figure 4-9 depicts the trends shown for ignition and combustion indices of the materials under study.

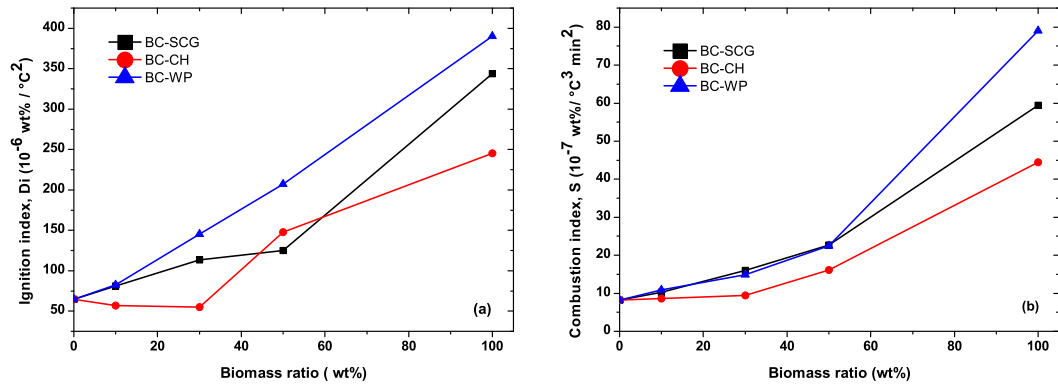


Figure 4-9: Ignition index (a) and combustion index (b) for the blends of bituminous coal (BC) with spent coffee grounds (BC-SCG), bituminous coal with coffee husk (BC-CH) and bituminous coal with wood pellets (BC-WP) under oxidising atmosphere at 20 °C/min.

In Figure 4-9a, it is evident an approximately linear relationship of ignition index (D_i) for BC-WP and in less proportion for BC-SCG blends to the extent the biomass ratio increase. For BC-CH blends, it is evident a slight decrease in the ignition temperature at ratios of 10 and 30 wt% to even lower values

than those for BC. Regarding combustion index (S) in Figure 4-9b, the trends are similar among the biomass materials without any increase proportional to the biomass ratio in the blend. To the extent the biomass ratio increases a better combustion performance is obtained for all the blends, with similar values for BC-WP and BC-SCG blends and reduced values for BC-CH blends. Indeed, for BC-CH, at 10 and 30 wt% there is no relevant change in the combustion index. It could be attributed to the lower values in the ignition index at low biomass ratios.

In general terms, higher values of ignition and combustion indices could be considered an indication of more stable combustion performance with more vigorous burning and quicker char burn out [Liu et al., 2018c] [Cai et al., 2016] [Moon et al., 2013]. In this study, both ignition and combustion indices improved with the inclusion of biomass without any linear relationship to the biomass ratio in the blend. Therefore, it reveals that by-products from coffee crop industry namely spent coffee ground (SCG) and coffee husk (CH) could improve the combustion performance of bituminous coal and provide useful information for energetic use at larger scales. Nevertheless, potential issues related to particulate matter, agglomeration due to high alkali metals content and poor densification characteristics have been reported [Jeguirim et al., 2016]. Despite the technical challenges to address about design and operation of reactors or required modifications of existing equipment, the energetic use of resources such as by-products from coffee crop would allow to achieve remarkable environmental and economic benefits.

Interaction of Coal and Biomass Under Oxidative Atmosphere

To establish the likely interaction between coal and biomass in addition to its extent, comparison of experimental and calculated values based on the additive model (see section 4.3.1) were performed. It assumes that there is no interaction between two materials during co-processing when there is no difference between the experimental and calculated values [Wu et al., 2016] [Hu et al., 2015b] [Jeong et al., 2015] [Song et al., 2014] [Aboyade et al., 2013]. Figure 4-10 shows the comparison of experimental and calculated TG

curves under oxidising atmosphere of the blends of coal and each biomass considered in this study.

It can be noticed that for all the blends the weight loss for experimental curves was higher than the calculated values with an increasing trend to the extent that the biomass ratio increases. Nevertheless, BC-WP blends show a bigger difference in comparison with BC-SCG and BC-CH. In fact, at 90/10 wt%, BC-WP blend shows a relevant difference. This kind of behaviour has been extensively reported in the literature as an indication of synergistic effects between the materials in the blends [Satyam Naidu et al., 2016] [Wang et al., 2016a] [Zhou et al., 2016] [Jeong et al., 2015]. The difference between experimental and calculated values did not show a linear relationship to the biomass ratio in the blend. Therefore, the combustion behaviour could not be described by additive relation of the pure materials. Similar conclusions have been reported by [Cong et al., 2019] [Satyam Naidu et al., 2016] [Wang et al., 2016a] [Aboyade et al., 2013] [Liu et al., 2013b]. To confirm the existence of synergistic effects during decomposition, experimental and calculated values for DTG curves were analysed and depicted in Figure 4-11.

Similar trends to those in TG curves (see Figure 4-10) were found in the analysis of DTG curves. All the blends show differences between experimental and calculated values in terms of the maximum rate of weight loss. Furthermore, it was observed the shift of experimental curves towards the left of the calculated ones, indicating a prominent effect leading to lower temperatures in comparison with corresponding calculated values. Nevertheless, no linear relationship to the extent of biomass ratio increased in the blend was identified. The shift effect was more prominent to the extent biomass ratio increased in the blend. Alike in TG curves in Figure 4-10, the BC-WP blend at 90/10 wt% showed a higher difference in comparison to the corresponding BC-SCG and BC-CH blends.

In previous studies of fuels co-processing have been reported the shift effect between experimental and calculated curves. In co-combustion experiments of lignite and rice husk char, it was reported the delay burning of char compo-

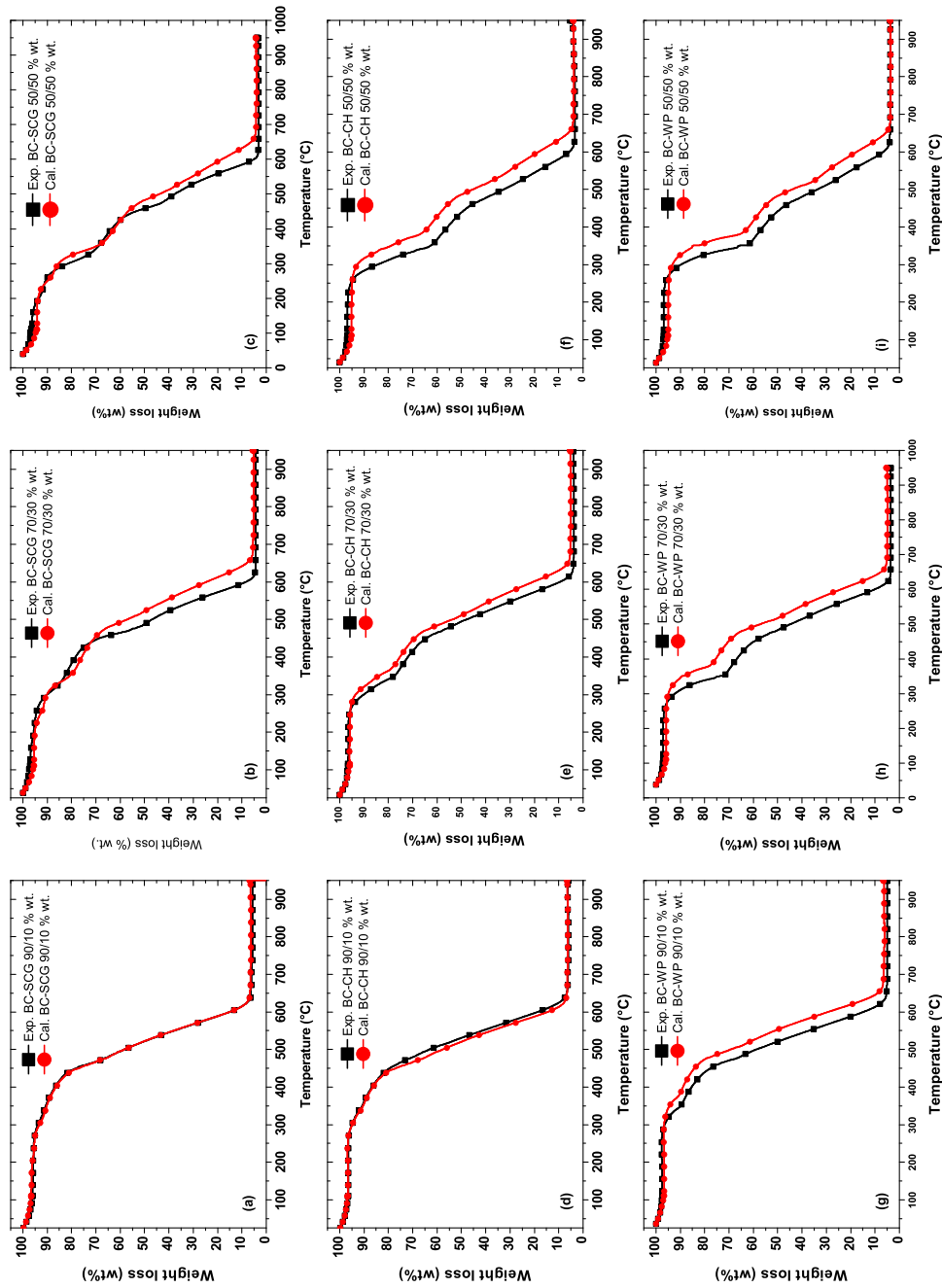


Figure 4-10: Comparison of experimental (Exp.) and calculated (Cal.) TG curves of bituminous coal (BC) blended at 10, 30 and 50 wt% with spent coffee grounds (SCG) (a, b, c), coffee husk (CH) (d, e, f) and wood pellets (WP) (g, h, i) under oxidising atmosphere (Air) at 20 °C/min.

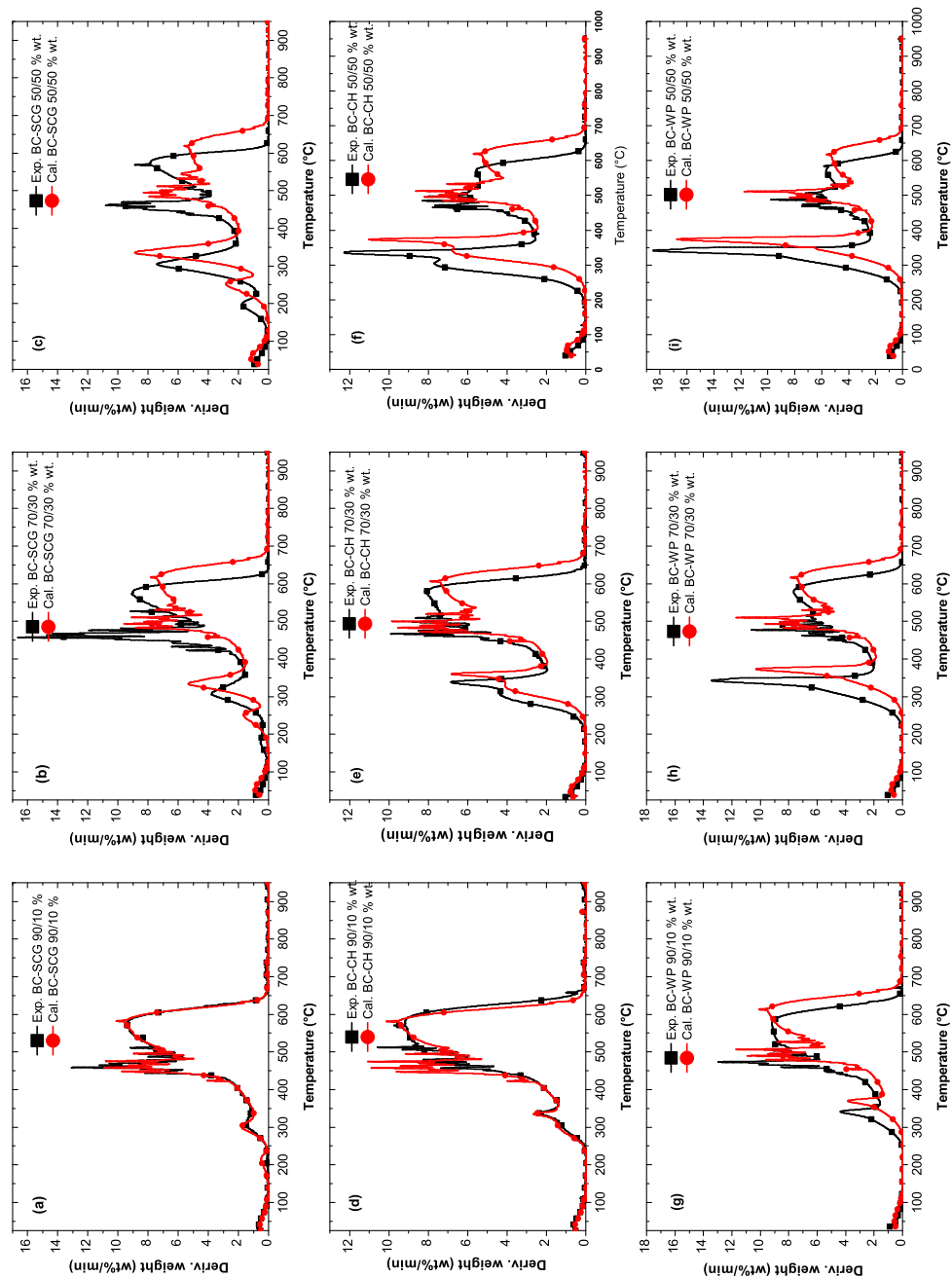


Figure 4-11: Comparison of experimental (Exp.) and calculated (Cal.) DTG curves of bituminous coal (BC) blended at 10, 30 and 50 wt% with spent coffee grounds (SCG) (a, b, c), coffee husk (CH) (d, e, f) and wood pellets (WP) (g, h, i) under oxidising atmosphere (Air) at 20 °C/min.

nents due to the shift of experimental curves to the right of calculated values leading to negative synergistic effect [Sarkar et al., 2014]. In contrast, during combustion experiments with blends of coal gauge and pine sawdust by [Zhang et al., 2016], it was reported positive synergistic effects due to the disparities between experimental and calculated values, which were more pronounced to the extent the biomass ratio increases, without any linear relation. Nevertheless, these disparities have been reported smaller when oxygen concentration and heating rate decrease and explained by the occurrence of thermal effects due to the preference of biomass combustion instead of coal [Zhang et al., 2016]. The following section describes the results from further experiments performed at different heating rates to confirm the existence of synergistic effects.

Effect of Heating Rates on Blends Combustion

Additional experiments at different heating rates were performed to confirm the existence of synergistic effect when by-products from coffee crop were blended with bituminous coal. The heating rate has a relevant influence on the thermal behaviour of fuels during decomposition. Higher heating rates could shift the TG and DTG curves to higher temperatures. In TGA experiments with SCG, [Li et al., 2014] reported the shift of the peaks in DTG curves to higher temperatures to the extent the heating rate was increased. It has been attributed to the presence of bigger temperature gradients across the particles at high heating rates due to the prevalence of thermal effect over chemical reactions, similar findings were reported by [Zhang et al., 2016].

In this study, the DTG curves of BC blended with SCG and CH at 50 wt% obtained at different heating rates namely 20, 5 and 1 °C/min were compared to confirm the difference between experimental and calculated values (see Figures 4-12 and 4-13). The prevalence of the difference between experimental and calculated values in DTG curves at different heating rates has been reported as evidence of synergistic effect [Kluska et al., 2018] [Liu et al., 2018a] [Zhang et al., 2016] [Li et al., 2014].

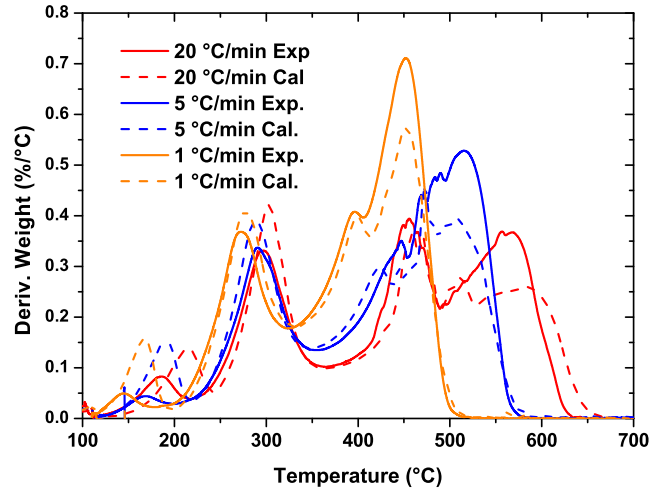


Figure 4-12: Comparison of experimental (Exp.) and calculated (Cal.) DTG curves of bituminous coal (BC) blended at 50 wt% with spent coffee grounds (SCG) under oxidising atmosphere (Air) at different heating rates.

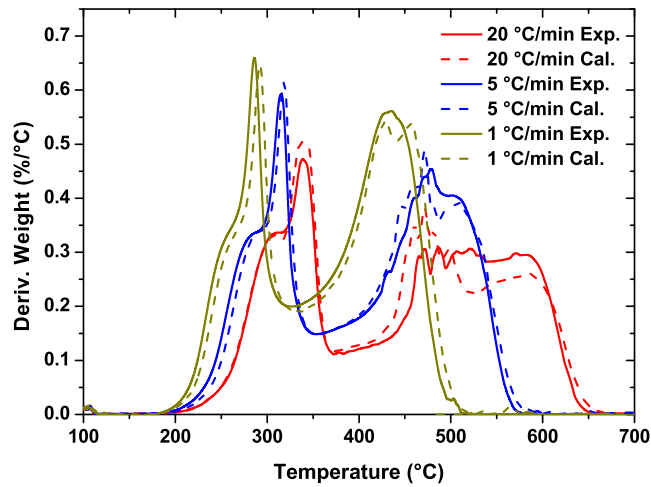


Figure 4-13: Comparison of experimental (Exp.) and calculated (Cal.) DTG curves of bituminous coal (BC) blended at 50 wt% with coffee husk (CH) under oxidising atmosphere (Air) at different heating rates.

A comparison of the results in Figures 4-12 and 4-13 reveals the effect of heating rate on combustion of the blends. To the extent the heating rate increases the shift of the DTG curve to higher temperatures and lower maximum peak values was observed in both blends. The shift of ignition and burnout temperatures along with higher maximum mass loss rate temperature toward higher values proves that combustion intensity can be improved increasing heating rate [Liu et al., 2018a] [Buratti et al., 2015]. Further-

more, the blend of BC and SCG showed an indication of synergistic effect due to the prevalence in the difference between experimental and calculated values of the DTG curves in the maximum mass loss rate despite the heating rate, this behaviour was not observed in the BC and CH blend.

4.4 Summary

From the previous discussion, it can be seen that the inclusion of either spent coffee grounds or coffee husk in coal combustion can enhance the combustion performance. The blends with spent coffee grounds were found to be more reactive than those with coffee husk and with similar devolatilisation, ignition and combustion index values to those for the blends with wood, used as the reference case. Further tests at different heating rates showed evidence of synergistic effects when spent coffee grounds were used. These results offer compelling evidence of the potential of by-products from the coffee crop, especially spent coffee ground for energetic applications. The materials characterisation tests showed that spent coffee ground can be an interesting fuel with a relatively higher heating value and volatile matter content. The results from this section can be useful to understand the behaviour of these blends under inert and oxidising conditions to determine their potential use with relevant information for the design and optimisation of thermochemical conversion systems at larger scales. Nevertheless, high nitrogen content arises as a challenge to address the use of spent coffee grounds as a fuel in terms of potential NO_x emissions. Furthermore, high content of alkali metals in spent coffee grounds raises some concerns in terms of potential ash issues. The next chapter investigates the relevance of the alkali metals content in the ash of spent coffee grounds in terms of ash fusibility characteristics.

Chapter 5

Ash Fusibility of Blends of Bituminous Coal and Biomass

A clear understanding of ash fusion characteristics of coal and biomass is essential to secure stable long-term operation of combustion facilities under co-processing schemes. The effect of adding biomass to coal combustion is one of the major challenges in co-processing because of the difference in ash composition and higher alkali metals content in biomass. It could lead to compounds with low fusion temperatures originating ash sintering and agglomeration issues. Although many research studies have focused on the effect of ash composition on the ash fusibility characteristics of coal and more recently several biomass resources, little has been reported about spent coffee grounds (SCG) ash composition and its effect on ash fusibility temperatures (AFT) when used in pure or blended with coal.

This chapter investigates the ash fusibility characteristics under oxidising conditions of blends of spent coffee grounds (SCG) at 40, 60 and 80 wt% with a bituminous coal (BC). For comparison purposes, blends of wheat straw (STW), well known for its high alkali metals content, and BC at the same mass ratios are also considered. Particular attention was paid to the blending ratio effect on AFT values. The results can provide insights into the ash fusion characteristics of these blends under oxidising conditions. It can be useful to determine their potential for a stable long-term operation and optimisation of thermochemical conversion systems at larger scales.

5.1 Introduction

The ash issues are mainly based on its deposits via slagging, fouling, sintering and agglomeration [Pintana and Tippayawong, 2016]. The characterisation of ash behaviour prior use is beneficial to determine adequate alternatives to minimise operational risks and establishing the suitability of a given fuel to be used in fluidised beds [Hupa, 2012] [Llorente and García, 2005]. Several approaches have been devised to characterise and predict ash behaviour of a particular solid fuel (i.e. ash fusibility test, dilatometry/shrinkage, sinter strength test, viscosity measurements, empirical indices as well as pilot-scale trials), each one with advantages and disadvantages in terms of cost, reliability and complexity [Pang et al., 2013] [Teixeira et al., 2012] [Llorente and García, 2005].

The AFT test is a broadly used method to characterise ash fuels behaviour despite its limitations, it describes considerably the ash behaviour [Yan et al., 2017] [Ma et al., 2017] [Niu et al., 2016a] [Vassilev et al., 2014]. This technique has shown to be adequate to predict the ash fusion behaviour from sintering/shrinkage to melting by the determination of four temperatures, namely initial deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) [Wang et al., 2017a] [Li et al., 2017b] [Niu et al., 2016a] [Vassilev et al., 2014] [Vassilev et al., 2013].

Several studies on ash fusibility test have been performed to characterise the behaviour of coal ash [Yan et al., 2017], biomass ash [Zhu et al., 2018a] [Dibdiakova et al., 2015] [Deng et al., 2013] as pure fuels. Other studies have investigated the ash fusion behaviour of blends of biomass/biomass [Zhu et al., 2018b], coal/coal [Li et al., 2017b] [Wang et al., 2017a] [Shen et al., 2015] [Santhosh Raaj et al., 2016] or coal/biomass [Ma et al., 2017] [Lu et al., 2017] [Xing et al., 2016a] [Li et al., 2015]. The difference in chemistry and mineralogy of the ash from different fuels is one of the main factors responsible for the variation in the sintering and fusion characteristics [Li et al., 2017b] [Vassilev et al., 2013].

The most relevant difference between coal and biomass ash fusion behaviour is related to the diverse fluxing or refractory roles of the major elements contained in the ash. The AFT values could differ for biomass or coal ash depending on the mineral species found for the same element [Vassilev et al., 2014]. It is clear that in co-combustion of fuels the ash chemistry varies with the type of fuel, the blending ratio and interaction of them [Li et al., 2017b] [Yan et al., 2017] [Hupa, 2012]. It could lead to higher or lower ash fusion temperatures than those of the individual fuels, without any linear relation to the blending ratio [Shen et al., 2015].

In the combustion of coal and biomass blends, one of the major challenges to address is the high alkali metals content in biomass [Vassilev et al., 2013] [Teixeira et al., 2012] [Llorente and García, 2005]. It could lead to compounds with low ash melting points increasing the risk of sintering, agglomeration or deposits formation in heat and power generation plants. The ash fusibility characteristics of coal and biomass blends differ greatly from that of the pure fuels [Ma et al., 2017]. Furthermore, the addition of biomass to coal combustion could reduce the ash use options due to undesired changes in ash composition [Vassilev et al., 2014] [Saidur et al., 2011]. In particular, this matter takes more relevance when herbaceous biomass is used due to the higher alkali-metal content in ash than woody fuels [Vassilev et al., 2013] [Hupa, 2012] [Llorente and García, 2005].

Despite chemical elements are rarely found in the fuel ash as the commonly reported oxides, it is an accepted practice to report the ash composition as a percentage of most common oxides of the forming elements [Hupa, 2012]. To differentiate the influence of these oxides in the ash fusibility, they are classified into acidic oxides (increasing the melting temperature) and basic oxides (decreasing the melting temperature) [Wang et al., 2016c] [Deng et al., 2013]. Acidic oxides include SiO_2 , Al_2O_3 , TiO_2 , which are considered receptors due to the high ionic potential with a tendency to form polymers, increasing AFT values, whilst basic oxides include CaO , MgO , Na_2O , K_2O , and Fe_2O_3 which are considered oxygen donators due to the low ionic po-

tential with a tendency to terminate polymer formation and to decrease the AFT values [Li et al., 2017a] [Ma et al., 2017]. In different stages of the ash melting process, different minerals may be produced by the reactions of these oxides and affect the ash fusibility in different ways [Wang et al., 2016c].

The evidence presented in this section suggests that more research efforts are required to achieve better understanding of SCG ash behaviour in pure or blended with bituminous coal. Furthermore, no comparison of the effect of SCG ratio in blends with BC in terms of modification of AFT values compared to other biomass resources has been reported. This chapter investigates the ash fusibility temperatures of BC blended with SCG at 40, 60, 80 % under oxidising conditions by AFT test. For comparison purpose, blends of BC and wheat straw (STW) at the same ratios are also considered.

5.2 Test Samples Preparation

Due to the difference in ash content in the fuels, the ash blends were prepared according to the ash content of the pure fuels and based on the blending ratio. For instance, for a blend of BC 60 wt% and SCG 40 wt%, namely BC60:SCG40, the actual ash ratio is BC 91.1 % and SCG 8.9 %. Since the ash content of BC and SCG are 7.56 % and 1.11 %, respectively. Therefore, the different ash fractions in the blend are 91.1 % of the BC ash (prepared at 815 °C) and 8.9 % of SCG (prepared at 550 °C). Table 5-1 shows the mass proportion used to prepare the ash blends samples based on the ash content of fuels (see Table 3-2).

5.3 Results and Discussion

The analysis of results was divided in two main sections. Initially, the analysis of ash from pure fuel samples was performed to determine the specific characteristics and content of these samples. Then the analysis for the blends was performed, including results from pure fuels for comparison purpose.

Table 5-1: Proportion of ash from bituminous coal (BC), spent coffee grounds (SCG) and wheat straw (STW) in the blends for AFT tests.

Fuel blend designation	Biomass ratio (wt%)	Mass proportions of ash in the blend (wt%)		
		BC	SCG	STW
BC60:SCG40	40	91.1	8.9	-
BC40:SCG60	60	82.1	17.9	-
BC20:SCG80	80	63.0	37.0	-
BC60:STW40	40	65.7	-	34.3
BC40:STW60	60	46.0	-	54.0
BC20:STW80	80	24.2	-	75.8

Furthermore, a comparison of findings with those reported in the literature for similar blends was considered.

5.3.1 Ash Fusibility Temperatures of Pure Fuels

The key characteristics to consider in the analysis are the difference in the melting/fusion events (temperature values) and the temperature range across which they occur during the heating up stage. Figure 5-1 depicts the fusibility temperatures for the pure fuels considered in the AFT experiments.

The different ash fusibility behaviour among the fuels ash showed in Figure 5-1 was mainly attributed to the variation in the biomass ash composition. Lower AFT values and a broader AFT range were observed for STW and SCG in comparison with BC. It is widely accepted that higher content of SiO_2 and Al_2O_3 , and lower content of CaO , Fe_2O_3 , MgO and K_2O in coal ash are responsible for increased AFT values [Vassilev et al., 2014]. Acidic oxides such as Al_2O_3 and SiO_2 are responsible for high AFT values of coal ash because these oxides with high ionic potential are prone to combine with oxygen to form polymers, causing the AFT values to increase [Ma et al., 2017] [Yan et al., 2017] [Wang et al., 2017a] [Lu et al., 2017] [Li et al., 2015] [Vassilev et al., 2013]. In comparison with BC ash, STW ash has a higher content of

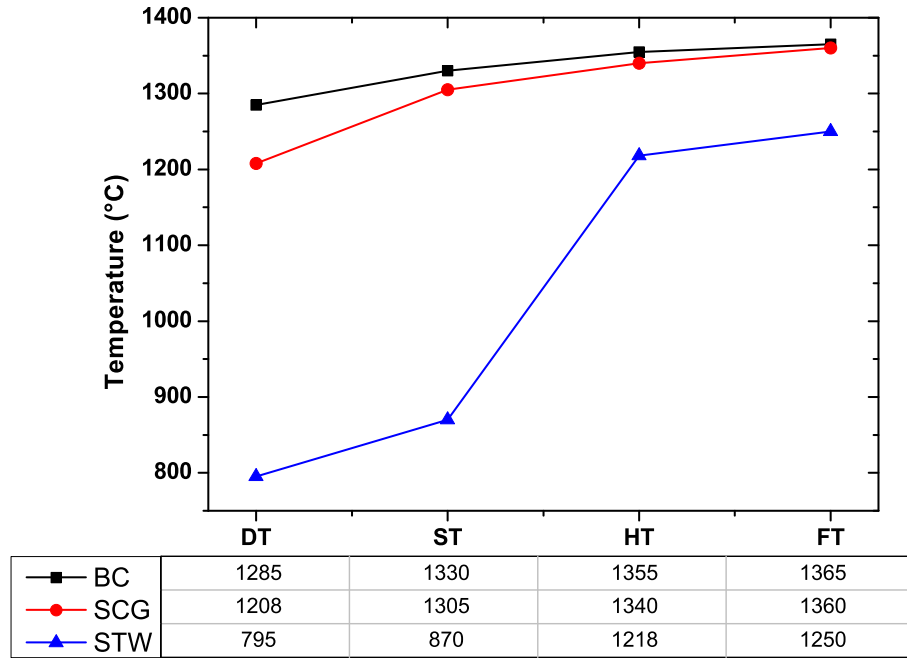


Figure 5-1: Ash fusion temperatures (deformation-DT, sphere-ST, hemisphere-HT, and flow-FT) for bituminous coal (BC), wheat straw (STW) and spent coffee grounds (SCG).

SiO_2 , K_2O , CaO , MgO , P_2O_5 and Cl , whereas lower content of Al_2O_3 and Fe_2O_3 . In biomass, the content of Na_2O is significantly lower than that of K_2O and can be ignored in general [Zhu et al., 2018b].

In AFT experiments under oxidising, inert and reducing conditions, respectively, [Li et al., 2017a], [Yan et al., 2017], and [Liu et al., 2013a] reported that low SiO_2/Al_2O_3 (S/A) ratios (1.0, 1.5 and 2.5, respectively) increased AFT values due to the formation of high-melting temperature compounds. Higher S/A ratio values led to slightly decreased or even unchanged AFT values. It was concluded that under the experimental conditions SiO_2 made little contribution to the modification of AFT values, and changes in AFT values were attributed mainly to higher Al_2O_3 content at low S/A ratio, which has a high melting point increasing the AFT values.

From Figure 5-1, it can be seen that between the biomass under study, SCG showed higher AFT values in comparison with STW, with similar behaviour to BC. This finding is in agreement with those from [Wei et al., 2018], who

showed increased AFT values for SCG. Despite high K_2O and P_2O_5 content, counting for more than 56 % of total ash in SCG, no SiO_2 content was detected in SCG samples. Numerous studies have reported that increased P_2O_5 content can decrease AFT values due to the development of low melting phase in the ash [Namkung et al., 2018]. Furthermore, high content of SiO_2 and K_2O in ash have been linked to low AFT values and ash sintering issues [Teixeira et al., 2012]. Nevertheless, the formation of potassium silicates with low AFT values has been reported to be limited by the availability of silicon in the fuel ash [Teixeira et al., 2012].

For STW, DT and ST are considerably low due to the high SiO_2 and K_2O content, while HT and ST are fairly high. Moreover, the difference between DT and ST is below 100 °C. The smaller the difference, the more sharply the viscosity of the biomass ash slag is changed with the temperature [Deng et al., 2013]. SCG showed a higher difference for DT and ST than BC, 97 °C and 45 °C, respectively. In general terms, SCG showed higher ST, HT and FT values in comparison with STW and other biomass resources reported in the literature. It could be explained by the relatively high CaO and MgO content in ash.

5.3.2 Ash Fusibility of Bituminous Coal and Wheat Straw Blends

This section describes the changes in AFT values to the extent STW ratio was increased in the blends. For comparison purpose, the AFT values for pure BC and STW were included in Table 5-2, which shows the chemical composition of the ash blends, calculated based on the ash composition of the pure fuels according to the equivalent coal and biomass blending ratio.

The addition of STW to BC in the blends leads to significant changes in the ash composition. To the extent STW ratio increased in the blends the Al_2O_3 and Fe_2O_3 content decreased. These two compounds broadly found in coal ash have shown high fusibility temperatures under oxidising conditions [Liu et al., 2013a]. Furthermore, SiO_2 , K_2O and Cl increased in the blends with

Table 5-2: Calculated chemical ash composition of bituminous coal (BC) and wheat straw (STW) blends, expressed as oxides.

Fuel blends (wt%)	Ash composition (wt%)												
	SiO_2	P_2O_5	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	Cr_2O_3	MnO_2	Cl
BC 100	43.21	0.27	11.84	35.41	4.03	0.83	0.18	0.90	2.28	0.96	0.04	0.05	0.00
BC80:STW20	46.72	0.69	9.97	29.70	4.68	1.24	0.15	3.40	2.28	0.80	0.04	0.05	0.26
BC60:STW40	50.57	1.15	7.92	23.46	5.41	1.69	0.12	6.14	2.29	0.63	0.03	0.05	0.55
BC40:STW60	54.81	1.65	5.67	16.58	6.20	2.18	0.08	9.15	2.29	0.45	0.03	0.05	0.87
BC20:STW80	59.49	2.21	3.18	8.99	7.07	2.73	0.04	12.48	2.29	0.24	0.02	0.05	1.22
STW 100	64.69	2.82	0.42	0.55	8.05	3.33	0.00	16.18	2.29	0.01	0.01	0.04	1.60

higher STW blending ratios. The coexistence of SiO_2 and K_2O , and Cl has been reported as one of the responsible factors for forming low-melting K-silicates, which decrease the AFT values [Zhu et al., 2018b] [Deng et al., 2013] or lead to sintering and agglomeration of bed material in fluidised beds [Teixeira et al., 2012]. Other compounds such as CaO , MgO and P_2O_5 increase to a lesser extent. Figure 5-2 depicts the calculated changing trends of the ash components in terms of STW blending ratio including the ash content of the fuels.

The main changes reported in Figure 5-2 are in the increasing trend in SiO_2 and K_2O content and decreasing behaviour for Al_2O_3 and Fe_2O_3 to the extent the STW ratio increases in the blend. These trends were easily visible even at low biomass blending ratios. It is mainly attributed to the high ash content in STW. Figure 5-3 presents the AFT values for the BC and STW blends. The biomass blending ratio varied in the range of 40 - 80 wt%. For comparison purpose, the AFT values for pure BC and STW were included.

The AFT values of the blends are lower than those of BC and differ greatly from those of the pure fuels. In comparison with BC, the addition of 40 wt% STW decreased DT by 205 °C with a difference of 135 °C between DT and ST. The addition of 60 wt% STW decreased DT by 327 °C in comparison with BC, with marginal changes in ST, HT, and FT in comparison with the addition of 40 wt% STW. Additionally, the difference between DT and ST

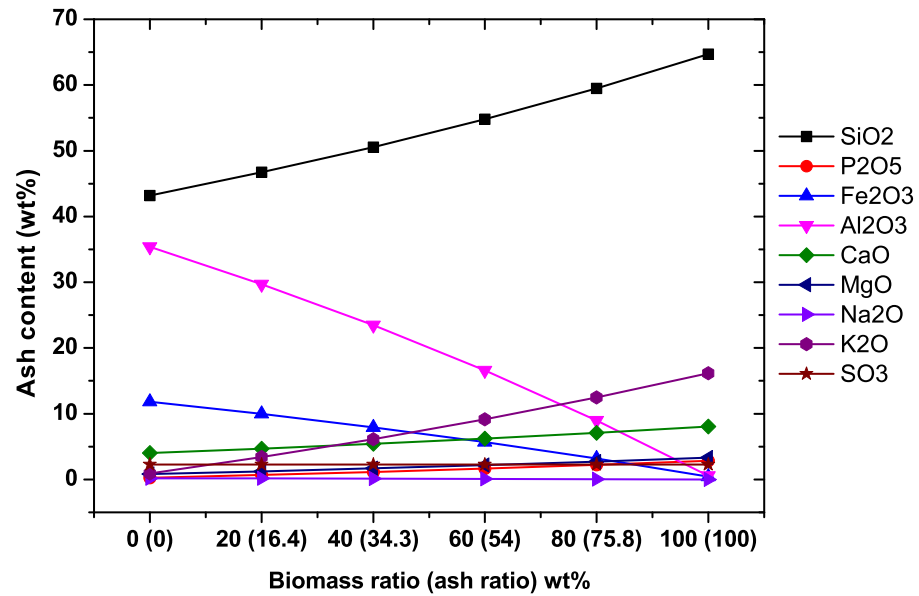


Figure 5-2: Calculated shift of ash composition (as oxides) by replacing coal with wheat straw (STW).

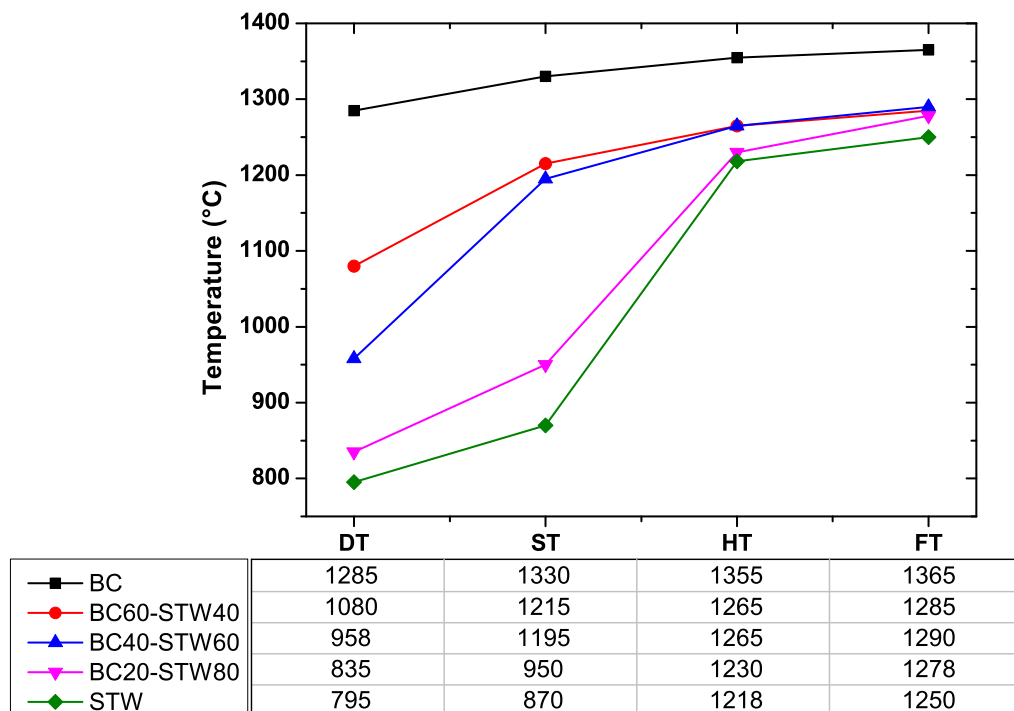


Figure 5-3: Ash fusion temperatures (deformation-DT, sphere-ST, hemisphere-HT, and flow-FT) for bituminous coal (BC) and wheat straw (STW) blends.

increased by 192 °C in comparison with BC. The addition of 80 wt% STW showed similar AFT behaviour to that of pure STW, with a decreasing trend for DT (123 °C), HT (35 °C) and FT (12 °C) in comparison with the addition of 60 wt% STW. Nevertheless, ST decreased by 245 °C in comparison with the addition of 60 wt% STW. In comparison with BC, the addition of 80 wt% STW decreased DT by 450 °C. At 80 wt% STW ratio the difference between DT and ST was 115 °C.

In general, the addition of STW ash to BC ash lowered AFT values in all the blends. It is evident a marked trend of decreasing AFT values even at low blending ratios. It is mainly attributed to the change in ash composition due to the high ash content in STW and the relevant content of SiO_2 , K_2O , and Cl , which could lead to the formation of low-melting alkali-silicates, consequently lowering the AFT values for the blends.

5.3.3 Ash Fusibility of Bituminous Coal and Spent Coffee Grounds Blends

This section describes the changes in AFT values to the extent SCG ratio was increased in the blends. For comparison purpose, the AFT values for pure BC and SCG were included in Table 5-3, which shows the calculated chemical composition of the ash blends based on the ash composition of the pure fuels according to the equivalent coal and biomass blending ratio.

Table 5-3: Calculated chemical ash composition of bituminous coal (BC) and spent coffee ground (SCG) blends, expressed as oxides.

Fuel blends (wt%)	Ash composition (wt%)												
	SiO_2	P_2O_5	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	Cr_2O_3	MnO_2	Cl
BC 100	43.21	0.27	11.84	35.41	4.03	0.83	0.18	0.90	2.28	0.96	0.04	0.05	0.00
BC80:SCG20	41.68	0.91	11.44	34.16	4.36	1.58	0.17	2.22	2.44	0.93	0.04	0.06	0.01
BC60:SCG40	39.35	1.89	10.83	32.25	4.88	2.71	0.16	4.22	2.69	0.87	0.04	0.08	0.02
BC40:SCG60	35.46	3.52	9.81	29.07	5.74	4.61	0.15	7.58	3.10	0.79	0.04	0.10	0.04
BC20:SCG80	27.22	6.98	7.65	22.31	7.56	8.63	0.11	14.70	3.97	0.61	0.03	0.16	0.07
SCG 100	0.00	18.40	0.52	0.00	13.57	21.91	0.00	38.20	6.84	0.00	0.00	0.34	0.20

The blending of SCG with BC leads to significant changes in the ash composition. To the extent SCG ratio increased in the blends; SiO_2 , Fe_2O_3 , and Al_2O_3 content decreased. It is attributed to the marginal content of these compounds in SCG. Nevertheless, due to the low ash content of SCG, the reduction of these compounds showed a slowly decreasing trend. In contrast, K_2O , CaO , MgO , and P_2O_5 showed an increasing trend, which was not relevant at low blending ratios. It is attributed to the low ash content of SCG. Interestingly, the S/A ratio showed a constant value of 1.22 regardless of the SCG blending ratio. It is because SiO_2 and Al_2O_3 content in the ash blends comes from BC only. Low S/A ratio values in ash have been linked to high AFT values [Yan et al., 2017]. Figure 5-4 depicts the calculated changing trends of the ash components in terms of SCG blending ratio including the ash content of the fuels in brackets.

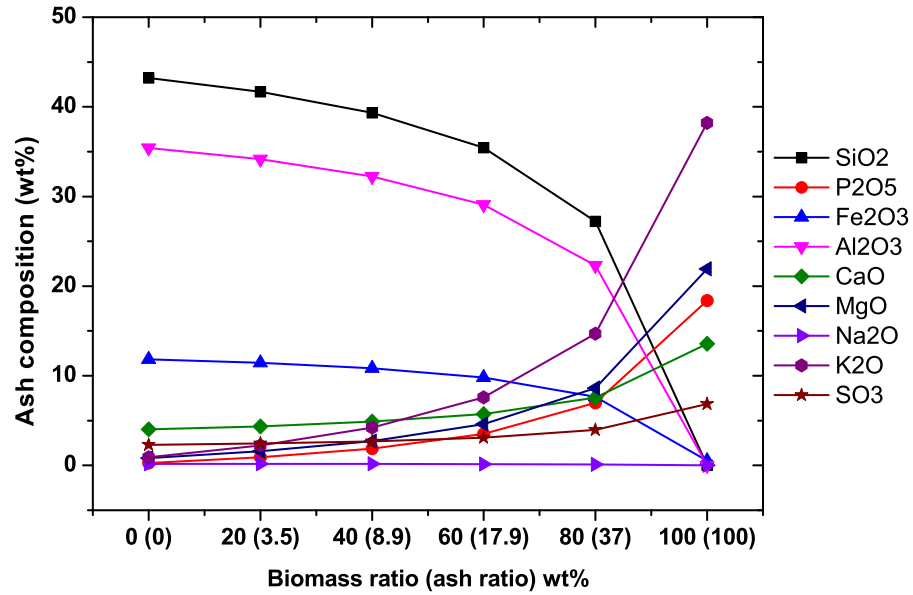


Figure 5-4: Calculated shift of ash composition (as oxides) by replacing coal with spent coffee grounds (SCG).

The AFT values for BC and SCG blends are presented in Figure 5-5. In comparison with BC, the addition of 40 wt% SCG decreased DT and ST by 120 and 87 °C, respectively. It represents a difference of 78 °C between DT and ST values, leading to an increase of 33 °C in DT and ST difference compared to BC. Furthermore, HT and FT decreased by 67 °C and 65 °C, respectively.

The addition of 60 wt% SCG decreased DT by 177 °C in comparison with BC and increased the difference between DT and ST to 165 °C, which increased by 120 °C compared to BC. Additionally, marginal changes in ST, HT and FT were observed in comparison with the addition of 40 wt% SCG.

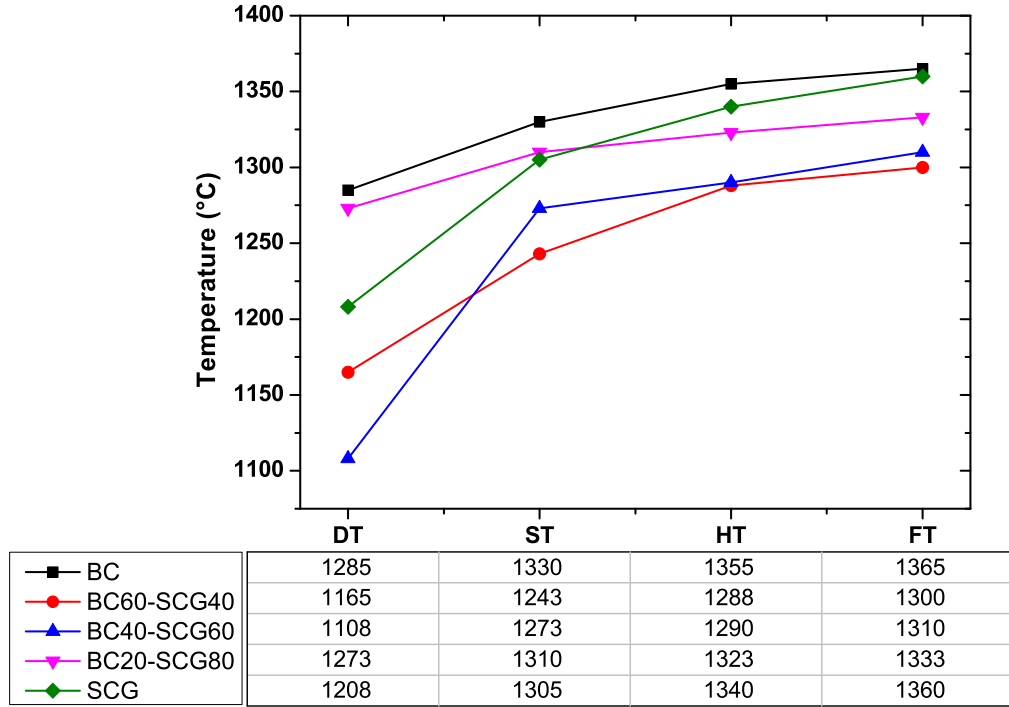


Figure 5-5: Ash fusion temperatures (deformation-DT, sphere-ST, hemisphere-HT, and flow-FT) for bituminous coal (BC) and spent coffee grounds (SCG) blends.

Unlike BC and STW blends, the AFT values of the BC and SCG blends did not show a constant decreasing trend. It is noteworthy that the 80 wt% SCG blending ratio showed an increased DT value similar to that from pure BC. This trend of BC:SCG was observed with repeated runs. Figure 5-6 shows the comparison of DT values of BC blended with STW and SCG to the extent the biomass ratio increases. There is a non-linear relationship in the changes of DT values for the blends of BC with either STW or SCG. As for STW, the higher the proportion of blending ratio, the lower the ash DT value. It was attributed to the relatively high ash content in STW and the high content of K_2O and SiO_2 in STW compared to BC. In co-combustion the content of ash in biomass plays a key role. [Luan et al., 2014] attributed the

diminishing of ash deposition problems to the low ash content in wood used during combustion experiments of coal and biomass blends.

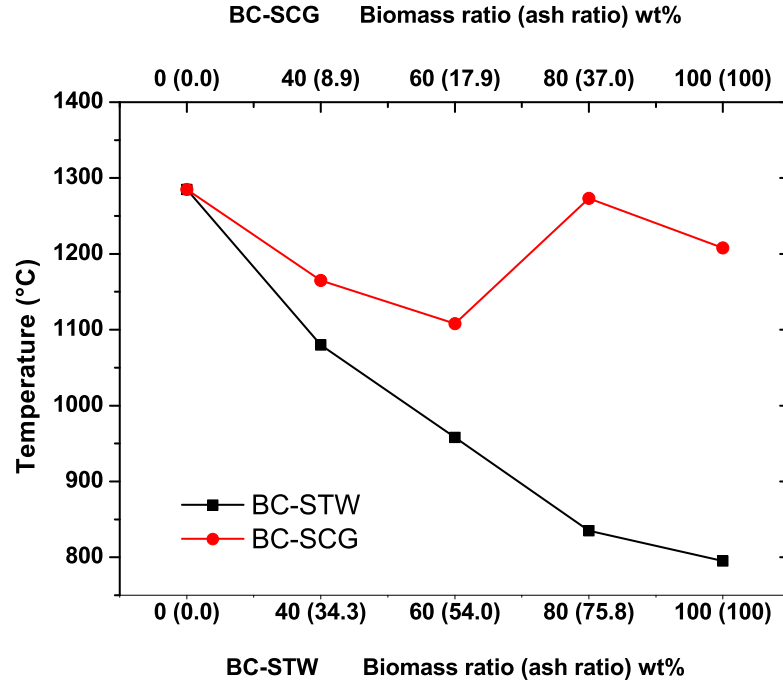


Figure 5-6: Comparison of deformation temperature (DT) for bituminous coal (BC) blended with spent coffee grounds (SCG) and wheat straw (STW).

As for SCG, despite the high K_2O content in SCG ash, the modification of AFT values for coal by K_2O content appears not to be significant as it occurred for STW ash. It is mainly attributed to the reducing availability of silicon in the ash blend to the extent the biomass ratio increases. Similar results were reported by [Teixeira et al., 2012] during co-combustion experiments in a BFB combustor and AFT experiments using blends of coal and olive cake compared to coal and straw pellets blends. In this study, DT values from blends with SCG initially decreased for blending ratios up to 60 wt%, then an increase in DT value for 80 wt% SCG blending ratio was observed. This behaviour has been reported as typical of eutectic melting during experiments conducting to investigate ash fusibility of coal blends [Shen et al., 2015]. In addition, [Song et al., 2010] reported similar trends during AFT experiments of coal ash blends varying the content of SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , and MgO , concluding that higher CaO and MgO content in the fuel

ash could increase the AFT values and reduce the risk of ash issues. Similarly, [Li et al., 2015] reported similar trends during experiments to investigate the behaviour of coal and biomass ash blends. It was attributed to the substitution of K by Ca in semi-molten aluminosilicates leading to the formation of higher melting temperature compounds.

Interestingly, the ash blend at 80 wt% SCG showed a similar DT value than that from pure BC. It is possible to suggest that some interactions among the ash from pure fuels may have taken place leading to high melting temperatures compounds. Similar findings were reported by [Ma et al., 2017] [Li et al., 2015] and [Li and Fang, 2015] during AFT studies of coal and biomass blends, and attributed to the formation of high-melting temperature mullite in higher amounts than compared to that of the original coal. Furthermore, during AFT experiments of biomass blends to investigate the effect of CaO and MgO , [Zhu et al., 2018b] reported the improved formation of high-melting Mg- or Ca-silicates as well as Mg- and Ca-Al-silicates, resulting in increasing AFT values. These results are consistent with those of other studies and suggest that the ash fusibility behaviour of ash blends is not additive and differ greatly from that of the pure fuels ash [Wang et al., 2017a] [Shen et al., 2015] [Li et al., 2015] [Liu et al., 2013a] [Haykiri-Acma et al., 2010]. It may be explained in the markedly different chemical and mineral composition of fuels ash and complex interactions due to the mineral evolution with the temperature increase.

5.3.4 Ash Characterisation - Indices

Originally devised for the coal industry, several indices based on the fuel ash composition are broadly used [Guo and Zhong, 2018] [Tchapda and Pisupati, 2014] [Teixeira et al., 2012]. One of the preliminary measures to predict the ash behaviour and likelihood of ash issues is the use of these indices, which are based on ash-forming elements present in the fuel ash. Despite these indices have varying levels of usefulness [Morris et al., 2018] [Pintana and Tippayawong, 2016], they have been used for predicting the ash fusion, slagging, deposit formation, fouling, agglomeration, sintering or corrosion

problems during thermochemical conversion of solid fuels [Pintana and Tippayawong, 2016] [Vassilev et al., 2014]. Nevertheless, the use of biomass as fuel or its inclusion in coal combustion raises new challenges in terms of new compounds contained in the ash, which could reduce the validity of these indices leading to unrealistic predictions.

In the literature, several indices based on the ash components have been proposed to predict the behaviour of fuels ash. One of the benefits of using ash indices is the possibility to obtain preliminary indications for ash issues in an inexpensive and easy way [Guo and Zhong, 2018]. Nevertheless, these indices do not consider the real behaviour and conditions of fuels processing [Morris et al., 2018] [Vassilev et al., 2014], such as the difference in the occurrence of mineral elements in biomass, mostly organically bound rather than associated with minerals as in common coals and ash formation mechanism [Vassilev et al., 2014] [Teixeira et al., 2012] or in the case of agglomeration, the combustion technology or bed material [Morris et al., 2018]. Among the most used and reported indices in the literature to predict ash issues are:

- **Base to acid ratio, $R_{B/A(+P)}$.** It explains the ash deposition potential and gives indications of the slagging propensity of ash [Xing et al., 2016a] [Teixeira et al., 2012]. Nevertheless, to have a better understanding of biomass influence it should be accounted that the addition of biomass to coal combustion increases the P_2O_5 concentration, significantly [Febrero et al., 2015] [Folgueras et al., 2015] [Vassilev et al., 2014] [Kupka et al., 2008]. The content of P_2O_5 in SCG ash used in this study is much higher than that observed for STW and BC. Severe slagging occurs when the $R_{B/A(+P)}$ has remained in the 0.75 - 2 range and moving away from this range, in either direction, decreases the slagging intensity [Kupka et al., 2008]. In general, the lower the ratio value, the higher the AFT values [Deng et al., 2013].

$$R_{B/A(+P)} = \frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3 + P_2O_5}{SiO_2 + Al_2O_3 + Ti_2O} \quad (5-1)$$

- **Slagging index, R_s .** It refers to deposit formation from adhering of sticky, melted or softened ash particles on heat transfer surfaces exposed to radiant heat [Pintana and Tippayawong, 2016]. S^d refers to the wt% of sulphur in ash on a dry basis. The use of indices based on sulphur content when biomass is involved have produced unrealistic predictions, it is due to the low sulphur content in most of the biomass resources [Teixeira et al., 2012]. Nevertheless, SCG used in this study showed higher values of sulphur content than those in BC. The interpretation of results is as follows $R_s < 0.6$ low slagging, $R_s = 0.6 - 2.0$ medium, $R_s = 2.0 - 2.6$ high, and $R_s > 2.6$ extremely high [Febrero et al., 2015] [Teixeira et al., 2012].

$$R_s = (R_{B/A(+P)})S^d \quad (5-2)$$

- **Fouling index, R_f .** Fouling refers to the dry deposition of ash particles or condensation of volatile inorganic components on heat transfer surfaces [Pintana and Tippayawong, 2016]. This index is considered a better approach to the effect of biomass on the deposition process due to the inclusion of alkali metals. Nevertheless, it disregards the influence of Cl and S content on the vaporisation of the alkali metal elements [Teixeira et al., 2012]. $R_f \leq 0.6$ low fouling, $0.6 < R_f \leq 40$ high, and $R_f > 40$ extremely high (tendency to sintering of deposits) [Febrero et al., 2015].

$$R_f = (R_{B/A(+P)})(Na_2O + K_2O) \quad (5-3)$$

- **Ash fusibility index, T_{AFI} .** This index can indicate the slagging tendency in terms of representative fusion temperatures namely initial deformation temperature (DT) and hemisphere temperature (HT) [Xing et al., 2016a] [Pintana and Tippayawong, 2016]. Unlike ash composition indices, it allows a better description of the real ash melting behaviour of fuels due to the use of actual experimental data, which take into account the existing interactions that influence the ash fusibility temperatures. Nevertheless, it should be considered that DT is depen-

dent on the atmosphere and AFT technique have some limitations in the prediction due to ashing process and conditions [Teixeira et al., 2012]. For ash, the slagging tendency is low for $T_{AFI} > 1340$ °C, medium for T_{AFI} in the range 1250 - 1340 °C, high for the range 1150 - 1250 °C, and severe for T_{AFI} values < 1150 °C [Xing et al., 2016a] [Folgueras et al., 2015].

$$T_{AFI} = \frac{4DT + HT}{5} \quad (5-4)$$

- **Alkali index, AI.** This index is based on the assessment of alkali oxides per unit of energy [Guo and Zhong, 2018] [Akram et al., 2015b]. It is used to have an indication of fouling, slagging or agglomeration occurrence, but it does not consider the influence of additives or alternative bed materials in the process, leading to poor predictions in those cases [Xing et al., 2016a]. When $0.17 < AI < 0.34$ agglomeration is possible, $AI > 0.34$ indicates certain agglomeration to occur [Morris et al., 2018].

$$AI = \frac{(Na_2O + K_2O)}{HHV} \quad (5-5)$$

- **Bed Agglomeration Index, BAI.** This index can give an indication of sintering and agglomeration of ash under thermal conversion conditions [Pintana and Tippayawong, 2016]. BAI lower values than 0.15 give an indication of agglomeration to occur [Morris et al., 2018].

$$BAI = \frac{Fe_2O_3}{Na_2O + K_2O} \quad (5-6)$$

- **Alkaline earth oxides to alkaline oxides, I.** Higher values than 2 should not present a risk of sintering [Akram et al., 2015b]. [Morris et al., 2018].

$$I = \frac{CaO + MgO}{Na_2O + K_2O} \quad (5-7)$$

- **Agglomeration Index 1, I1.** It gives an indication of agglomeration based on the probability that an excess of alkali metals over sulphur and chloride leads to the formation of alkali metal silicates [Morris et al., 2018]. It assumes that all the S and Cl present in the fuel react with the fuel alkali species and ignore both the release of S and Cl in the forms of HCl and SO_2 and their combination with other cations [Niu et al., 2016a]. If $I1 > 1$, alkali-induced agglomeration is possible [Morris et al., 2018] [Akram et al., 2015b].

$$I1 = \frac{Na + K}{2S + Cl} \quad (5-8)$$

- **Agglomeration Index 2, I2.** It describes the probability of the formation of a refractory outer coating [Niu et al., 2016a]. It is based on the coating of SiO_2 bed particles by an inner layer rich in alkali silicates and a refractory outer layer rich in Ca , P , and Mg , with higher melting temperatures, reducing the probability of agglomeration. A fuel with a ratio in which $(Ca + P + Mg)$ is larger than $(K + Na + Si)$ is believed to form such a non-sticky outer layer. [Niu et al., 2016a]. If $I2 > 1$, there is a high agglomeration potential [Morris et al., 2018].

$$I2 = \frac{Na + K + Si}{Mg + P + Ca} \quad (5-9)$$

Table 5-4 summarises the indices values for the fuels used in this study. The slagging potential in terms of the $R_{B/A(+P)}$ and R_s showed similar trends. BC was the fuel with the lowest slagging potential, followed by STW. As for pure SCG, the estimation of these indices was not applicable due to the negligible detection (see Table 3-3) of the oxides in the denominator of the equation, see equation 5-1. Either BC:STW or BC:SCG blends showed low slagging potential at low blending ratios with an increasing trend in both cases. Moreover, BC20:SCG80 blend showed a severe slagging potential, which appears to be extremely high when sulphur content was taken into account in R_s .

Table 5-4: Index values of bituminous coal (BC) blended with spent coffee ground (SCG) and wheat straw pellets (STW).

Fuel blends	Indices*								
	$R_{B/A(+P)}$	R_s	R_f	T_{AFI}	AI	BAI	I	$I1$	$I2$
BC 100	0.23	0.47	0.24	1173	0.03	11.00	4.52	0.23	5.89
BC80:SCG20	0.27	0.74	0.64	-	0.05	4.78	2.49	0.74	4.81
BC60:SCG40	0.34	1.17	1.49	1024	0.08	2.47	1.73	1.25	3.74
BC40:SCG60	0.48	1.97	3.72	1006	0.11	1.27	1.34	1.77	2.66
BC20:SCG80	0.91	4.33	13.48	1250	0.15	0.52	1.09	2.28	1.59
SCG 100	-	-	-	1013	0.19	0.01	0.93	2.79	0.51
BC80:STW20	0.26	0.52	0.93	-	0.09	2.81	1.67	0.96	5.68
BC60:STW40	0.30	0.57	1.88	1033	0.18	1.27	1.13	1.70	5.47
BC40:STW60	0.35	0.63	3.20	879	0.26	0.61	0.91	2.43	5.27
BC20:STW80	0.40	0.70	5.05	844	0.39	0.25	0.78	3.17	5.06
STW 100	0.47	0.77	7.64	826	0.55	0.03	0.70	3.90	4.85

* $R_{B/A(+P)}$, Base-to-acid Ratio. R_s , Slagging Index. R_f , Fouling Index. T_{AFI} , Ash Fusibility Index.

AI , Alkaline index. BAI , Bed agglomeration index. I , Alkaline earth oxides to alkaline oxides.

$I1$, Agglomeration Index 1. $I2$, Agglomeration Index 2.

Both groups of blends namely BC:STW and BC:SCG showed an increasing trend in R_f values to the extent biomass ratio increases. Nevertheless, the lower ash content in SCG contributed to have similar R_f values to those in BC:STW blends up to 60 wt% biomass ratio regardless of the higher K_2O content in SCG ash. Nevertheless, higher SCG ratios showed a significant increase of fouling risk with R_f values from BC:SCG blends doubling those from BC:STW.

The ash fusibility index T_{AFI} showed severe deposition tendency for all the blends, in this decreasing order STW > SCG > BC. All the BC:STW blends showed severe deposition tendency. As for BC:SCG blends, higher T_{AFI} index values were observed, giving an indication of a severe deposition tendency, which decreased to medium for the BC20:SCG80 blend.

The alkali index values gave an indication of low probability of ash issues for BC:SCG. Inversely, the opposite trend was observed for BC:STW blends with an increasing trend to the extent the biomass ratio increases. No indication of sintering or agglomeration was observed based on *BAI* values for both groups of blends, with a lower risk for BC:SCG blends. Similarly, BC:SCG showed less risk of sintering based on *I* values compared to BC:STW blends, it could be mainly attributed to higher *CaO* and *MgO* content in SCG ash. *I1* values showed a risk of alkali-induced agglomeration for blending ratios higher than 20 wt% for all the blends with an increasing trend to the extent the biomass ratio increases. Despite *I2* values showed a risk of agglomeration for all the blends, a markedly decreasing trend was observed for BC:SCG to the extent biomass ratio increases. It was mainly attributed to the increment of *CaO* and *MgO* in the blends to the extent the biomass ratio increases.

The present analysis undoubtedly reveals that these chemical indices can be only preliminary indicators for ash issues. The use of indices has limitations when predicting ash issues [Vassilev et al., 2014]. Indeed, these indices originally devised for the coal industry displayed contradictory results when extensively applied to biomass fuels [Garcia-Maraver et al., 2017]. In this study, SCG and STW showed a markedly trend to produce slagging, fouling and agglomeration. None of the indices could describe the observed trend in the DT values of BC:SCG blends. Based on these results, the co-processing of fuels showed not to be relevant in terms of changing the trends of ash issues for the biomass used in this study. Therefore, the applicability of ash indices should be considered with caution and only as a preliminary estimation.

Further analysis was performed using a ternary diagram to illustrate the changes in the ash blends composition (see Table 5-3). Ternary diagrams are an additional preliminary approach to predict the behaviour of fuels based on the ash composition [Du et al., 2014] [Scala and Chirone, 2008]. Although there are several diagrams based on the main ash compounds, multicomponent phase diagrams that include the major components are considered to be more accurate [Niu et al., 2016a]. Figure 5-7 shows the ternary diagram originally proposed by [Link et al., 2018] with the total content of alkaline

oxides $Na_2O + K_2O$, alkaline earth oxides $CaO + MgO$ and acidic and intermediate oxides $SiO_2 + Al_2O_3 + Fe_2O_3 + P_2O_5$ in each corner. The contribution of other oxides and Cl to the average composition was neglected.

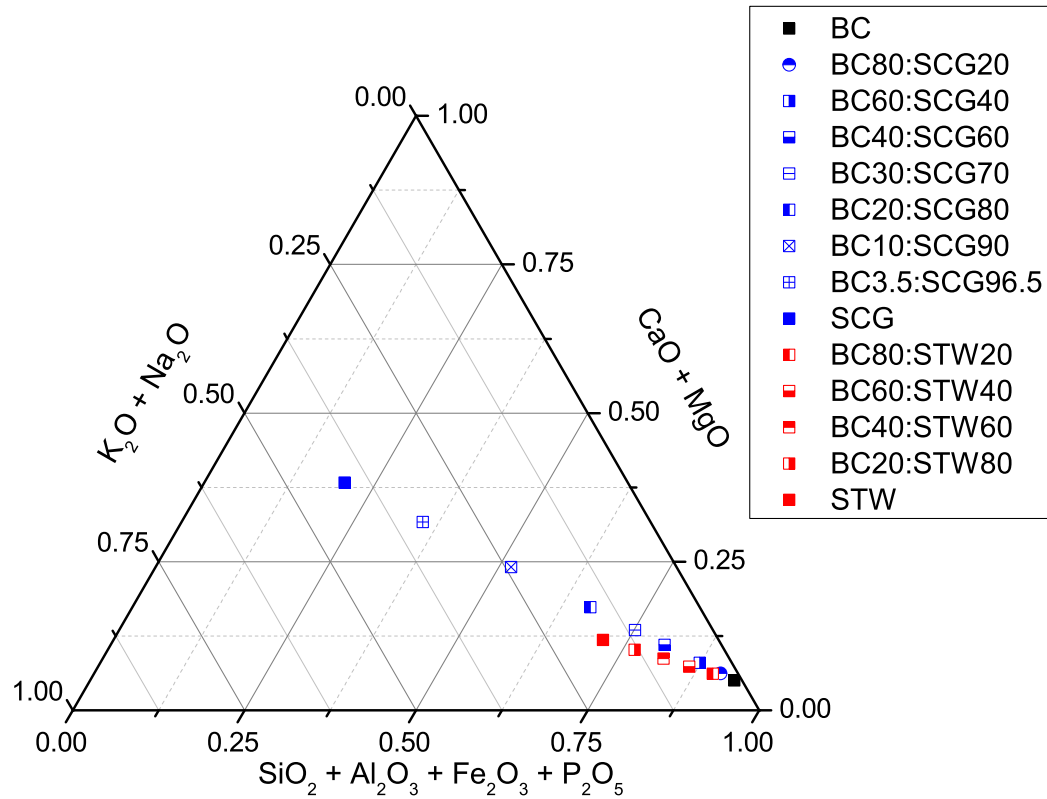


Figure 5-7: Ternary diagram of ash blends (closed symbols correspond to pure fuels ash, opened symbols correspond to different blends).

From Figure 5-7, it is evident the change in ash composition of the blends of BC with either STW or SCG to the extent the biomass ratio increases. Despite the low ash content, the addition of SCG ash showed a broad change of the compounds in the ash blends due to the different ash composition compared to BC. It is attributed to the increasing content of CaO and MgO in the blend to the extent the SCG ash ratio increases. Higher content of CaO favours the formation of Ca-Silicates or Ca-K-Silicates instead of K-Silicates with lower melting temperatures [Vassilev et al., 2014] [Vassilev et al., 2013] [Teixeira et al., 2012]. In contrast, the addition of STW ash with high SiO_2 and K_2O content showed a narrow change of the compounds in the ash blends, resulting in decreasing AFT values of the blends due to the formation of low

melting temperatures compounds. Similar trends were reported by [Zhu et al., 2018b], during AFT experiments of blends of corn straw and sawdust, and further studies of the effects of SiO_2 , K_2O , CaO , and MgO as additives.

From the results in this chapter can be concluded that the content of CaO and MgO in SCG ash contributes to increase the ash fusibility behaviour of BC:SCG blends. Despite the high K_2O content in SCG, BC:SCG blends showed higher AFT values than those from BC:STW blends. Interestingly, DT for BC:SCG blends was observed to increase to higher values than pure BC at biomass blending ratios between 70 - 90 wt%. This can be explained by the relatively high content of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO in the blends. Several studies have indicated a positive effect on DT with increased content of those compounds in the ash due to the possibility to form high melting temperatures compounds [Niu et al., 2016a] [Vassilev et al., 2014]. In contrast, BC:STW blends showed a decreasing trend in AFT values to the extent the STW blending ratio increased. It was attributed to the increased content of SiO_2 , and K_2O and the reduction of compounds with high melting points such as Al_2O_3 and Fe_2O_3 . Similar findings have been reported as promoting the progressing of low melting species leading to low AFT values [Zhu et al., 2018b] [Luan et al., 2014].

Furthermore, ash composition indices showed poor reliability to predict or explain the real behaviour of fuel ash issues and incapable to describe the particular behaviour of AFT values from BC:SCG ash blends. This confirms that these indices could be used as preliminary indicators of ash issues only because the modes of element occurrence and real combustion conditions are neglected. These results reveal that simplified generalisations about the fuel ash behaviour may not be possible and specific ash fusibility characterisation of fuels should be performed case-by-case. As a conclusion, the evidence in this chapter shows that SCG could be a good quality fuel with low ash content, which may be used in co-processing schemes without severe ash issues. Nevertheless, results from the studies in this chapter do not consider the real processing conditions under larger scales including the interactions of fuels, the effect of compounds occurrence and temperature gradients.

5.4 Summary

The use of SCG as a fuel in co-processing arises as an interesting alternative due to the low ash content and high ash fusibility temperatures when blended with coal. The high content of CaO , MgO , and P_2O_5 in SCG with negligible content of SiO_2 and Cl complements the high content of Al_2O_3 and Fe_2O_3 in coal leading to higher ash fusion temperatures reducing the common ash issues from biomass. The ash indices used in this study showed to be useful just a preliminary measure to predict the occurrence of ash issues. Further analyses of ash composition and blending ratio in a ternary diagram showed the change in ash composition of BC:SCG blends in a broad range despite the low ash content of SCG. The fuels characterisation showed that SCG can be an interesting fuel with a relatively higher heating value, high volatile matter content and reduced ash content with high melting temperatures compounds. Therefore, SCG has potential to be a good quality fuel which can be used in pure or in co-processing with other fuel with reduced ash issues and improved combustion performance.

These results can be useful to understand the behaviour of these ash blends under oxidising conditions providing relevant information for the design and optimisation of thermochemical conversion systems at larger scales. Nevertheless, high nitrogen content arises as a challenge to address about the use of spent coffee grounds as a fuel in terms of potential NO_x emissions. Furthermore, high content of alkali metals in spent coffee grounds raises some concerns in terms of potential ash issues. The next chapter investigates the performance of SCG as fuel in co-combustion with BC in a fluidised bed reactor in terms of GHG emissions and agglomeration tendency.

Chapter 6

Co-combustion Experiments in a Fluidised Bed Combustor

6.1 Introduction

Co-combustion of coal and biomass is considered quite a promising alternative to accelerate the decarbonisation of energy systems in the short-term. It has been demonstrated in more than 150 installations worldwide for a broad variety of feedstocks in several combustor types [Sahu et al., 2014] [Miller, 2011] [Loo and Koppejan, 2008]. Woody and herbaceous biomass have shown to be feasible to replace up to 20 % and 10 % of the total energy input (energy basis), respectively [Karampinis et al., 2015]. In most of the cases, reduced modifications have been needed to achieve stable operation of the equipment with a negligible effect on combustion efficiency at modest replacement levels (i.e. 3 - 5 wt%) [Karampinis et al., 2015] [Loo and Koppejan, 2008]. Nevertheless, increasing the blending ratio entails challenges linked to fuel preparation, combustion efficiency, and ash sintering and agglomeration due to troublesome elements in biomass ash.

6.2 Experimental Campaign

This section describes the experimental campaign conducted for the combustion experiments in the BFB combustor. It was divided in three stages:

- **Comparative study of biomass fuels - Stage I.** It entails combustion experiments of bituminous coal (BC) blended with biomass to investigate the effect of blending ratio. The analysis of results was based on the most representative flue gas emissions (CO_2 , CO , and NO_x), combustion performance, agglomeration tendency, and ash behaviour. Three different biomass resources were used namely commercial wood pellets (WP) and wheat straw pellets (STW) at 15 and 40 wt% along with in-house manufactured spent coffee grounds pellets (SCG) blended at 40 wt%. Due to limited availability of SCG only the blend with 40 wt% was considered. Experiments using pure bituminous coal (BC) were carried out as a reference case. Garside 14/25 sand was used as bed material in all cases.
- **Comparative study of ilmenite as an alternative bed material - Stage II.** Based on the results from the first stage, the blend of BC with STW at 40 wt% was selected due to the existence of agglomerates for the operating time. The performance of ilmenite as alternative bed material in comparison to silica sand in terms of the most representative flue gas emissions (CO_2 , CO , and NO_x), combustion performance, and agglomeration tendency was investigated.
- **Comparative study of ilmenite as an additive - Stage III.** Similarly to the study in stage II, the blend of BC with STW at 40 wt% was selected to perform the comparative studies of additives. The experiments were carried out using kaolin, bauxite, and ilmenite as additives at 10 wt% in a Garside 14/25 sand bed to investigate the agglomeration tendency in the bed, the most representative flue gas emissions (CO_2 , CO , and NO_x), and combustion performance.

Each co-combustion experiment consisted of two runs of ~ 5 hours of fuel combustion using the same bed material to confirm the repeatability. The fluidisation air flow rate used at operating conditions was set to be 640 l/min. Fuel feed began after the bed was preheated with the electric heaters to a temperature over 600 °C. The fuel feed rate was adjusted to maintain a constant temperature of 900 ± 20 °C. In a steady operation, the excess air was

in the range of 75 - 110 % to maintain the bed temperature. The combustion performance was determined by the loss of efficiency due to unburnt carbon (UBC) in ash according to [Kuprianov et al., 2011] and CO emissions according to [Guo and Zhong, 2018] (see Equations 6-2 and 6-1). In addition, further SEM/EDX and XRF analysis were performed to characterise the agglomerates and ash obtained.

$$Efficiency\ loss\ due\ to\ CO\ emissions = \left(\frac{CO}{CO_2 + CO} \right) 100 \quad (6-1)$$

Where CO_2 and CO are the average concentration values in the flue gas during combustion experiments. Although there are some fluctuations in the course of the experiment, the measuring results are basically stable.

$$Efficiency\ loss\ due\ to\ UBC = \frac{32,866}{LHV} \left(\frac{UBC}{100 - UBC} \right) A \quad (6-2)$$

Where UBC is the unburnt carbon content in the ash in wt%. LHV is the low heating value. A is the fuel ash content in wt% on as received basis.

6.3 Results and Discussion

6.3.1 Combustion Operation

Temperatures and drop pressure across the BFB reactor were the primary measurements to monitor the combustion experiments. Figure 6-1 shows the typical temperature and drop pressure profiles of the BFB reactor during one of the combustion experiments. It includes the start-up, fuel combustion, and corresponding temperatures decrease after the stop of fuel feed during the shutdown. The increase of fluidisation air flow rate every 20 minutes can be observed (corresponding to the red dashed lines, namely, (1) 200, (2) 260, (3) 320, (4) 380, (5) 440, (6) 500, and (7) 640 l/min) according to the experimental combustion procedure described in section 3.4.4. Similarly, dark dashed lines depict the onset and end of fuel feed after reaching approximately 600 °C in the bed (i.e. T2 and T3).

Fluctuations observed in the temperatures, and an increase in the drop pressure during the start-up stage correspond to the increase of air flow rate. The majority of the temperature fluctuations occurred at the onset of bed fluidisation, corresponding to an initial decrease in the bed temperatures, which then increase again. It is attributed to the change in the hydrodynamic regime and bed expansion (see Figure 2-3 (bottom)). In fluidised beds, the onset of fluidisation is indicated by the presence of larger fluctuation of the bed pressure [Montes et al., 2016]. Similarly, fluctuations observed in the temperatures during fuel combustion stage correspond to fuel feed adjustments to maintain operating temperature (i.e. 900 ± 20 °C).

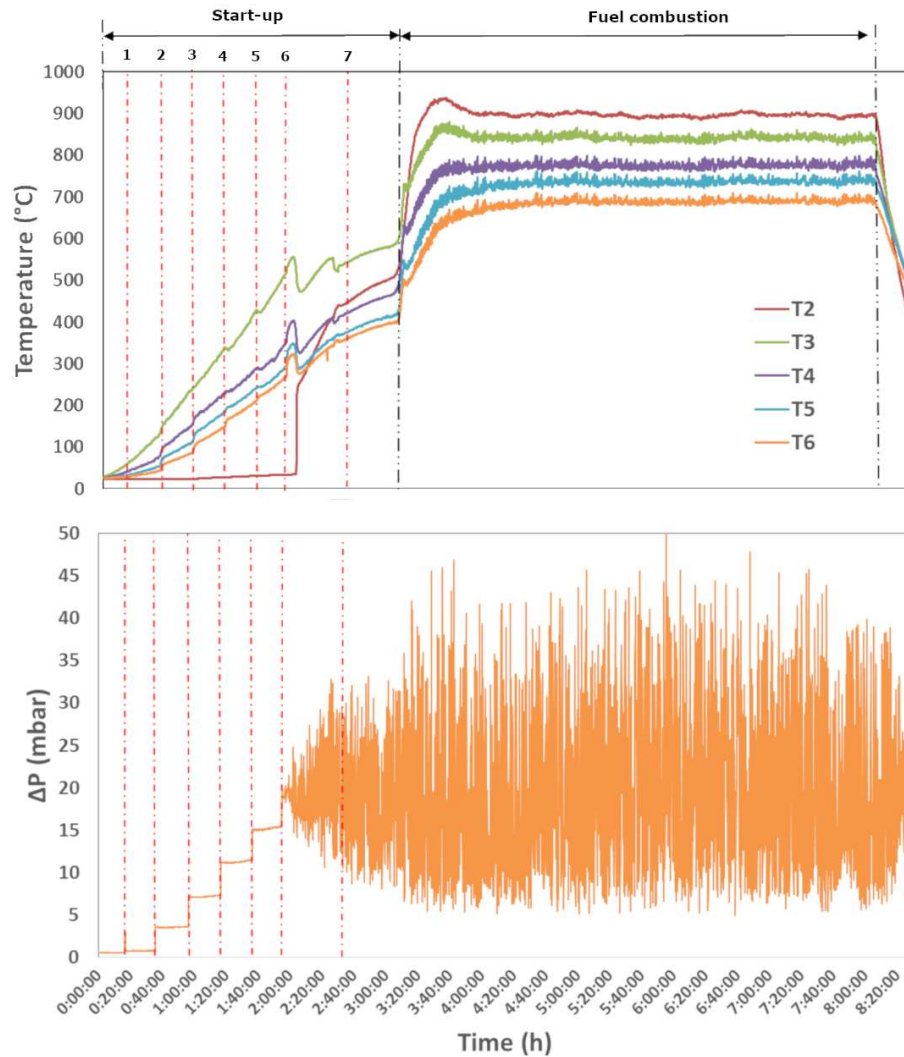


Figure 6-1: Typical temperature profile (top) and drop pressure profile (bottom) across the BFB reactor.

Likewise, the typical flue gas emissions profiles are shown in Figure 6-2. Events previously described such as onset and end of fuel feed, and fluctuation due to fuel feed adjustment can be observed.

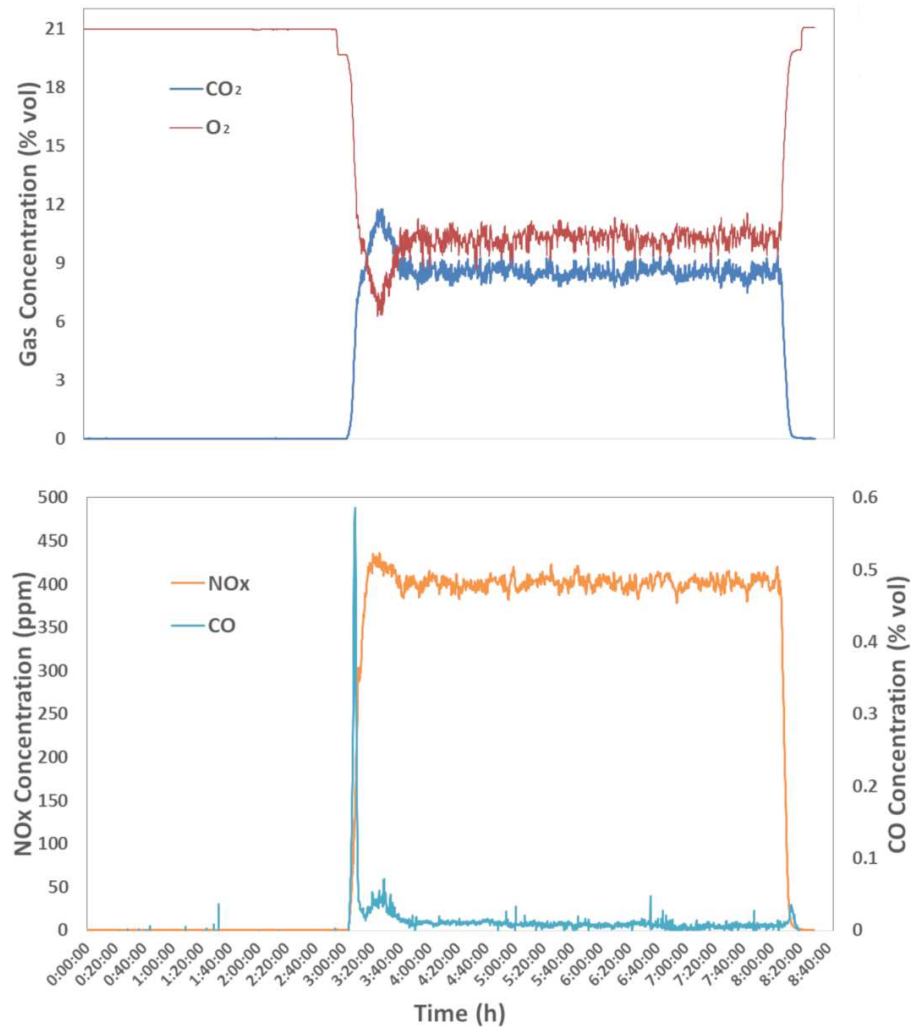


Figure 6-2: Flue gas composition, CO_2 and O_2 concentration (top), and NO_x and CO concentration (bottom) at the outlet of the BFB reactor.

Information obtained through the data-logging system provided the raw data to perform the analysis of results and support the discussion from the different stages of the experimental campaign presented in the following sections. Table 6-1 shows the average values of results from the experimental campaign.

Table 6-1: Average values of experimental campaign results from the fluidised bed combustion experiments at steady state

Experiment	Run	Run time (h)	Bed temp. (°C)	Furnace temp. (°C)	Max. bed temp (°C)	Pressure drop (mbar)	Air flow rate (l/min)	Fuel feed rate (kg/h)	Excess air (%)	Flue gas composition, 10% O ₂		
										CO ₂ (%vol)	CO (ppm)	NO _x (ppm)
100 % BC	1	4.78	899	843	937	19.27	640	2.14	92.7	8.76	100	406
	2	4.55	894	837	917	19.73	640	2.14	104.5	9.34	150	441
Stage I: Comparative study of biomass resource and ratio, Fuel : 60 wt% BC + selected material, Bed material: 100 wt% silica sand												
40 wt% WP	3	4.00	892	851	909	19.54	640	2.45	102.90	9.48	140	336
	4	4.60	891	853	920	19.35	640	2.55	81.3	9.64	150	299
15 wt% WP	5	4.85	895	849	913	19.52	640	2.05	97.1	9.09	90	389
	6	4.30	888	841	915	19.55	640	2.13	111.9	8.88	80	385
40 wt% STW	7	4.38	898	866	926	19.58	640	2.65	94.4	9.49	110	308
	8	4.27	902	869	921	19.82	640	2.61	87.7	9.26	120	296
15 wt% STW	9	4.88	901	853	925	20.00	640	2.29	91.3	9.09	90	372
	10	4.70	892	849	912	19.35	640	2.33	99.1	9.09	80	362
Stage II - Spent coffee ground combustion performance. Fuel: 60 wt% BC - 40 wt% SCG, Bed material: 100 wt% silica sand												
40 wt% SCG	11	4.57	909	856	932	19.59	640	2.35	79.3	8.98	100	398
	12	4.57	909	860	938	19.42	640	2.33	83.8	9.47	80	378
	13	4.41	903	855	927	19.71	640	2.39	85.7	9.28	120	356
	14	4.20	901	851	929	19.59	640	2.38	82.9	9.25	90	377
Stage III - Comparative study of additives, Fuel: 60 wt% BC - 40 wt% STW, Bd material: 90 wt% silica sand + selected additive.												
10 wt% Kaolin	15	4.01	897	860	928	19.29	640	2.54	76.5	9.81	100	274
	16	4.30	899	863	923	19.73	640	2.71	78.9	9.24	70	265
10 wt% Bauxite	17	4.55	903	857	929	19.48	640	2.72	84.9	9.33	80	303
	18	3.90	900	860	928	20.04	640	2.79	82.2	10.42	80	301
10 wt% Ilmenite	19	4.25	905	857	929	19.50	640	2.51	103.4	10.25	40	286
	20	4.26	907	862	944	19.98	640	2.64	82.0	9.04	100	257
Stage IV - Comparative study of alternative bed material. Fuel: 60 wt% BC - 40 wt% STW.												
100 wt% Ilmenite	21	4.27	904	865	930	20.10	640	2.66	87.4	9.01	210	448
	22	4.67	901	858	927	18.55	640	2.52	112.5	9.21	160	510

6.3.2 Stage I: Effect of Biomass Resource and Ratio

In this section the effect of biomass resource and blending ratio was examined using Garside 14/25 sand as bed material. Initially, two main fuel blends were investigated namely BC-WP and BC-STW blended at 15 and 40 wt%. Secondly, BC-WP and BC-STW blends at 40 wt% were compared to BC-SCG at the same blending ratio. The analysis of results was based on the effect of blending ratio in terms of most representative flue gas emissions (CO_2 , CO , and NO_x), combustion performance, and agglomeration tendency.

Temperature Profile

Figure 6-3 illustrates the temperature profiles across the height of the BFB reactor using different fuel blends and biomass ratios at steady state. All the blends attained the maximum temperature just 100 mm above the air distributor plate, suggesting the combustion of the fuel in the dense bed as expected for fuel blends with predominant ratios of coal with low volatile matter. Afterwards the temperature reaches a maximum value, it gradually decreases in the freeboard. It was probably due to the air dilution effect of the high excess air and heat loss through the reactor walls.

To the extent biomass ratio increases the combustion of the fuel blends continued in the gas phase across the freeboard, similar results have been reported from co-combustion experiments of coal and biomass by [Vamvuka et al., 2017] [Atimtay and Kaynak, 2008] [Patumsward and Cliffe, 2001]. This phenomenon was more noticeable to the extent biomass ratio increased in the blend leading to higher temperatures (see Figure 6-3a and b). It is attributed to higher volatile matter content from biomass.

The temperature profile of WP blended at 15 wt% closely follows the profile of BC. It should be noticed that there was no detrimental effect on combustion efficiency because increased mixing in the bed by the high air flow rate, which was more relevant than similar temperatures values. This observation agrees with the results of [Patumsward and Cliffe, 2001], who investigated

the co-combustion of coal with waste from olive oil production in a fluidised bed combustor. Blends at 40 wt% (see Figure 6-3c) showed increased combustion temperatures in the freeboard compared to pure BC as expected for higher biomass blending ratios. It was attributed to higher volatile matter from biomass increasing the reactivity of coal. These results agree with the findings of previous co-combustion studies of coal and biomass in fluidised beds by [Suheri and Kuprianov, 2015] [Badour et al., 2012] [Li et al., 2008].

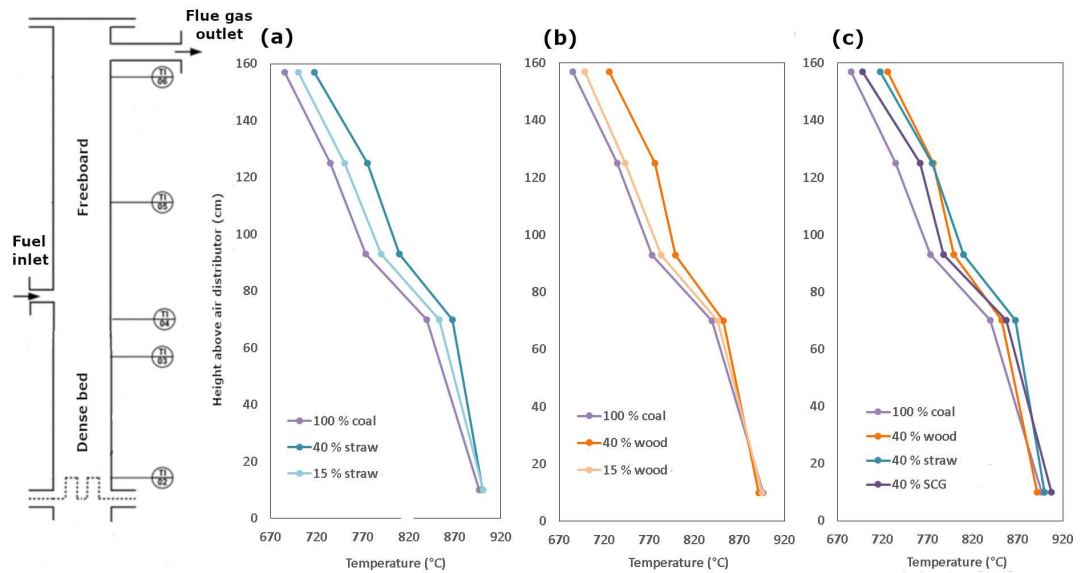


Figure 6-3: Temperature profile across the height of the BFB reactor using different fuel blends and biomass ratios at steady state, (a) BC:STW, (b) BC:WP, and (c) blends at 40wt%.

CO₂ Emissions

In co-combustion to keep the same heat input as coal, higher amounts of biomass are required. It results in no relevant changes in the CO₂ emissions in comparison with the combustion of pure coal. In Figure 6-4a, the CO₂ emissions are illustrated in terms of energy-based emission factors. It could be observed an increase in the CO₂ emissions to the extent that the blending ratio increases for all blends. It is explained in the fact that for a fixed heat input to the combustor, the increase in CO₂ emissions is due to an increase in the mass of CO₂ in the flue gas associated to the larger biomass use with increasing co-combustion ratio, which generally yields higher emis-

sions compared with pure coal combustion [Dahlquist, 2013]. Nevertheless, the CO_2 emitted from biomass does not contribute to the net increase in the CO_2 atmospheric level due to the CO_2 neutral nature of biomass [Sahu et al., 2014] [Scala, 2013] [Moradian et al., 2013] [Loo and Koppejan, 2008]. In general, biomass addition to coal combustion systems provides a reduction in gas emissions of CO_2 , SO_2 , and NO_x [Guo and Zhong, 2018] [Lackner et al., 2010]. Among the biomass resources tested, SCG appears as the most suitable due to high fixed carbon content and heating value.

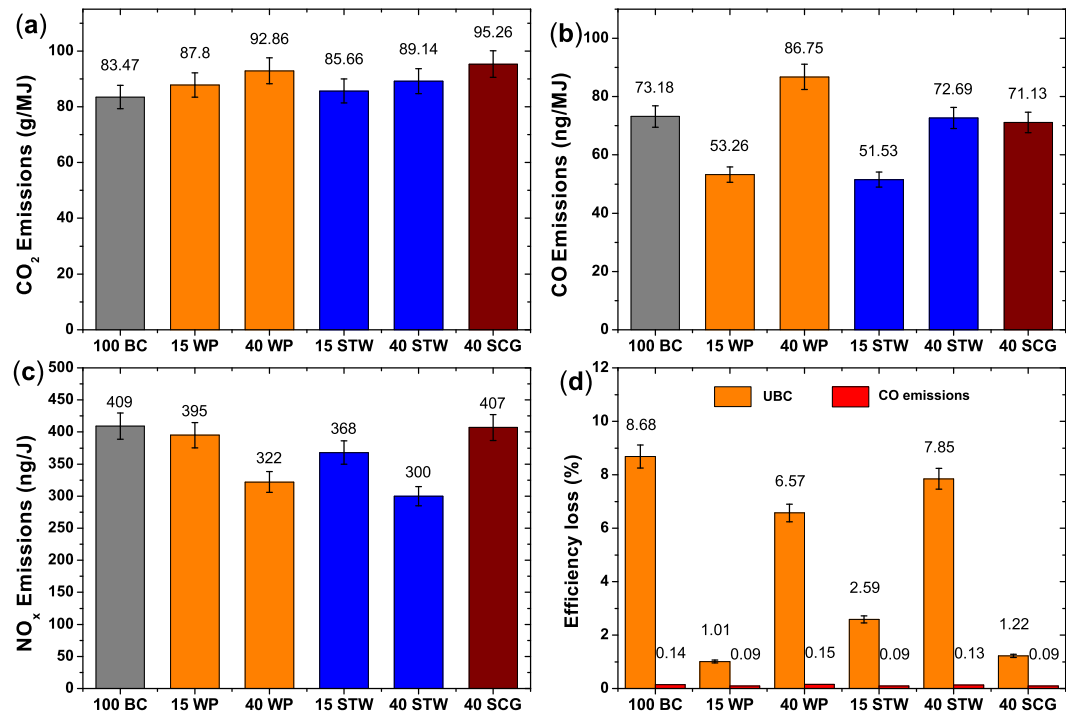


Figure 6-4: Emissions of CO_2 (a), CO (b), NO_x (c) per energy input, and loss of efficiency due to unburnt carbon (UBC) and CO emissions (d) using bituminous coal (BC) blended with wood (WP) pellets and wheat straw (STW) pellets at 15 wt% and 40 wt%, and spent coffee grounds (SCG) pellets at 40 wt%.

CO Emissions

In co-combustion, CO emissions increase with increasing the blending ratio [Okasha et al., 2014] [Scala, 2013] [Li et al., 2008] [Gogebakan et al., 2008]. The results illustrated in Figure 6-4b show lower CO emissions at 15 wt% biomass ratio for both blends than those from pure coal. It is attributed

to the increase of reactivity in the blend due to higher content of volatile matter from biomass [Okasha et al., 2014] [Scala, 2013]. Similar findings were reported by [Atimtay and Varol, 2009] and [Patumsward and Cliffe, 2001] from co-combustion experiments of olive cake with coal in a fluidised bed combustor.

At higher biomass ratios, larger amounts of volatiles and fines are available and could escape the bed to burn in the freeboard, requiring longer residence time and improved mixing [Lackner et al., 2010]. In such cases, the geometry of the reactor plays a critical role [Atimtay and Varol, 2009] [Loo and Koppejan, 2008] [Oka, 2004]. An increase in the cross-sectional area of the freeboard in relation to the bed improves lateral mixing in the freeboard and increases the freeboard temperature, thereby decreasing *CO* emissions [Scala, 2013] [Basu, 2006]. Air excess and air staging are other parameters that could be adjusted to decrease *CO* emissions both enhancing the rate of *CO* oxidation to *CO*₂ [Kuprianov et al., 2011] [Lackner et al., 2010] [Basu, 2006]. Nevertheless, the current research was not specifically designed to evaluate factors related to either excess air or air staging. The experiments were carried out at the same operating temperature and excess air range without air staging to investigate agglomeration tendency.

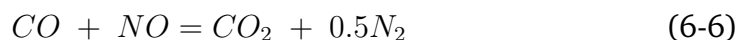
Co-combustion with STW and SCG at 40 wt% showed lower *CO* emissions than WP at the same ratio. This may be due to the different ash composition of STW and SCG compared with WP, and the synergistic effects of compounds with the coal. The present findings seem to be consistent with earlier observations which found evidence of synergistic effects when SCG was used (see Chapter 4). Furthermore, this is in good agreement with results from [Atimtay and Kaynak, 2008], during co-combustion of peach and apricot stones with coal in a fluidised bed. Additionally, it may represent an additional advantage due to the low ash content of SCG compared to STW and similar to WP, reducing ash handling requirements during operation. Nevertheless, it should be considered that WP contains more volatile matter than SCG and STW.

NO_x Emissions

The effect of co-combustion on NO_x emissions is illustrated for the blends to the extent biomass ratio increases in Figure 6-4c. It is well known that NO_x levels are particularly determined by nitrogen content in the fuel [Hrdlička et al., 2016]. Co-combustion of BC with biomass reduces the NO_x emissions in comparison with pure coal combustion due to lower nitrogen content of WP and STW. This is consistent with conclusions from [Guo and Zhong, 2018], who reported that NO_x emissions decreased significantly during the combustion of coal and biomass blends due to the low nitrogen content in biomass. Despite higher nitrogen content in SCG than BC (see Table 3-2), co-combustion experiments of BC blended with SCG at 40 wt% did not show a relevant change in NO_x emissions in comparison with pure coal combustion. It could be explained by the release of nitrogen as ammonia (NH_3) during biomass combustion. This could represent a lower demand for ammonia injection into the combustor to reduce NO_x emissions under co-combustion conditions [Moradian et al., 2013].

Lower conversion rates of NH_3 to NO compared to HCN , which is the main product of coal fuel nitrogen, promote the NO_x reduction during co-combustion [Karampinis et al., 2014] [Houshfar et al., 2012]. Higher volatile matter in biomass promotes the rapid release of volatiles leading to a high concentration of hydrocarbon radicals, resulting in the reduction of NO (see Equations 6-3, 6-4 and 6-5). Additionally, high levels of volatiles would reduce the oxygen availability for char oxidation leading to high concentrations of CO , which can react with NO to produce N_2 (see equation 6-6) [Liu et al., 2018b] [Guo and Zhong, 2018] [Dahlquist, 2013].





Furthermore, the reduction reaction of NO and CO can be catalysed by inorganic impurities and even the char at high temperatures [Liu et al., 2018b] [Dahlquist, 2013] [Lackner et al., 2010] [Atimtay and Kaynak, 2008]. Higher inorganic impurities proportion in SCG, may be the explanation for no significant change in NO_x emissions when SCG was blended with BC compared to pure BC combustion despite the higher nitrogen content in SCG. Similarly, higher ash content in STW may be the explanation for lower NO_x emissions when STW was blended with BC compared to the values from the blends with WP. Similar findings were reported by [Sirisomboon et al., 2010] and [Atimtay and Kaynak, 2008] from fluidised combustion experiments using rice husks with elevated fuel-ash and peach and apricot stone with coal.

Although a few studies have used SCG in pure or co-combustion in fluidised beds, some studies performed in other combustion technologies could shed light on SCG potential as a fuel. In experiments in a wood pellet boiler using SCG in pure and blended with sawdust, [Limousy et al., 2013] reported good combustion efficiency when SCG was blended at 50 wt% with sawdust achieving NO_x and CO emissions similar to those obtained during wood pellets combustion. It was mainly attributed to the catalytic effect of ash compounds, despite the high nitrogen content of SCG. In addition, [Byul et al., 2017], [Allesina et al., 2017], [Jeguirim et al., 2016] and [Jeguirim et al., 2014b] reported similar findings from combustion experiments of SCG in pure and blended in small scale residential combustors, confirming the potential of SCG to reduce harmful emissions when used as a fuel.

Combustion Performance

Biomass addition to coal combustion generally results in higher combustion efficiencies due to the higher volatile matter content of biomass in comparison with coal [Lackner et al., 2010] [Ghani et al., 2009]. The loss of efficiency due to unburnt carbon (UBC) and CO emissions to the extent biomass ratio increases is shown in Figure 6-4d. The results of this study showed that

100 wt% BC gives the highest efficiency loss. It can be seen that lower values were obtained with the blends at 40 wt% and 15 wt% of WP and STW. The blend of SCG at 40 wt% show similar values to those of the blends of WP and STW at 15 wt%. The highest efficiency loss of BC found in this study could be explained in the fact that the overbed feeding configuration is not the best option for less reactive fuels causing a relatively low combustion efficiency, particularly in BFB combustors [Basu, 2006]. Nevertheless, overbed feeding configuration allows the use of larger fuel particle size than underbed systems making the fuel preparations simpler and less expensive [Basu, 2013] [Scala, 2013].

These results showed that to the extent the biomass ratio in the fuel blend increases, larger amounts of volatiles and fines are available. They could escape the bed to burn in the freeboard leading to higher temperatures in the furnace at higher biomass ratios than those from pure coal or low blending ratios. Furthermore, biomass addition to coal combustion systems commonly results in higher combustion efficiencies due to higher volatile matter content of biomass compared to coal. Biomass rapidly burns and results in highly porous char accelerating the char combustion as well [Lackner et al., 2010]. Nevertheless, biomass ratio at 40 wt% for WP and STW showed higher efficiency loss. These results are in agreement with those observed in *CO* emissions and show that the gain in combustion efficiency is mainly attributed to the reduction in UBC and partially to the reduction of *CO* concentration. Several studies on co-combustion of coal and biomass in fluidised beds have reported similar trends [Kuprianov et al., 2011].

Based on the analysis of gas emissions and efficiency loss, it can be concluded that the best performance of the BFB combustor at the operating conditions is achievable with WP and STW blended at 15 wt%. Interestingly, SCG blended at 40 wt% with BC showed similar efficiency loss values to WP and STW blended at 15 wt%, but no significant reduction in either *CO* or *NO_x* emissions were found compared to pure coal combustion.

Agglomeration Tendency

The analysis of agglomeration tendency in this stage was based on visual observation. There was no evidence of defluidisation during the experiments. After each experiment (i.e. two runs), corresponding to ~ 10 hours of combustion operation, the bed material was examined to verify the existence of agglomerates. The results showed no agglomerates when pure BC or the blends with biomass at 15 wt% were used. As for the blends of BC with biomass at 40 wt%, agglomerates of 3 cm were only found in the bed material when STW was used (see Figure 6-9a).

These agglomerates seemed to be completely fused with a reduced porous structure. This finding suggests the formation of melts and later agglomeration along with the occurrence of intense sintering and secondary reactions after the agglomerates have formed tending to strengthen the agglomerates. As for SCG, two additional runs were performed at the same conditions to provide an extended operation time (i.e. 20 hours) with the same bed material, nevertheless no agglomerates were found after the experiments.

SEM-EDX Analysis of coating layers. To investigate the existence and composition of coating layers when the blend of BC with SCG at 40 wt% further SEM/EDX analysis was performed. Selected bed particle samples were collected after 20 hours using Garside 14/25 as bed material. Then the samples were embedded in epoxy resin, cut and polished for SEM/EDX analysis of bed particles cross-section (see Figure 6-5).

The results from EDX mapping analysis clearly show the existence of cracks in the bed particles. The presence of cracks has been linked to mechanical and chemical stress, which can lead to attrition and fragmentation of bed particles [Chi et al., 2019]. *Si*, *Fe*, *K*, *Al*, and *Ca* and *Mg* to a lesser extent appear to be the dominant elements in the cracking and coating layer. These results are in agreement with findings from the AFT studies using SCG (see section 5.3.3), leading to the formation of high melting temperature compounds. No *S* and *Cl* were found in the coating layer.

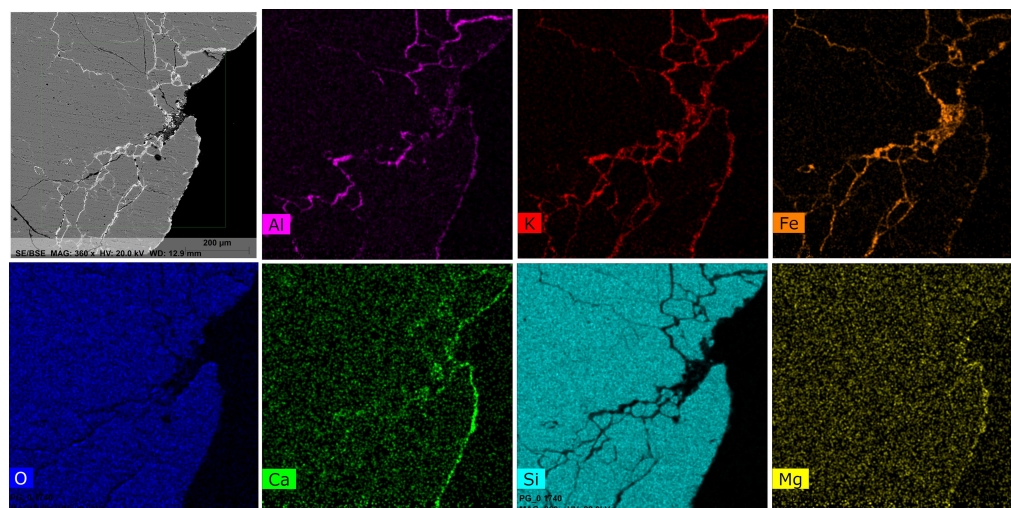


Figure 6-5: EDX elemental mapping of Garside 14/25 bed material samples from combustion of BC blended with SCG at 40 wt% after 20 hours of operation.

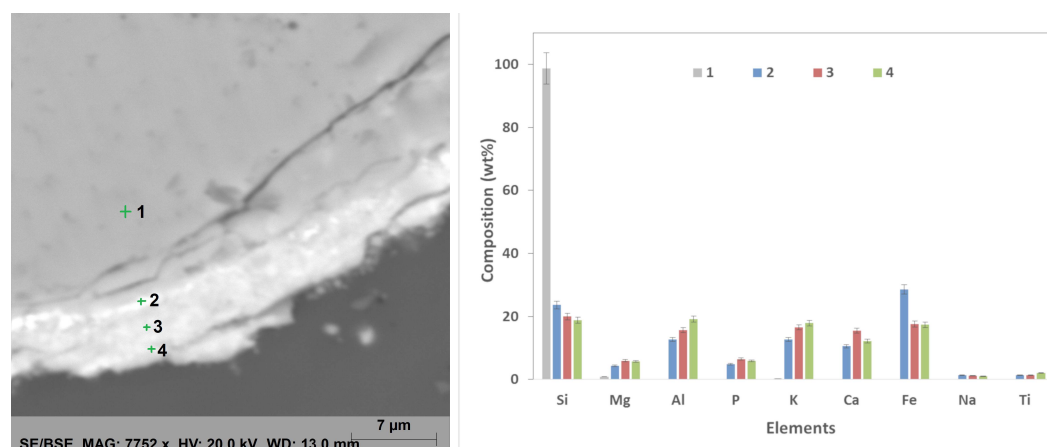


Figure 6-6: EDX elemental spot analysis of Garside 14/25 bed material samples from combustion of BC blended with SCG at 40 wt% after 20 hours of operation.

Further analysis by EDX spot analysis shown in 6-6 revealed the existence of a thin coating layer ($< 10 \mu\text{m}$). Indeed, it consisted of a two-layer structure with a substantial content of *Si*, *K*, *Ca*, and *Fe* in the innermost layer, indicating the role of an adhesive $K_2O\text{-}CaO\text{-}SiO_2$ system in the formation of the primary coating layer on the silica sand particles. Iron found in this layer could be mainly derived from the fuel blend (see Table 5-3). Nevertheless,

the precipitation of *Fe* to the surface of the bed particles was suggested in earlier studies conducted in our research group using the same bed material [Afilaka, 2015]. The iron on the sand particle surface could further react with the potassium compounds to form the coating layer (see reactions 6-10, 6-11, and 6-12). When moving to the outermost layer the content of *K* along with the elements enhancing the melting temperatures of existing compounds such as *Al*, *Ca*, *Fe*, and *Mg* showed an increasing trend. It could explain the reduced agglomeration tendency when the blend of BC with SCG at 40 wt% was used.

XRF Analysis of Cyclone Ash. To investigate the modification of cyclone ash quality when SCG was blended with BC, further analysis of elemental composition (XRF) was performed. The results showed in Figure 6-7 reveal an increase in *K*, *Mg*, *Ca*, and *P* with lower content of *Si*, *Al* in ash when SCG at 40 wt% was used compared to pure BC. Higher content of alkaline and alkaline earth metals in the ash can impose limitations regarding ash utilisation or increase disposal costs [Fuller et al., 2018] [Cheremisinoff, 2012].

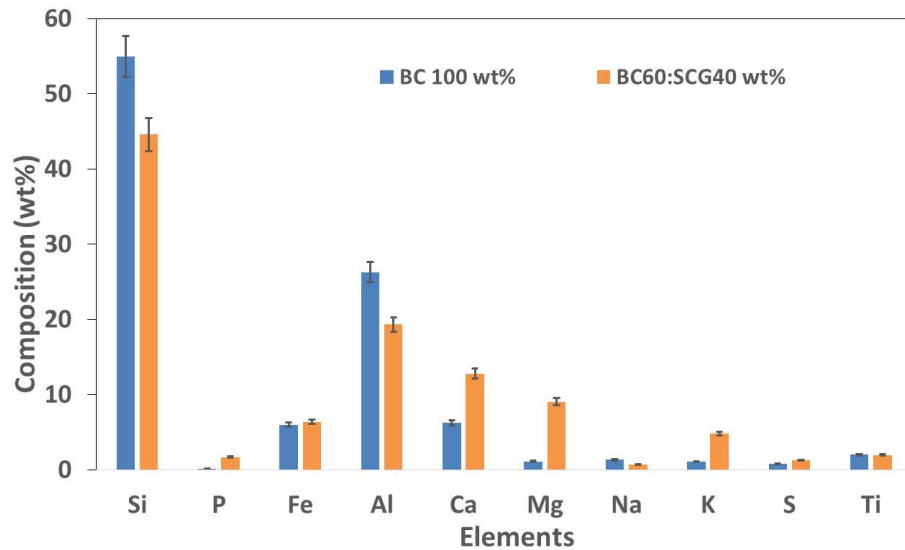


Figure 6-7: Elemental composition (XRF) of cyclone ash from combustion of BC blended with SCG at 40 wt%, using Garside 14/25 as bed material.

6.3.3 Stage II - Performance of Ilmenite as Alternative Bed Material

This section investigates the performance of ilmenite as an alternative bed material compared to Garside 14/25 sand. Based on the results from Stage I in terms of the presence of agglomerates, the blend consisting of BC blended with STW at 40 wt% was used in all experiments. The operating bed temperature was maintained at 900 ± 20 °C by varying fuel feeding rate. No relevant difference between the bed materials was found in terms of temperature profiles, and CO_2 (see Figure 6-8a). Therefore, the analysis of results was based on the most representative flue gas emissions (CO , and NO_x), combustion performance, and agglomeration tendency.

CO Emissions

Figure 6-8b illustrates the reduction in CO emissions when ilmenite was used as bed material compared to Garside 14/25. This reduction is attributed to the potential of oxygen carriers to increase the carbon conversion, which is determined by the reactivity of the oxygen carrier with CO [Wang et al., 2017b]. Similar results have been reported by [Hughes et al., 2017] and [Wang et al., 2017b] using ilmenite as bed material. It has a positive effect on the reduction of unburnt carbon, increasing the combustion efficiency. This effect has been reported to be more prevalent at low excess air levels [Hughes et al., 2017] [Ryden et al., 2016]. It is explained in the fact that the rate of reaction of CO with oxygen is much faster than with the oxygen carrier, so when oxygen (as gaseous O_2) is available it tends to control the overall rate of CO conversion [Ryden et al., 2016]. Due to practical constraints and the interest to investigate the agglomeration tendency at operating temperature, the modification of excess air was not considered in this study.

NO_x Emissions

The effect of ilmenite as bed material on NO_x emissions is illustrated in Figure 6-8c. The results showed higher NO_x emissions when ilmenite was used compared to Garside 14/25. These results are consistent with those

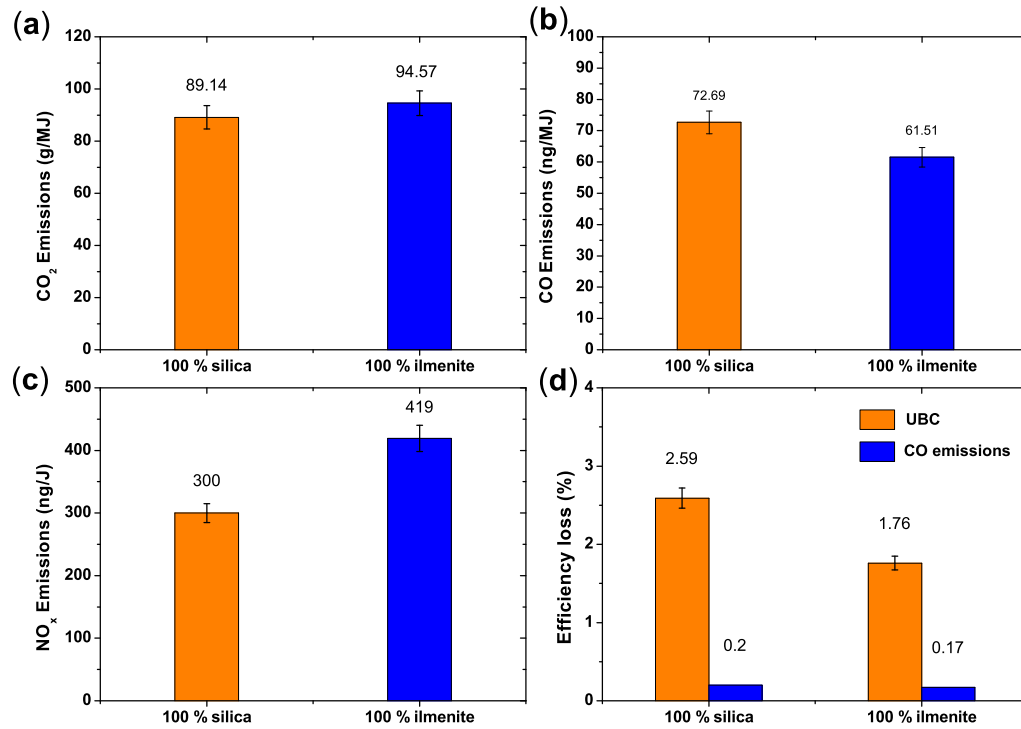


Figure 6-8: Comparison of Ilmenite and Garside 14/25 as bed materials in terms of emissions of CO_2 (a), CO (b), NO_x (c) per energy input, and loss of efficiency due to unburnt carbon (UBC) and CO emissions (d) using bituminous coal (BC) blended with wheat straw (STW) pellets at 40 wt%.

of [Hughes et al., 2017] [Wang et al., 2017b], which used ilmenite as bed material with single air supply, coal and wood char as fuels, respectively. As shown in Figures 6-8b and c, the level of NO_x emissions increased with a decreasing concentration of CO . It may suggest that the presence of ilmenite promotes NO formation by consuming reducing gas species (i.e. H_2 and CO), forming oxidising products (i.e. H_2O and CO_2). Oxygen carriers in the bed can lead to oxidising conditions in parts of the reactor that normally would be reducing [Rydén et al., 2016]. In addition, it has been reported that oxygen carriers can enhance the conversion rate of NH_3 , leading to higher levels of NO under Oxygen Carrier Assisted Combustion (OCAC) conditions [Wang et al., 2017b].

Combustion Performance

Figure 6-8d shows the efficiency loss due to unburnt carbon (UBC) and CO emissions for Garside 14/25 and ilmenite. These results show better combustion performance due to reduced loss of efficiency when ilmenite was used compared to Garside 14/25. These findings seem to be consistent with those reported from other studies, which found enhanced carbon conversion rate and higher efficiency combustion in experiments using various oxygen carriers (i.e. ilmenite, manganese ore, and two oxide scales from the steel production industry) in a small fluidised bed reactor with wood char as fuel [Wang et al., 2017b]. Similar results were reported by [Hughes et al., 2017], in combustion experiments under atmospheric and pressurised conditions in FBC systems using two coals, with more profound results under conditions of low excess air. Additionally, similar results have been reported by [Larson et al., 2014] and [Lind et al., 2013] during experiments conducting to upgrade raw gas from biomass gasification.

Agglomeration Tendency

Likewise to the experiments with 100 wt% Garside 14/25 (stage I), visual inspection of the bed material after 10 hours of operation was performed. It revealed agglomerates when ilmenite as bed material was used. Figure 6-9 shows the agglomerates found in both cases for comparison purpose. It must be said that for the operation time no evidence of defluidisation was observed during the experiments.

A comparison between the agglomerates formed from the same fuel blend and similar operating conditions using both bed materials showed smaller agglomerates when ilmenite was used than those from Garside 14/25. In addition, agglomerates from ilmenite showed a porous structure and appeared to be quite weak and were easily broken into smaller ones. A porous structure indicates the existence of a burning fuel particle inside, initiating the agglomeration process [Scala and Chirone, 2008]. Agglomerates from Garside 14/25 appeared to be completely fused as a result of heavy deposition and melting, without visible bridges connecting the particles. It suggests the

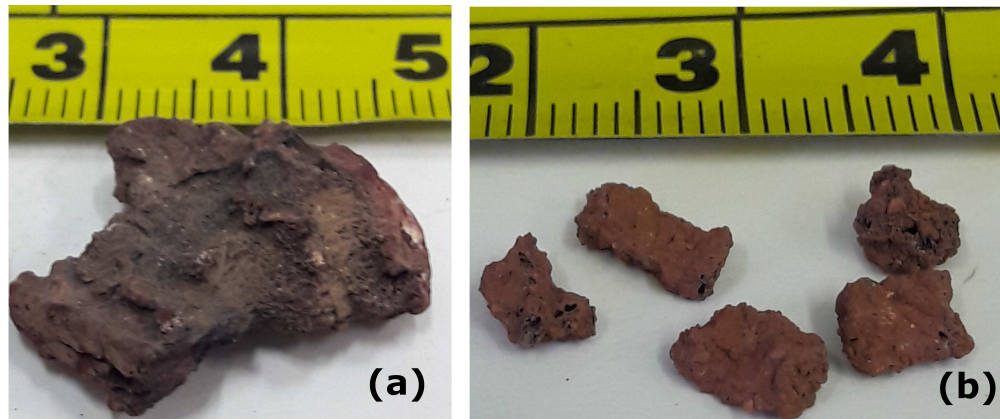


Figure 6-9: Comparison of samples of agglomerates produced from combustion of BC blended with STW at 40 wt% after 10 hours of operation using (a) Garside 14/25, and (b) ilmenite 100 wt% as bed material (scale in cm).

formation of melts and later agglomeration along with the occurrence of intense sintering and secondary reactions after the agglomerates have formed tending to strengthen the agglomerates.

SEM-EDX Analysis of Agglomerates. To investigate the composition of the agglomerates, selected samples collected after the experiments using Garside 14/25 and ilmenite as bed material were embedded in epoxy resin, then cut and polished for SEM observation and EDX analysis of agglomerate cross-section. Figure 6-10 shows the SEM/EDX analysis of agglomerated bed material using Garside 14/25 and ilmenite.

When Garside 14/25 was the bed material (see Figure 6-10a), a dense melt phase mainly composed of *Fe* with reduced amounts of *Si*, *Al* and *K* was observed. Similar findings were reported by [Afilaka, 2015], who conducted coal combustion experiments in the same BFB combustor using the same sand bed. It was reported that the iron content from the sand bed could be responsible for the agglomeration formation due to the presence of $FeO - Al_2O_3 - SiO_2$ alkali silicates leading to the formation of melts and later agglomeration along with the occurrence of intense sintering.

Agglomerates from ilmenite (Ilm) as bed material showed bridges between the bed particles (see Figure 6-10b), with *Si* and *K* as the predominant ele-

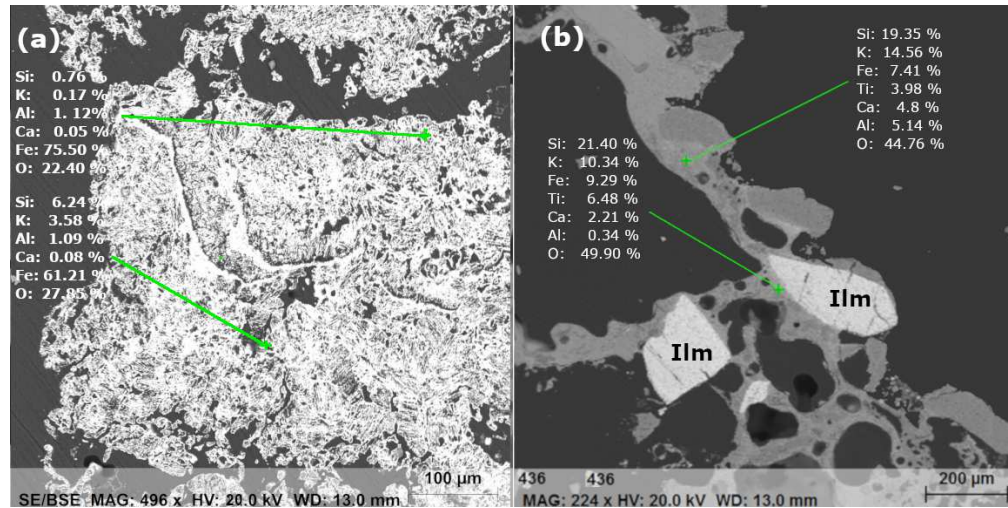


Figure 6-10: SEM/EDX micrograph showing the cross-sectional surface as well as the elemental spot analysis of the binder region of agglomerated (a) Garside 14/25, and (b) ilmenite bed materials obtained from the combustion of BC blended with STW at 40 wt% after 10 hours of operation.

ments in the binder. In addition, representative quantities of Fe , Ti , Ca and Al were found in the binder, suggesting the diffusion of these elements. It is widely accepted that these elements could react with K forming compounds with higher melting temperatures [Vassilev et al., 2014]. In fact, it has been reported that if the alternative bed material contains a sufficient amount of iron oxide (Fe_2O_3), the iron will react preferentially with alkali metals evolving to form $X_2Fe_2O_4$ which melts at a higher temperature of 1135 °C [Basu, 2006]. Furthermore, during straw combustion experiments using TiO_2 as an additive, a significant reduction of K vapourisation was reported by [Wiinikka et al., 2009].

This finding suggests the interaction of ash components with the ilmenite. Similar results were found by [Zevenhoven et al., 2018], who reported a Fe and Ti rich phase in the bridges between particles during experiments to investigate the influence of potassium-containing components on ilmenite bed material under oxidising conditions in a lab-scale fluidised bed reactor. To analyse the chemical composition of agglomerates and the binder linking the ilmenite bed particles, the EDX mapping technique was used with results presented in Figure 6-11. The distribution of Si , K , Ca , Al , Fe , Ti , and O

across the surface of the agglomerated bed material sample was identified as presented. The intensity of the colour across a particular area indicates a higher content of the element in that region.

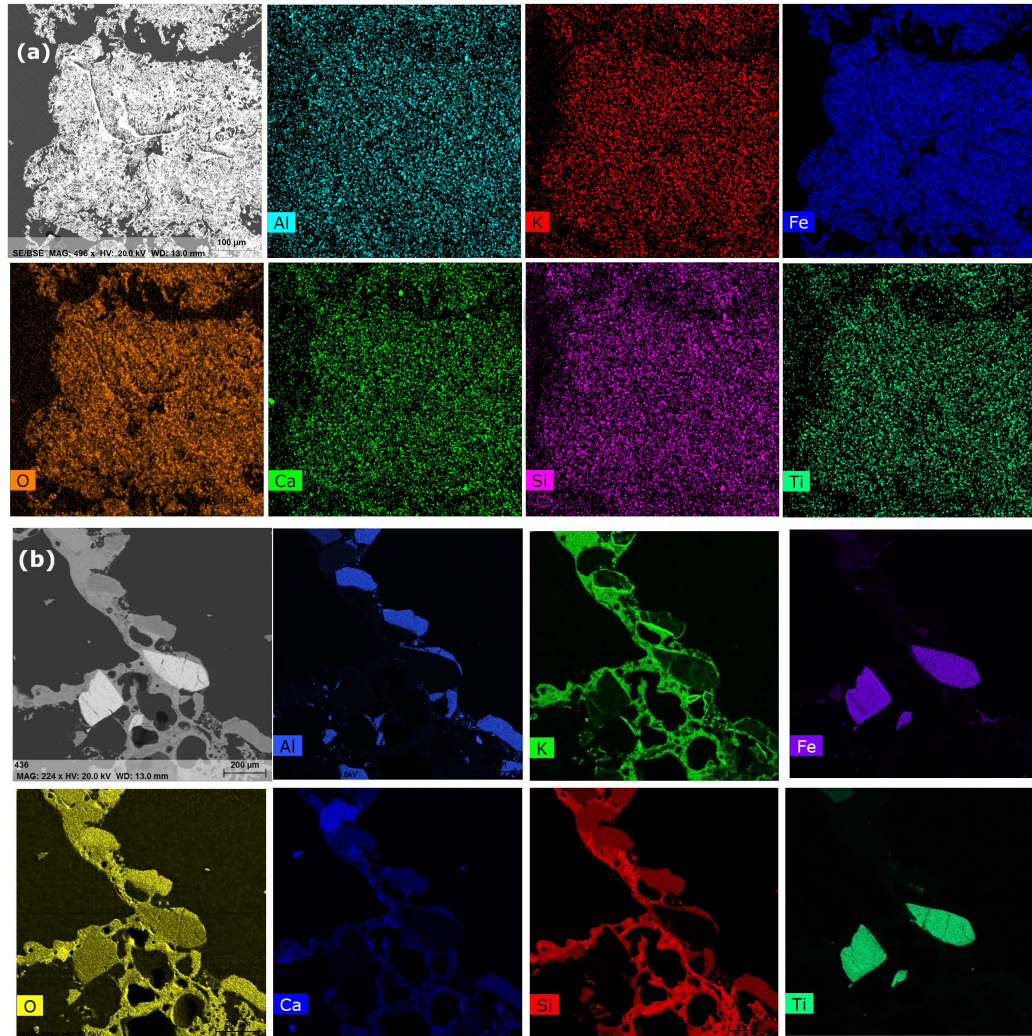


Figure 6-11: EDX elemental mapping of agglomerates samples from combustion of BC blended with STW at 40 wt% after 10 hours of operation, using (a) Garside 14/25, and (b) ilmenite as bed material.

The results from EDX mapping analysis confirm the predominantly presence of *Fe* when Garside 14/25 was used as bed material (Figure 6-11a). As for Ilmenite, *K* and *Si* are the dominant elements in the binder region, with a lesser intense presence of *Al* and *Ca* (Figure 6-11b). Because the reduced proportions of *Fe* and *Ti* in the binder compared to the ilmenite bed parti-

cles, only those areas with the highest proportion are plotted. The presence of a *Fe* and *Ti* enriched layer on ilmenite particles surface has been reported before by [Zevenhoven et al., 2018] [Thunman et al., 2013]. Nevertheless, studies with longer exposure times have reported the migration of *Fe* to the outer layer of the particles, indicating a segregation phenomenon of *Fe* from *TiO₂*, and the inward migration of *K* during biomass combustion [Corcoran et al., 2018b], this segregation can decrease the oxygen transport capacity of ilmenite [Yu et al., 2018]. For the operating time in this research, no evidence of *Fe* segregation in the bed particles was observed. The distribution of *O* across the agglomerates samples can be considered an indication of the presence of studied elements in their oxidised forms.

Ilmenite bed particles showed evidence of cracks. It has been reported as a consequence of mechanical and chemical stress, leading to attrition and fragmentation of bed materials [Knutsson and Linderholm, 2015]. Attrition has been identified as a limiting factor for the build-up of ash on ilmenite particles. It may cause the breakage of the formed layer, providing the possibility for *Fe* to migrate towards locations with high oxygen potential [Corcoran et al., 2018b] [Adanez et al., 2012]. In contrast, finer particles of bed material can act as the cores for ash coagulation leading to an increase of the agglomeration tendency [Chi et al., 2019]. Cracks in the ilmenite bed particles may ease the diffusion of elements from the fuel ash into the particles [Corcoran et al., 2018b].

Figure 6-12 shows the SEM/EDX elemental mapping of an ilmenite bed particle after 10 hours of operation to investigate the existence of cracks and the migration of elements into the particle. The results show *Ca* and *K* to be the most active ash elements to interact with ilmenite. Similar findings during combustion experiments in a CFB using wood as fuel and ilmenite as an additive were reported by [Corcoran et al., 2018b]. No interaction of the ash elements *Si* and *P* was detected. As expected significant amounts of *Fe* and *Ti* were found across the particle.

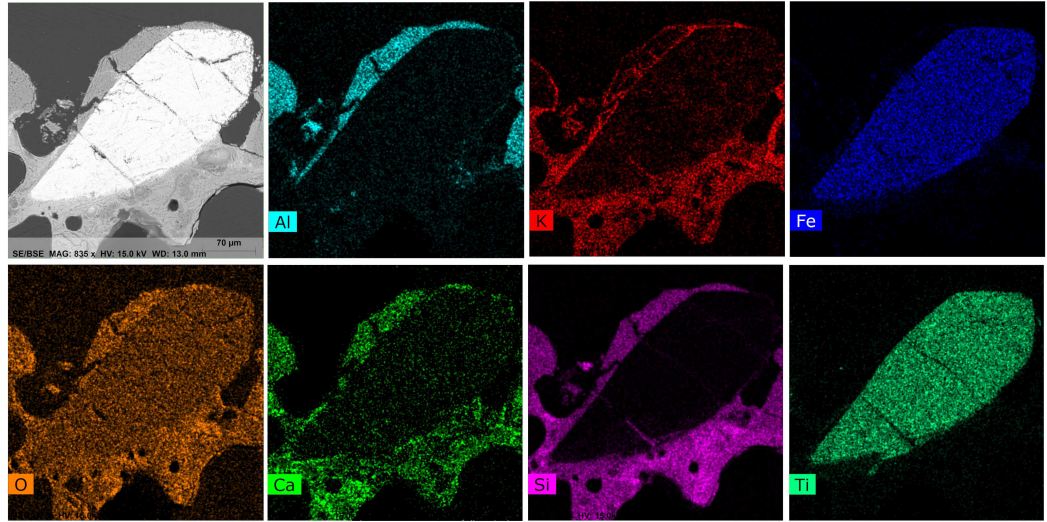


Figure 6-12: SEM/EDX elemental mapping illustration of cracks and the interaction of ash elements within the cross section of the ilmenite particle obtained from the combustion of BC blended with STW at 40 wt% after 10 hours of operation.

XRF Analysis of Cyclone Ash. To investigate the modification of cyclone ash quality when Garside 14/25 and ilmenite were used as bed material further analysis of elemental composition (XRF) was performed. For comparison purpose ash from the combustion of pure coal was included. The results showed in Figure 6-13 reveal a reduction in *K* and *Ca* content in ash when ilmenite was used in comparison to Garside 14/25. As expected higher *Fe* and *Ti* content was found in ash when ilmenite was used. The lower content of *K* in ash may suggest the potential of ilmenite to capture alkali metals in the bed to form higher melting compounds. In addition, it confirms earlier findings of *K* and *Ca* as the most active elements to interact with ilmenite. In comparison with ash from combustion of pure coal, the ash when ilmenite was used as bed material reveals reduced content of *Al*, and higher content of *K* and *Ti*. Higher *K* content in the ash can impose limitations regarding ash utilisation or increase disposal costs [Fuller et al., 2018] [Cheremisinoff, 2012].

Based on the results from this section, it can be concluded that the difference in appearance observed between the agglomerated samples is a result more

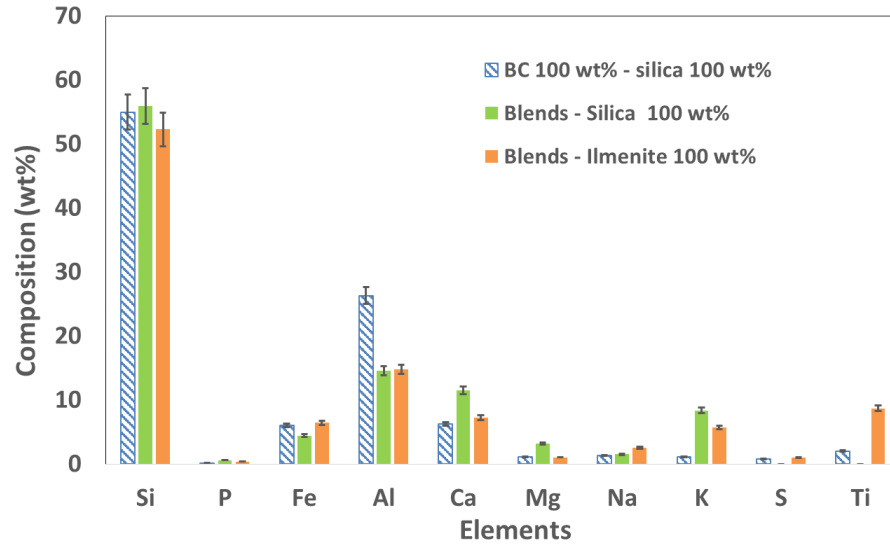


Figure 6-13: Elemental composition (XRF) of cyclone ash from combustion of BC blended with STW at 40 wt%, using Garside 14/25 and ilmenite as bed material (Bituminous coal (BC) at 100 wt% using Garside 14/25 was included for comparison purpose).

related to difference in the variation of their chemical composition. Ilmenite as bed material led to reduce the agglomerates size by forming high melting point compounds which hinder the K-rich molten substance attachment and result in heterogeneous coating layers in the agglomerates. These agglomerates appeared to be quite weak and were easily broken into smaller ones. In contrast, agglomerates from Garside 14/25 as bed material showed a dense melt phase mainly composed of *Fe* with reduced amounts of *Si*, *Al* and *K*, and closely connected structure. These results suggest that ilmenite is likely to have similar or less tendency towards agglomeration and defluidisation than silica sand.

6.3.4 Stage III - Performance of Ilmenite as Additive

The effect of ilmenite as an additive was investigated and compared to bauxite and kaolin using Garside 14/25 sand as bed material. The blend consisting of BC with STW at 40 wt% was used in all experiments. Kaolin and bauxite were used due to their acknowledged potential to decrease agglomeration tendency by capturing alkali metals [Marinkovic et al., 2016] [Splithoff, 2010]. The additives were blended at 10 wt% in all cases. No relevant

difference was found among the additives in terms of temperature profiles, CO_2 (see Figure 6-14a), and NO_x emissions (see Figure 6-14c). Therefore, the analysis of results was based on the effect of ilmenite as an additive on CO emissions, combustion performance and agglomeration tendency compared to kaolin and bauxite.

CO Emissions

Figure 6-14b shows a decrease in CO emissions when additives were used compared to the reference case. As expected ilmenite showed the lowest CO concentration. It is attributed to the enhanced reactivity of the oxygen carrier with CO , suggesting the improvement of combustion performance with ilmenite as an additive. As for kaolin and bauxite, the reduction in CO emissions is attributed to a catalytic effect due to their influence on char conversion. A positive influence of bauxite on fuel conversion has been suggested by [Marinkovic et al., 2016], during biomass gasification experiments in a dual fluidised bed system. An unexpected finding was the lower value in CO emissions when ilmenite was used as an additive compared to that from the experiments with ilmenite as bed material (see Figure 6-8b). [Hughes et al., 2017] reported similar results during coal combustion experiments using ilmenite as an additive and bed material. This behaviour was attributed to variation in the temperature profile, rate, and extent of pyrolysis and oxygen concentration.

Combustion Performance

Figure 6-14d shows the loss of efficiency due to unburnt carbon (UBC) and CO emissions for kaolin, bauxite, and ilmenite. The values obtained for Gar-side 14/25 at 100 wt% are included for comparison purpose. These results show better combustion performance due to reduced efficiency loss when bauxite and ilmenite were used. In experiments in a dual fluidised bed system, [Marinkovic et al., 2016] reported an enhanced carbon conversion and some degree of oxygen transport capacity in bauxite. Similarly, [Berdugo Vilches et al., 2016] reported higher char conversion rates in bauxite, despite its significantly lower oxygen transport capacity compared to ilmenite

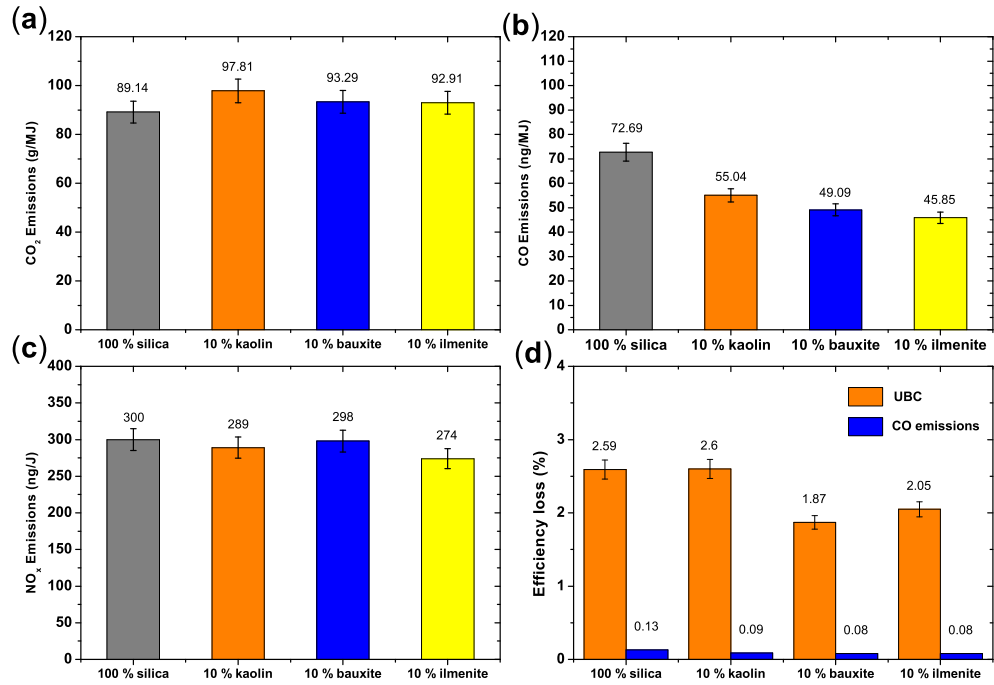
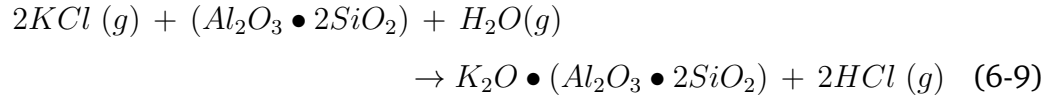
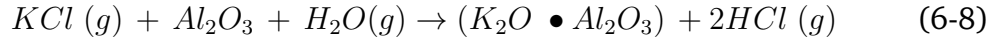
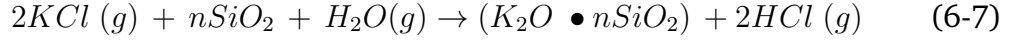


Figure 6-14: Comparison of kaolin, bauxite and ilmenite as additives at 10 wt% in terms of emissions of (a) CO_2 , (b) CO , (c) NO_x per energy input, and (d) loss of efficiency due to unburnt carbon (UBC) and CO emissions using bituminous coal (BC) blended with straw pellets (STW) at 40 wt%.

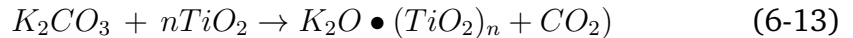
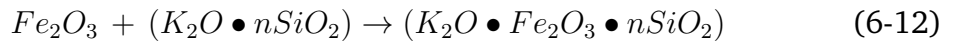
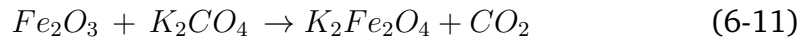
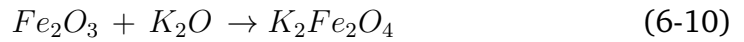
during experiments in a dual fluidised bed system. It was linked to the ability of the alkali metals to be partially released from bauxite due to be physically bound to the material. Ilmenite has been reported as effective to reduce UBC when used as an additive during coal combustion experiments in a fluidised bed by [Hughes et al., 2017], and during biomass combustion experiments in a dual fluidised bed gasification system and CFB by [Larsson et al., 2014] and [Thunman et al., 2013], respectively. It has been attributed to the high oxygen transport capacity.

Agglomeration Tendency

Naturally occurring aluminium-based materials such as kaolin and bauxite have been extensively studied as alkali-adsorbing materials in combustion systems [Marinkovic et al., 2016] [Fournel et al., 2015]. The following reactions have been reported as the most likely to occur with alkali chloride [De Fusco et al., 2016] [Spliethoff, 2010] [Boström et al., 2009]:



Among the tested aluminium-based materials, kaolin has shown better alkali-adsorbing capacity due to the irreversibility of alkalis to kaolinite, which is the dominating mineral in kaolin [Boström et al., 2009], and higher saturation levels [Marinkovic et al., 2016]. Ilmenite, as a natural occurring iron-based material is mainly composed of different kinds of iron oxides as the active phases with some impurities such as SiO_2 , Al_2O_3 , CaO , TiO_2 (see Table 3-4). Therefore, in addition to the reactions 6-7, 6-8, and 6-9 the following reactions may be the most likely to occur with alkali metals:



The results from visual inspection of the bed materials after 10 hours of operation with BC blended with STW at 40 wt% as fuel revealed the presence of small agglomerates shown in Figure 6-15.

A comparison between the agglomerates formed from the same fuel blend and similar operating conditions using the three additives, showed smaller agglomerates when the additives were used than those from 100 wt% Gar-side 14/25 bed material (see Figure 6-9a). Agglomerates from ilmenite ap-

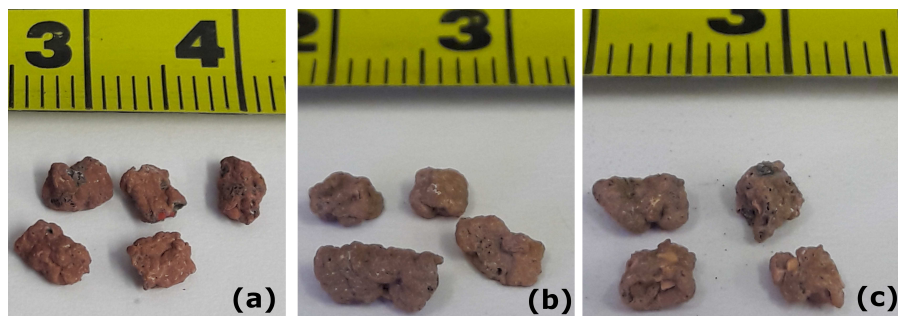


Figure 6-15: Comparison of samples of agglomerates produced from combustion of BC blended with STW at 40 wt% after 10 hours of operation using Garside 14/25 as bed material and additives at 10 wt%: (a) ilmenite, (b) bauxite, and (c) kaolin (scale in cm).

peared to be weak and were easily broken into smaller ones in a similar way to the agglomerates found when it was used as alternative bed material.

SEM-EDX Analysis of Agglomerates and Cyclone Ash. To analyse the chemical composition of the binder linking the bed particles in agglomerates, samples of few mm size (a mixture of fuel ash, silica bed, and additive) were analysed by EDX mapping technique with results presented in Figure 6-16. The distribution of *Si*, *K*, *Ca*, *Al*, *Fe*, *Ti* and *O* across the surface of the agglomerated bed samples was identified as presented. The SEM micrographs are included at the top left hand side of the image. The intensity of the colour across a particular area indicates a higher content of the element in that region.

The results from EDX mapping analysis show the predominantly presence of *K* and *Si* in the binder region for all the additives. It can be an indication of the presence of fused K-silicates. Nevertheless, an intense presence of *Ca* and *Al* to a lesser extent was observed. These results indicate that *Ca* and other refractory elements such as *Al* and *Mg* may exist as K-Al-Silicates, K-Ca/Mg silicates, and K-Ca-Silicates with higher melting temperatures than K-silicates in the binder.

XRF Analysis of Agglomerates and Cyclone Ash. Further elemental composition (XRF) analysis of the cyclone ash and agglomerates are presented in Figure 6-17. The agglomerates appear to have a similar composition for all

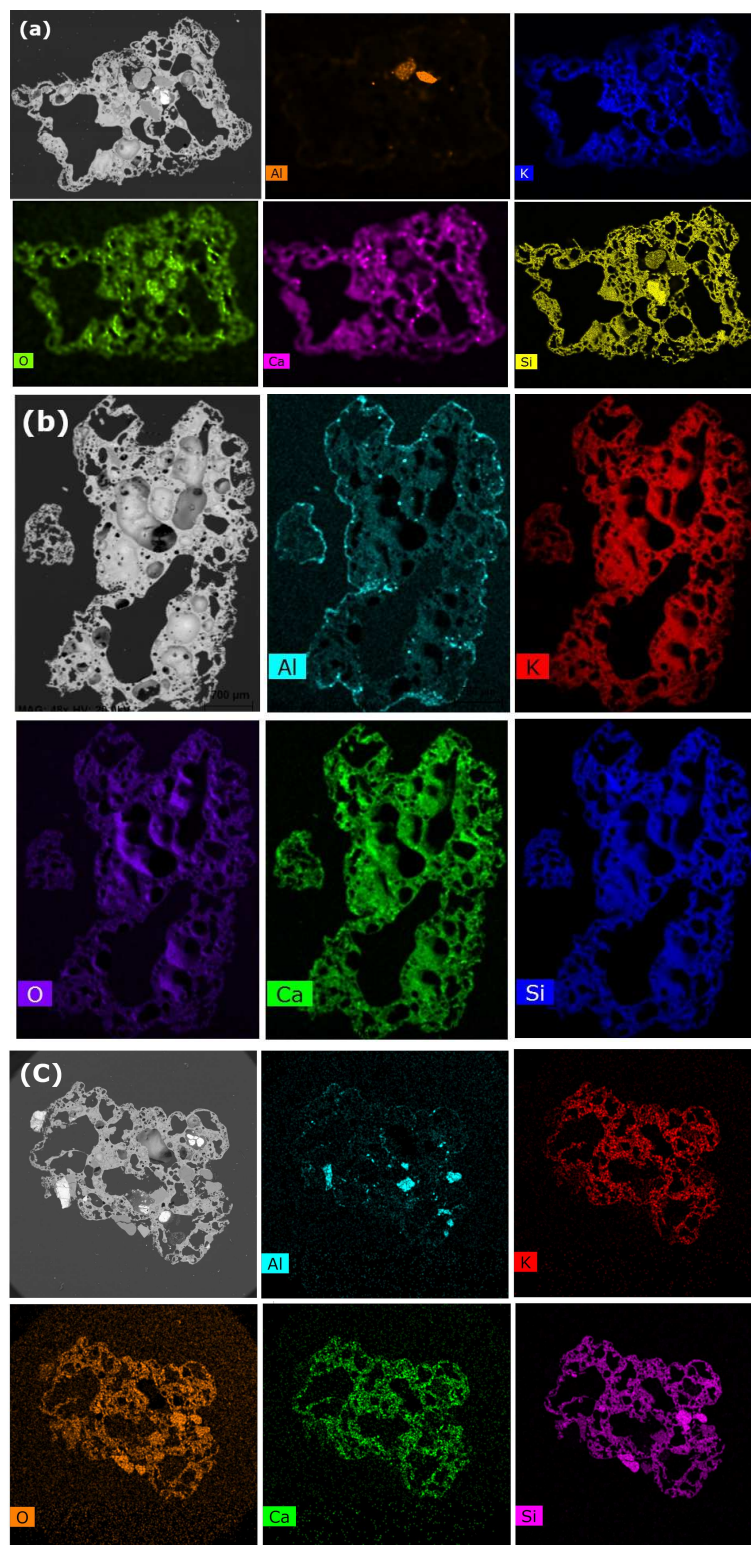


Figure 6-16: EDX elemental mapping of agglomerates samples from combustion of BC blended with STW at 40 wt% after 10 hours of operation, using Garside 14/25 as bed material and additives at 10 wt%: kaolin (a), bauxite (b), and ilmenite (c).

the additives with predominantly content of *Si*, *Ca*, *K* and reduced content of *Al* and *Mg*. Agglomerates when ilmenite was used, showed to have a slightly higher content of *Fe* and *Ti* (see Figure 6-17a). These results offer additional evidence to confirm the findings from the EDX mapping analysis, suggesting the existence of K-silicates, K-Ca-silicates, K-Al-silicates and to a lesser extent the existence of K-Mg-silicates, and K-Ca/Mg silicates. As for the cyclone ash (see Figure 6-17b), *Si*, *Al*, *K* and reduced content of *Ca* and *Fe* was detected. In this case, the predominantly compounds appear to be K-Al-silicates and K-Ca-silicates. These results suggest that ilmenite as an additive is likely to have similar potential to capture alkali metals in higher temperatures structures, reducing the risk of agglomeration and defluidisation than kaolin and bauxite for the operating conditions in this research.

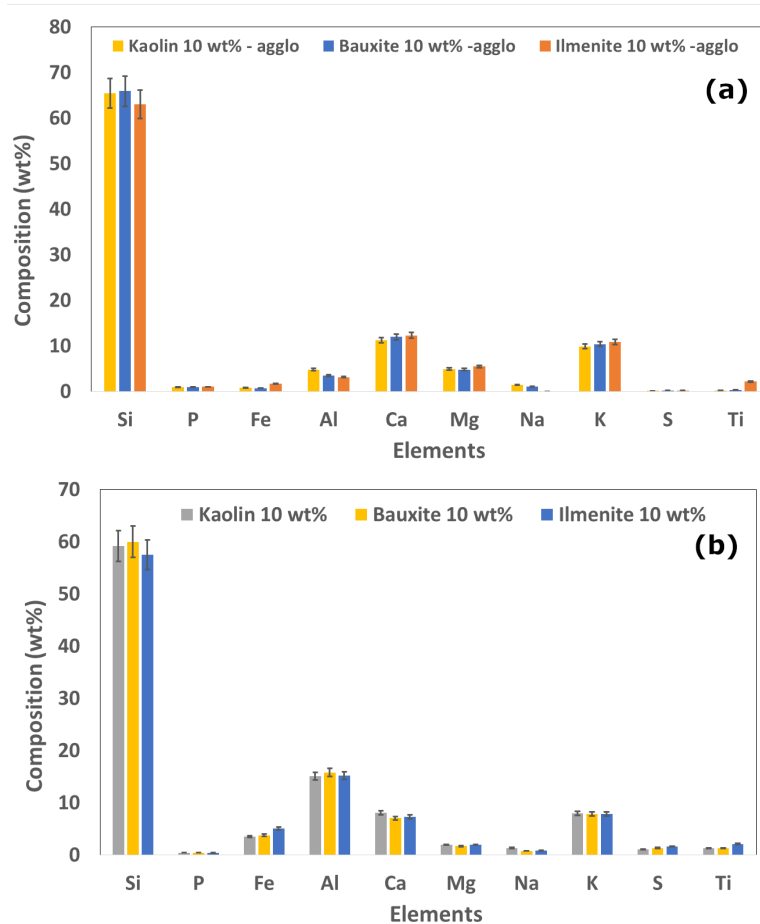


Figure 6-17: Elemental composition (XRF) of (a) agglomerates and (b) cyclone ash from combustion of BC blended with STW at 40 wt% after 10 hours of operation, using Garside 14/25 as bed material and additives at 10 wt%.

6.4 Summary

The results of co-combustion experiments in a pilot-scale BFB combustor to investigate the potential of spent coffee ground (SCG) as a fuel, and ilmenite as an additive and alternative bed material were presented and discussed. Biomass combustion was found to be different from coal combustion due to the difference in physical and chemical properties. The differences are clearly shown in the temperature profiles, gas emissions, and combustion performance. The results using silica sand as bed material showed that coal and SCG blends can be combusted for energy applications with improved combustion efficiency compared to blends of coal with wheat straw or wood commercial pellets. Nevertheless, high N content in SCG represents a challenge in terms of NO_x emissions that should be addressed.

Further experiments investigated the effect of ilmenite as an additive and alternative bed material. The results showed improved combustion performance due to reduced values of unburnt carbon in ash and CO emissions when ilmenite was used in comparison with the reference case. It was attributed to the improved oxygen transport capacity of ilmenite. Nevertheless, higher NO_x emissions in comparison with the reference case were observed when ilmenite was used as alternative bed material.

Furthermore, ilmenite showed to have similar potential to reduce the risk of agglomeration when used as an additive and alternative bed material in comparison with kaolin and bauxite, and silica sand, respectively. SEM/EDX and XRF analysis of agglomerates and ash showed the predominantly presence of K and Si in the binder region in all cases, with other refractory elements (i.e. Ca , Al , Mg , Fe , and Ti) to a lesser extent. It could be considered an indication of the existence in the binder of K-Ca-silicates, K-Al-silicates, K-Mg-silicates, K-Ca/Mg silicates, and Fe- Ti-bearing compounds with higher melting temperatures.

Chapter 7

Conclusions and Future Work

7.1 Introduction

This study set out to investigate the combustion behaviour of coal and biomass blends using a pilot-scale bubbling fluidised bed reactor. The analysis of results was based on the most representative flue gas emissions, combustion performance, and fuel ash behaviour. Additionally, the effect of biomass ratio in the blend in terms of reactivity and ash behaviour have also been investigated by thermogravimetric (TGA) and ash fusibility temperatures (AFT) studies. Research activities focused on the study of by-products from coffee crops as fuel and ilmenite as an additive and alternative bed material for fluidised bed combustion. The following sections describe the conclusions that can be drawn from this study and provide insights for future research.

7.2 Conclusions

The results of this study support the idea that co-combustion of coal and biomass is a feasible alternative in the short-term to decrease the environmental effect of coal combustion. Conclusions from the literature review indicate that despite the broad existing knowledge about solid fuels combustion, there are still unsolved challenges about the processing of solid fuels in pure or in co-combustion schemes. Biomass fuels have shown to be effective to enhance the reactivity of coal under co-processing conditions with additional benefits in terms of emissions reduction. Nevertheless, ash related

issues have hindered the increase of the biomass ratio in the blends. Moreover, concerns about the use of woody biomass in terms of intensive use of resources and land have prompted the interest in other kinds of resources such as herbaceous biomass.

Fluidised bed combustion is an efficient technology that allows processing of a broad range of fuels with different characteristics. The use of biomass in pure or in co-processing with coal in fluidised beds raises concerns about ash related issues due to the content of alkali and alkaline earth metals. This is one of the main challenges facing fluidised bed combustion due to the risk of ash sintering and agglomeration. Although additives and alternative bed materials have shown to be an effective measure for reducing the agglomeration tendency, there is no agreement about the most effective material. Furthermore, the use of a specific additive or alternative bed material to decrease the agglomeration tendency may have negative effects on other aspects resulting in additional issues. This indicates a need to gain a better understanding of the interactions between either additives or alternative bed materials with troublesome ash elements.

The results presented in this thesis cover three major sections: (1) thermogravimetric (TGA) studies of coal blended with by-products from coffee crop under inert and oxidising conditions, (2) ash fusibility temperatures (AFT) studies of ash blends of coal with wheat straw and spent coffee grounds, and (3) fluidised bed combustion experiments of blends using coal with three different biomass fuels in a fluidised bed reactor. The following sections describe the findings from the studies carried out in this research.

7.2.1 Thermogravimetric Studies

The thermal decomposition of blends of coal with by-products of coffee crop (spent coffee ground (SCG) and coffee husk (CH)) was investigated upon inert and oxidising atmospheres to evaluate their potential for energetic applications. Comparison of the results shows that although both by-products from coffee crop have the potential to improve the combustion performance

of coal, spent coffee grounds is the most interesting. SCG showed the lowest initial devolatilisation temperature. It is attributed to the higher heating value and reactivity due to high hemicellulose content and synergistic effects, leading to lower devolatilisation and ignition temperatures along with improved combustion performance. The thermal behaviour characteristics of the blends showed no linear correlation to the biomass ratio. These results provide evidence of similar or better devolatilisation and combustion indices than those obtain when wood from commercial pellets are used. It makes several noteworthy contributions to the conversion of this abundant biomass resource into energy. In fact, these findings may be useful for the configuration and the designing of processing equipment at larger scales.

7.2.2 Ash Fusibility Studies

Coal ash blended with ash from spent coffee grounds (SCG) and wheat straw (STW) was tested in an ash fusibility furnace. The effect of ash blending ratio was systematically investigated. As expected biomass ash showed lower fusibility temperatures compared to the coal ash. Ash from the biomass fuels showed differences in chemical composition and was found to be different from coal ash. Interestingly, despite the higher K_2O content in SCG ash, it showed higher ash fusibility temperatures than STW ash, with similar values to those from coal ash. This trend led to different ash fusibility temperatures between the blends at the same blending ratio. In contrast to STW ash, SCG ash showed to increase the fusibility temperatures of the ash blends at high blending ratios. Moreover, the vector-based image processing application developed in this study clearly has an advantage over the by-default method in terms of the tracking of changes in the samples. These results provide evidence of SCG potential to be a good quality fuel for co-combustion due to the reduced ash content. Furthermore, SCG ash showed significant amounts of CaO , MgO , and P_2O_5 ; and negligible content of SiO_2 and Cl , which favours the formation of high melting temperatures compounds. These findings might help to understand the behaviour of ash blends under oxidising conditions providing relevant information for the design and optimisation of thermochemical conversion systems at larger scales.

7.2.3 Fluidised Bed Combustion Experiments

The results of co-combustion experiments in a pilot-scale BFB combustor to investigate the potential of spent coffee grounds (SCG) as a fuel, and ilmenite as an additive and alternative bed material were presented and discussed. Biomass combustion was found to be different from coal combustion due to the difference in physical and chemical properties. The differences were clearly shown in the temperature profiles, flue gas emissions, combustion performance, and agglomeration tendency.

SCG showed to be a promising biomass fuel due to the satisfactory characteristics of the in-house manufactured pellets, relatively high heating value, and reduced ash content. Furthermore, the experimental results showed that blends of coal and SCG pellets could be combusted for energy applications with improved combustion efficiency compared to blends of coal with wheat straw or wood commercial pellets. Although blends with SCG showed higher NO_x emissions compared to other biomass fuels, no increase was found when compared to pure coal. Moreover, this study demonstrated that despite the significant amount of K in SCG ash, extended operation time could be achieved in fluidised beds with reduced agglomeration tendency when using blends of coal and SCG pellets at higher operating temperature than the used in most commercial applications. The substantial content of refractory elements such as Ca and Mg in SCG ash compensates to a certain point its high alkali metals content (K). It has helped in quick formation of high melting compounds leading to a reduced agglomeration tendency.

Experiments using coal blended with wheat straw pellets at 40 wt% were performed to investigate ilmenite performance as an additive and alternative bed material. Kaolin and bauxite, and silica sand were used as additives and bed material for comparison purpose, respectively. The experimental results showed that ilmenite led to lower CO emissions and reduced efficiency loss either as an additive or alternative bed material compared to the other additives and silica sand. Furthermore, the results of this study indicated that ilmenite could decrease the need for excess air to achieve complete com-

bustion. In addition, this study demonstrated the potential of ilmenite to reduce the agglomeration tendency in fluidised beds. Much smaller and easy to break agglomerates were found compared to those from the combustion of the blend using silica sand as bed material. Further analysis showed substantial differences in the structure and composition of the agglomerates and cyclone ash from the experiments when ilmenite was used compared to the other materials tested. These results suggest that ilmenite is likely to have equal or less tendency towards agglomeration and defluidisation than silica sand as bed material or kaolin and bauxite as an additive, with potential to capture alkali metals in higher melting temperatures structures. Nevertheless, high NO_x emissions and high attrition rates of ilmenite particles need to be addressed.

7.3 Future Work

The results of the co-combustion of coal and biomass blends included in this thesis have shown that it is certainly feasible to use spent coffee grounds as a fuel, and ilmenite as an additive or alternative bed material in a pilot-scale bubbling fluidised bed. Taking into account the findings, discussion and conclusions of this research the following are some recommendations that can be used as a guideline to future research work.

- Future research might be undertaken to perform thermogravimetric analysis of by-products from the coffee crop. A natural progression of this work is to study blends with different ranks of coal at higher blending ratios and other biomass fuels. It might include a kinetic assessment of devolatilisation, and oxidation, which would help to understand the changes in activation energy and reactivity of the blends.
- A future study investigating the kinetic and physical characterisation (e.g. surface area and porosities) of char from by-products of coffee crop produced during devolatilisation would be interesting. It will allow to gain a better understanding of the effect of varying parameters, and could help to understand the processes during char burnout.

- More research is needed to assess the manufacture of pellets of spent coffee grounds in pure or blended with other biomass fuels. More work will need to be done to determine factors affecting their mechanical durability, thermal characteristics, and their potential to meet environmental regulations. Further research might explore the feasibility of pre-treatments such as torrefaction to improve energy density.
- Further research regarding long-term combustion operation of spent coffee grounds pellets in pure or blended with other fuels in fluidised beds would be interesting. It might investigate the effect of varying operating parameters including blending ratio, combustion conditions, and bed materials. Future work is thus needed to achieve a deeper and more comprehensive understanding of spent coffee grounds potential to be a biomass fuel.
- More research is needed to study the long-term operation of ilmenite as an additive and alternative bed material. It could consist of combustion studies of fuels in pure or in blends to investigate effects of parameters such as excess air, and air staging on its potential to enhance the combustion performance, and decrease harmful emissions.
- Future research may use ilmenite as an additive at higher proportions to investigate the effect on combustion performance, harmful emission, and agglomeration tendency under varying operational conditions.
- Further experimental investigations are needed to assess the ash quality and its potential use when ilmenite is used in fluidised bed combustion.

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Appendix A

Ultimate and Proximate Analysis of Fuels as received

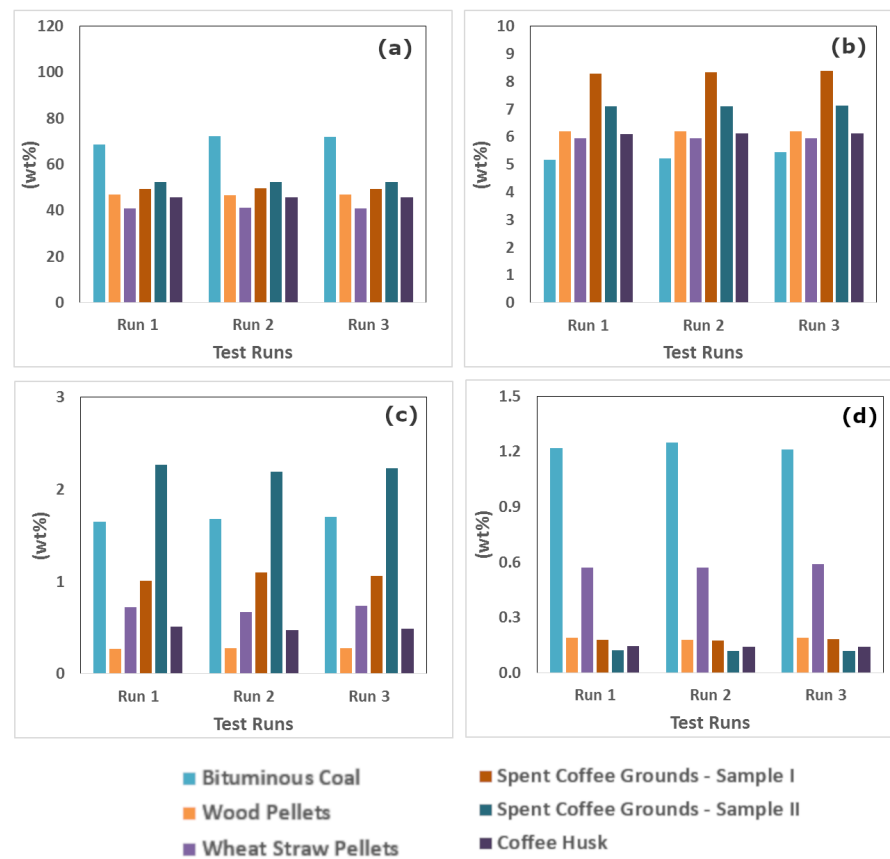


Figure A-1: Experimental runs of ultimate analysis for fuels tested; (a) carbon content, (b) hydrogen content, (c) nitrogen content, and (d) sulphur content.

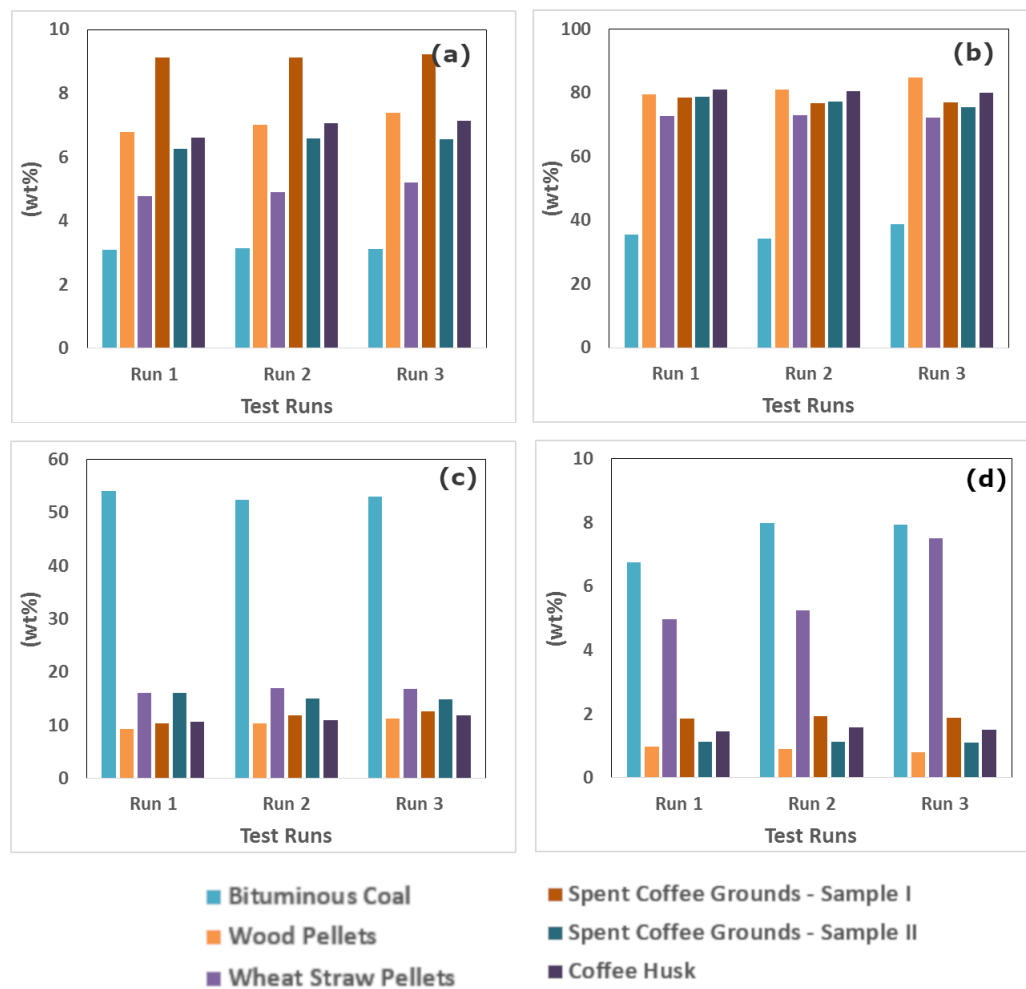


Figure A-2: Experimental runs of proximate analysis for fuels tested; (a) moisture content, (b) volatile matter content, (c) fixed carbon content, and (d) ash content.

Appendix B

Fuel Feeding Calibrations

Preliminary experiments conducting to calibrate de fuel feeding system according to the biomass resource blended with coal were performed. This process consisted of previous preparations of the blends to be used in the FBC experiments and corresponding pouring in the hopper. Then, the blends were fed into the reactor by the setting a program of different speeds of the feeder screw. Conveyed fuel blends were collected and weighed every 2 minutes over a fixed period of 30 minutes. The results obtained are presented in Figures **B-1**, **B-2**, **B-3**, **B-4**, and **B-5**.

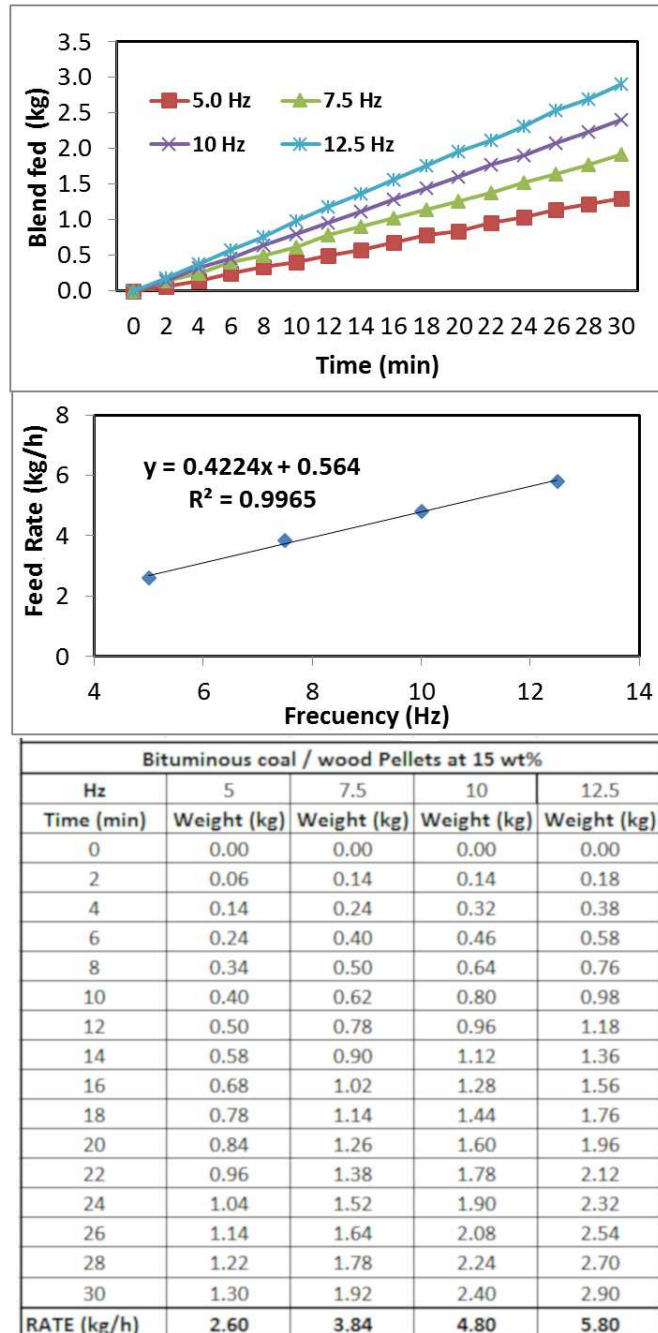


Figure B-1: Fuel feeding calibration, bituminous coal blended with wood pellets at 15 wt%.

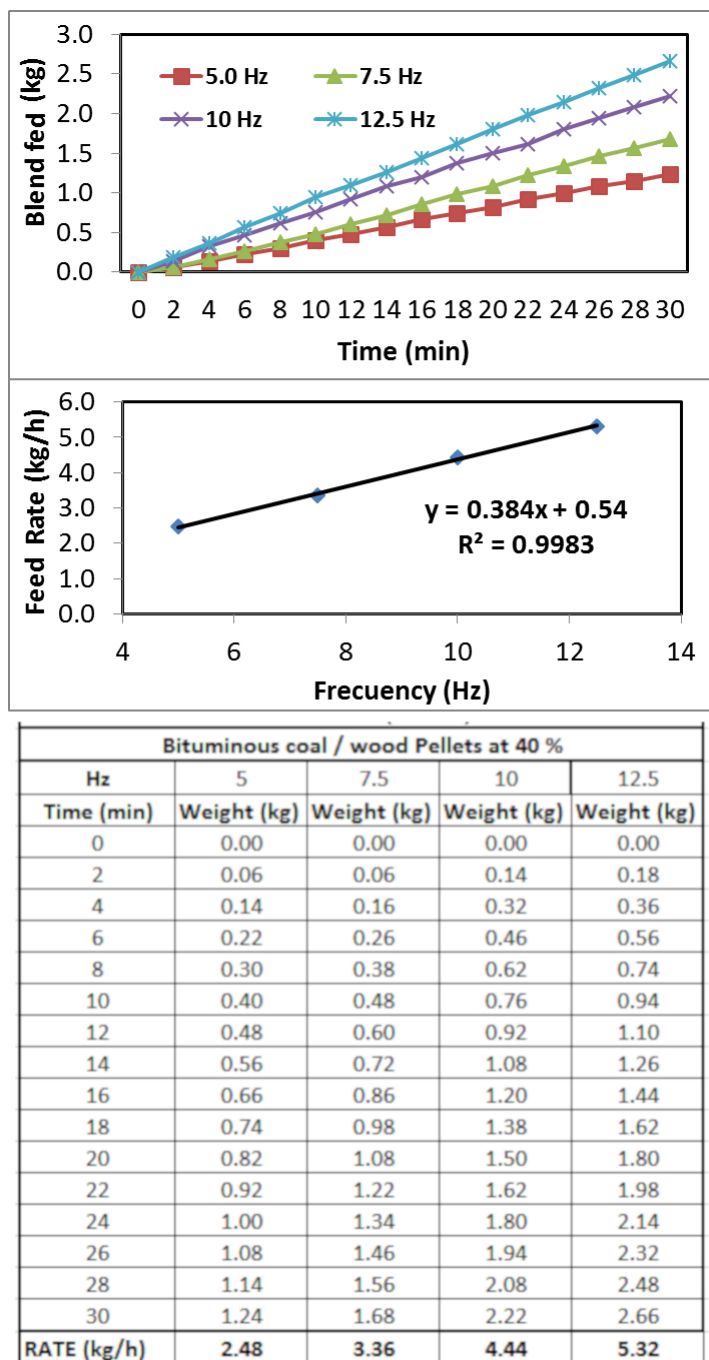


Figure B-2: Fuel feeding calibration, bituminous coal blended with wood pellets at 40 wt%.

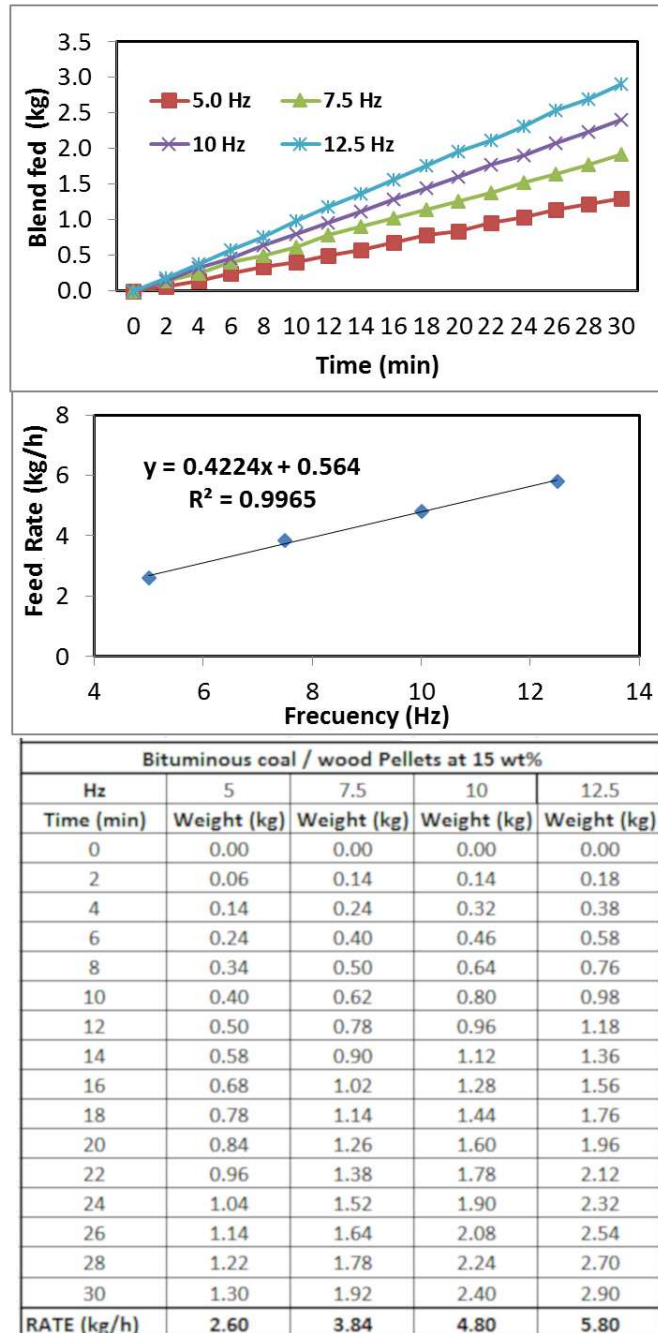


Figure B-3: Fuel feeding calibration, bituminous coal blended with wheat straw pellets at 15 wt%.

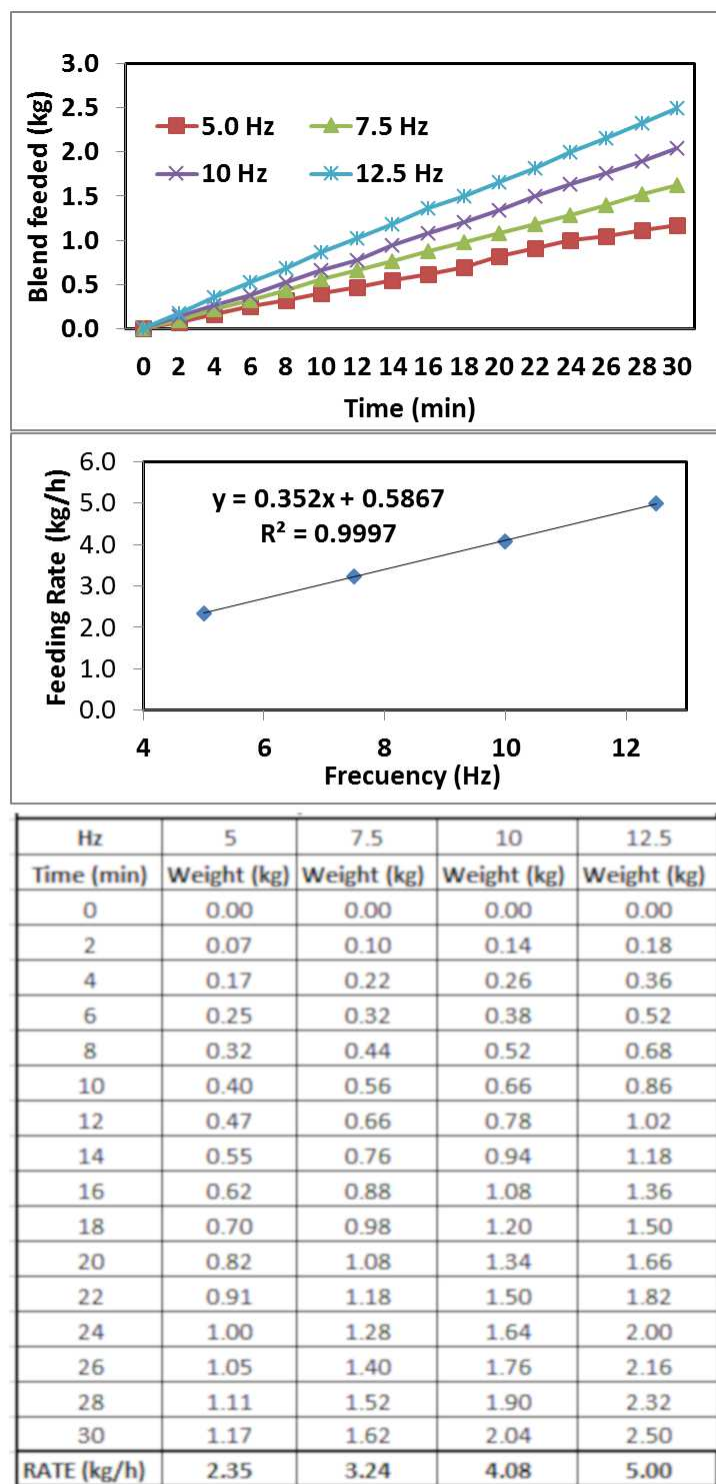


Figure B-4: Fuel feeding calibration, bituminous coal blended with wheat straw pellets at 40 wt%.

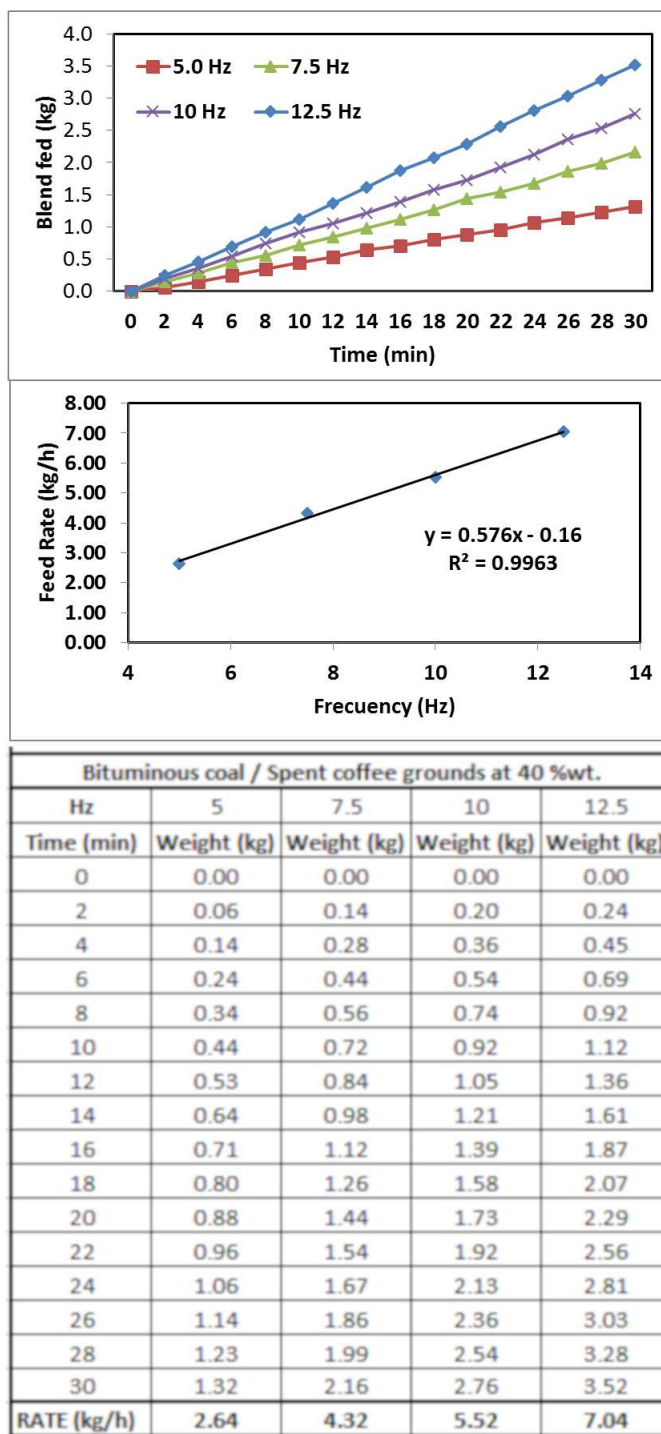


Figure B-5: Fuel feeding calibration, bituminous coal blended with spent coffee grounds pellets at 40 wt%.

Appendix C

Sieving Analysis for Garside 14/25 Sand and Ilmenite

Table C-1: Particles size distribution of garside 14/25 and ilmenite as received

	As received			
	Garside 14/25		Ilmenite	
				
Particle size (mm)	Weight (g)	Grading (%)	Weight (g)	Grading (%)
1.18	115.90	3.80	0.00	0.00
1.00	384.30	12.60	41.13	1.37
0.85	1550.93	50.85	389.95	13.00
0.60	872.00	28.59	1857.51	61.93
0.30	84.49	2.77	607.14	20.24
0.21	30.81	1.01	51.39	1.71
0.15	9.15	0.30	30.18	1.00
0.00	2.44	0.08	22.23	0.74

Appendix D

Calculations

Excess air ratio

The value of excess air ratio is calculated from measurement of oxygen concentration in the flue gas.

$$Excess\ air = \left(\left(\frac{20.9}{20.9 - O_{2meas}} \right) - 1 \right) 100 \quad (D-1)$$

Where O_{2meas} is the measured oxygen (%vol).

Emissions Conversion Factor

$$X_{ref} = X_{meas} \frac{20.9 - O_{2ref}}{20.9 - O_{2meas}} \quad (D-2)$$

Where X_{ref} is the referenced concentration, X_{meas} corresponds to measured concentration, O_{2ref} is the reference O concentration (10 %), O_{2meas} is the measured oxygen (%vol), and 20.9 is the percentage of O_2 in the air.

Energy-based Emissions Conversion Factor

$$EF(g/MJ) = \frac{Q}{22.4} \frac{X}{\dot{m}} \frac{M}{HHV} \frac{60}{1} \quad (D-3)$$

Where Q is the volumetric air flow rate (l/min), X corresponds to measured concentration (CO_2 , CO , or NO_x) (%vol), M corresponds to the molecular weight of the chemical species ($CO_2 = 44$ g/mol, $CO = 28$ g/mol, or $NO_x = 46$ g/mol), molar volume is 22.4 l/mol at standard temperature and pressure (STP) (taken as 0 °C and 1 atm), $\dot{m}$ is the fuel feeding rate (kg/h), and HHV is the high heating value of the fuel (MJ/kg).

Appendix E

Classification of Fluidised Particles

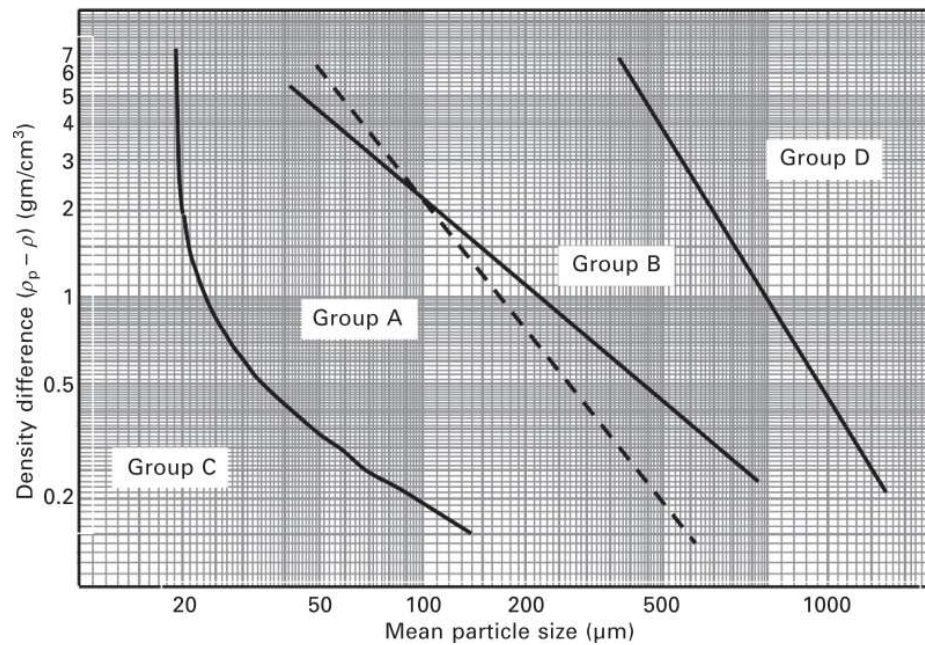


Figure E-1: Geldart classification of particles for air at ambient conditions [Scala, 2013]

Appendix F

Flue Gas Sampling Arrangement

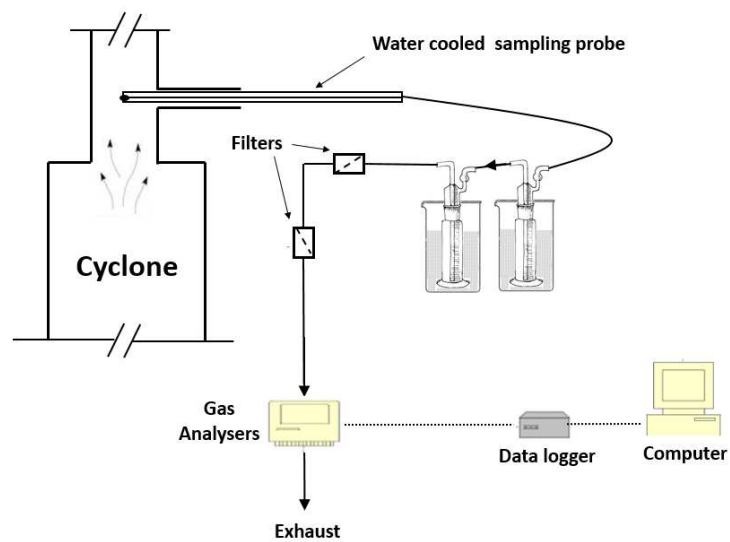


Figure F-1: Schematic Diagram of Gas Sampling Arrangement