

# The influence of biomass additions on the pyrolysis behaviour of an inertinite rich South African coal

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*"I venture to define science as a series of interconnected concepts and conceptual schemes arising from experiment and observation and fruitful of further experiments and observations. The test of a scientific theory is, I suggest, its fruitfulness."*

**By James Bryant Conant (1893-1978)**

## Declaration

I, Thabo Zacharia Sehume, hereby declare that the dissertation entitled:

**“The influence of biomass additions on the pyrolysis behaviour of an inertinite rich South African coal”**, is submitted to the North-West University. It is my own original revision and has not been submitted to any higher educational institutional for a degree.

Signed at Potchefstroom

.....

T.Z. Sehume

.....

Date

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## Abstract

The influences of selected biomasses (hardwood chips, softwood chips, pinewood chips and sugarcane bagasse) on the degradation of an inertinite-rich South African coal were studied. The pyrolysis process is important since it is a precursor for most thermal processes (such as combustion). The coal and the four types of biomass were pulverised to a particle size of less than 75  $\mu\text{m}$ . A thermogravimetric analyser coupled to a quadrupole mass spectrometer (TG-MS) was used to investigate the devolatilisation behaviour of the coal, biomass and their blends (0, 20, 40, 60, 80 and 100% wt./wt.) in a temperatures range of ambient temperature to 1100  $^{\circ}\text{C}$ . The biomasses consist of ligno-cellulosic components, which contain 27.8-39.9 wt. % cellulose, 17.4-21.1 wt. % hemi-cellulose and 8.0-32.4 wt. % lignin, which were in the range of reported values in literature. The TGA results indicated that biomass samples reacted at lower temperatures compared to coal, as cellulose and lignin decomposed between 152-660  $^{\circ}\text{C}$  and 113-900  $^{\circ}\text{C}$  respectively.

Chars were characterised using different analytical methods (for instance proximate and mineral analyses). The sugarcane bagasse and blend of sugarcane bagasse in coal samples indicated a significant large content of ash in comparison to other samples. This may be attributed to the particle size selection of  $<75\ \mu\text{m}$  and environmental or harvesting conditions used to maintain or harvest the crops. The results obtained from XRF indicated significant contents of silica ( $\text{SiO}_2$ ) and aluminium ( $\text{Al}_2\text{O}_3$ ) for the parent and blended chars, where these oxides confirm the presence of the clay minerals. From the XRD carbon crystallite results, it was observed that at higher temperatures the chars undergo structural ordering. The carbon aromaticity of the chars increased from biomasses (pinewood chips had the lowest aromaticity value) to coal, and the blended chars showed carbon aromaticity values in between that of the parent materials. As expected, these results showed biomasses to have a larger reactivity than coal alone, which can be attributed to the biomasses low thermal resistance and higher surface areas.

The parent and blended samples from wood origin have reacted at lower temperatures than these from herbaceous origin. This behaviour can be attributed to the composition of the biomass as well as the biomass' ash composition. The possible synergistic or inhibiting effects that may arise during the pyrolysis process were investigated by comparing the calculated weighted averages of the mass loss data with the experimentally determined results. The calculated weighted blend thermal behaviour (mass loss curves) of the 20, 40,

60 and 80% wt./wt. coal-biomass blends indicated that the pyrolysis behaviour of the biomass is not influenced to any meaningful extent by the presence of the coal and vice versa, as a maximum average deviation of only 2.8% is observed. These results may be attributed to the experimental conditions (i.e. low heating and high flow rates) applied. The MS results indicated the release of the main gases (compounds containing the ions of  $\text{H}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2^+$ ) during the pyrolysis process. The hydrogen evolution of all the samples was mainly above 650 °C, which was in the last stage of the pyrolysis process. The second  $\text{CO}_2$  MS peaks (due to the degradation of the coal) and the DTG results were compared to evaluate the influence of the biomass on the coal reactivity with respect to  $\text{CO}_2$  evolution. The results indicated a small increase in the coal's reactivity due to the presence of the biomass samples. The largest decrease in the temperature at maximum rate of  $\text{CO}_2$  evolution was observed for the pinewood chip-coal sample (-43 °C), followed by hardwood chip-coal (-36 °C), softwood chip-coal (-31 °C) and sugarcane bagasse-coal blends (-32 °C). The decrease in temperature at maximum rate of  $\text{CO}_2$  evolution (thus the specific reaction steps involving  $\text{CO}_2$ ) seems to be due to a catalytic effect of inorganic compounds in the biomass samples and/or secondary reactions between biomass thermal products and the coal at higher temperatures.

**Keywords:** inertinite-rich coal, biomass, pyrolysis, TG-MS, synergistic effects and mineral matter

## Opsomming

Die invloed van verskeie biomassa (hardehoutspaander, sagtehoutspaander, dennehoutspaander en suikerriet bagas) op die degradasie van inertiniet-ryke Suid Afrikaanse steenkool was bestudeer. Die pirolise proses is belangrik omdat dit die voorafgaande reaksie vir meeste van die termiese prosesse soos verbranding is. Beide die steenkool en biomassa monsters is fyngehaal tot kleiner as 75  $\mu\text{m}$ . 'n Termogravimetriese analiseerder, gekoppel aan 'n kwadropool massaspektrometer (TG-MS), is gebruik om die tendens waar vlugtige stowwe verwyder word vanuit steenkool, biomassa en hul mengsels (0, 20, 40, 60, 80, 100 %) te ondersoek in 'n temperatuurgebied van om 1100 °C. Die biomassa bestaan uit lignien bevattende sellulose wat 27.8-39.9 massa % sellulose, 17.4-21.1 massa % hemi-sellulose en 8.0-32.4 massa % lignien bevat wat ooreenstem met literatuurwaardes. Die TGA resultate het aangetoon dat die biomassa monsters by 'n laer temperatuur gereageer het in vergelyking met steenkool, omdat sellulose en lignien tussen 152-660 °C en 113-900 °C onderskeidelik ontbind.

Verskeie analitiese metodes is gebruik om die kooks te karakteriseer, soos bv. proksimale en mineraal analyses. Die suikerriet bagas en mengsels van die suikerriet bagas in steenkoolmonsters het die grootste as inhoud getoon in vergelyking met die ander monsters. Hierdie verskynsel kan voorkom as gevolg van die klein partikel grootte van <75  $\mu\text{m}$  of as gevolg van die toestand waarmee die oes ingesamel is. Die resultate verkry vanaf XSF analise het aansienlike silika ( $\text{SiO}_2$ ) en aluminium ( $\text{Al}_2\text{O}_3$ ) inhoude vir die oorspronklike sowel as die gemengde kooks getoon wat 'n bevestiging is vir die teenwoordigheid van klei minerale. Vanaf die XSD koolstof kristalliet resultate kon waargeneem word dat kooks strukturele ordening ondergaan by hoër temperature. Die koolstof aromatisiteit van die kooks neem toe vanaf biomassa (dennehoutspaander bevat die laagste aromatisiteit) na steenkool, terwyl die gemengde kooksmonsters se koolstof aromatisiteit waardes tussen dié van die stammateriale val. Soos verwag wys hierdie resultate dat biomassa hoër reaktiwiteit toon as steenkool alleen en dit kan die gevolg van lae termiese weerstand en groter oppervlak areas van biomassa wees.

Die stammonsters sowel as gemengde monsters vanaf hutoorsprong het by laer temperature gereageer as die monsters afkomstig van kruidagtige oorsprong. Hierdie tendens kan die gevolg wees van die biomassa se samestelling asook die asinhoud. Die moontlike sinergistiese of inhiberende effek wat kan voorkom tydens pirolise is ondersoek deur die berekende geweegde gemiddelde van die massaverlies data met die eksperimenteel bepaalde resultate te vergelyk. Die berekende geweegde mengsel se termiese gedrag (massaverlies kurwe) van die 20, 40, 60 en 80 % massa/massa. steenkool-

biomassa mengsel het aangedui dat die pirolise gedrag van biomassa tot geen betekenisvolle mate beïnvloed word deur die steenkool se teenwoordigheid nie en ook andersom, omrede 'n maksimum gemiddelde afwyking van slegs 2.8% waargeneem is. Hierdie resultate kan toegereken word aan die eksperimentele kondisies soos lae verhittings- en hoë vloeitempo's. Die MS resultate toon die vrystelling van die hoofgasse (komponente wat ione van  $H_2^+$ ,  $CH_3^+$ ,  $H_2O$  en  $CO_2^+$  bevat) gedurende die pirolise proses. Die waterstof ontwikkeling van al die monsters was hoofsaaklik bo 650 °C, hierdie gasontwikkeling vind plaas gedurende die laaste stadium van die pirolise proses. Die tweede  $CO_2$  MS piek, wat die gevolg van steenkool degradasie is, en die DTG resultate is vergelyk om die invloed van biomassa op die steenkool se reaktiwiteit in terme van  $CO_2$  vorming te evalueer. Die resultate het 'n klein toename in die steenkool se reaktiwiteit getoon as gevolg van die biomassa se teenwoordigheid. Die grootste afname in temperatuur by die maksimum tempo van  $CO_2$  ontwikkeling is waargeneem vir die dennehoutspaander-steenkool mengsel (-43 °C), gevolg deur hardehoutspaander-steenkool (-36 °C), sagtehoutspaander-steenkool (-31 °C) en suikerriet bagas-steenkool mengsels (-32 °C). Die afname in temperatuur by die maksimum tempo van  $CO_2$  ontwikkeling (dus die spesifieke reaksiestappe wat  $CO_2$  vorm) is skynbaar as gevolg van die katalitiese effek van anorganiese komponente in die biomassa monsters en/of die sekondêre reaksies tussen biomassa termiese produkte en die steenkool by hoër temperature.

**Sleutelwoorde:** inertiniet-ryke steenkool, biomassa, pirolise, TG-MS, sinergistiese effek en minerale.

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## Chapter 1

### Problem Statement and Hypothesis

An in-depth understanding of the pyrolysis process where coal and biomass are converted into more valuable products is required. An investigation will be conducted to study the influence of biomass addition to coal under thermal degradation (devolatilisation) process conditions, as well as to identify some of the product gases evolved. This chapter contains a problem statement, hypothesis, aims, and objectives for the purpose of the dissertation.

#### 1.1 Problem Statement and Substantiation

Coal utilisation has led to rising concerns about CO<sub>2</sub> emissions causing global warming. The use of biomass is considered to be renewable and assists in reducing CO<sub>2</sub> emissions compared to coal, because biomass is suggested to be CO<sub>2</sub> neutral with regard to greenhouse gas balance [Usón *et al.*, 2004; Zhu *et al.*, 2008; Biagini *et al.*, 2002, Sonobe *et al.*, 2008]. The well-known gasification process of coal occurs primarily through two overlapping stages: pyrolysis and conversion of the char residue [Ciferno and Marano, 2002]. The knowledge of pyrolysis characteristics could be important for better understanding of thermochemical conversion of coal co-utilised with a renewable energy source [Yang *et al.*, 2007]. One of the important features of biomass renewable energy source is the high content of alkali metal in some of the plant biomass material. Alkali metals, such as potassium, are found to reduce the coal's ash melting point and they are considered to be one of the factors which can influence the gasification process [Keown *et al.*, 2005]. The biomass metal salts retained after devolatilisation could be used as a cheap catalyst for further co-gasification of coal and biomass [Raveendran and Ganesh, 1998; Zolin *et al.*, 2001]. However, Keown *et al.* [2005] observed that these metal salts tend to volatilise during pyrolysis. Studies done by Nielsen *et al.* [2000] showed that the volatilisation of these metal salt species from biomass may cause other problems during thermochemical conversion (e.g. slagging and fouling). In order to reduce the negative impact caused by these metal salts during pyrolysis, biomass may be co-utilised with coal. Mixing coal with biomass feedstock may also assist industries in producing synthesis gas and address issues regarding coal shortage. Studies have shown that coal and biomass exhibit similar trends under heat treatment, but with differences in quantitative values (i.e. total yields and distribution of products) [Moghtaderi *et al.*, 2004].

There is limited research being performed to take full advantage of the catalytic properties of inherent alkaline compounds in plant biomass during the co-pyrolysis process. Most existing studies focus on fast pyrolysis of biomasses to produce bio-oil and possible synergetic

effects that rise from coal/biomass use during co-gasification process [Collot *et al.*, 1999; De Jong *et al.*, 1999; Ciferno and Marano, 2002; Moghtaderi *et al.*, 2004]. A comprehensive understanding of gaseous products formed during pyrolysis process due to co-utilisation of biomass and coal is required. The study of thermal treatment of coal, biomass, and coal-biomass blends could provide important information on how to elucidate industrial problems such as clogging of filters, catalyst poisoning, hot corrosion, erosion, and gas emissions [Gray *et al.*, 1996].

## 1.2 Hypothesis

It is hypothesised that the addition of plant biomass will have an influence on the degradation of the coal during pyrolysis process. The alkaline compounds in the plant biomass are also suspected to exhibit catalytic properties during preparation of the coal char. Differences in the composition of the biomass feedstock (chemical structure of cellulose, hemicellulose, and lignin) will influence the resulting low molecular mass gas products formed during the co-pyrolysis process.

## 1.3 Aims and Objectives

Aims and objectives of this dissertation include:

- ❖ Determining the physical-chemical characteristics of coal, biomass and coal/biomass blend chars by using different analytical techniques.
- ❖ Determining the influence of the biomass additives on coal's degradation during thermal treatment under N<sub>2</sub> atmosphere.
- ❖ Determining possible interactions between the coal-biomass blends during the pyrolysis process.
- ❖ Using a thermogravimetric analyser coupled to a mass spectrometer (TG/MS) to determine the effects of biomass loadings on the low molecular weight gases evolved from the coal during the pyrolysis process.
- ❖ Determining which biomass species exhibits the greatest influence on the evolution of gaseous species during the co-pyrolysis of coal and biomass.

## 1.4 Outline of the Study

Figure 1.1 is a schematic representation of the outline of the study. The experiments were carried out in such a manner to provide clarity about the investigation of biomass influence on coal during pyrolysis. Four types of plant biomass were selected for this study based on their seasonal availability (hard woodchip, soft woodchip, pine woodchip, and sugar cane bagasse). The experimental data was recorded simultaneously using a thermogravimetric analyser coupled to a mass spectrometer (TG/MS). The coal sample was blended with selected biomasses separately in the proportions of 0:100, 20:80, 40:60, 60:40, 80: 20 and 100:0 (wt. %: wt. %). To reduce the effects of mass and heat transfer limitations, small masses of coal and biomass samples (about 25 mg) were loaded into  $\text{Al}_2\text{O}_3$  ceramic pans [Munir *et al.*, 2009]. Samples of coal, biomass and coal/biomass blends were charred in a nitrogen atmosphere. The temperature range used for all experiments was from ambient to 1100 °C at a heating rate of 10° C/min. The resulting char residue (80% biomass to 20% coal) obtained from the tube furnace was subjected to BET surface area, XRD, XRF, and scanning electron microscopy (SEM) analyses. Raw biomass samples were analysed to determine present inorganic species and ligno-cellulosic components (cellulose, hemicellulose, and lignin).

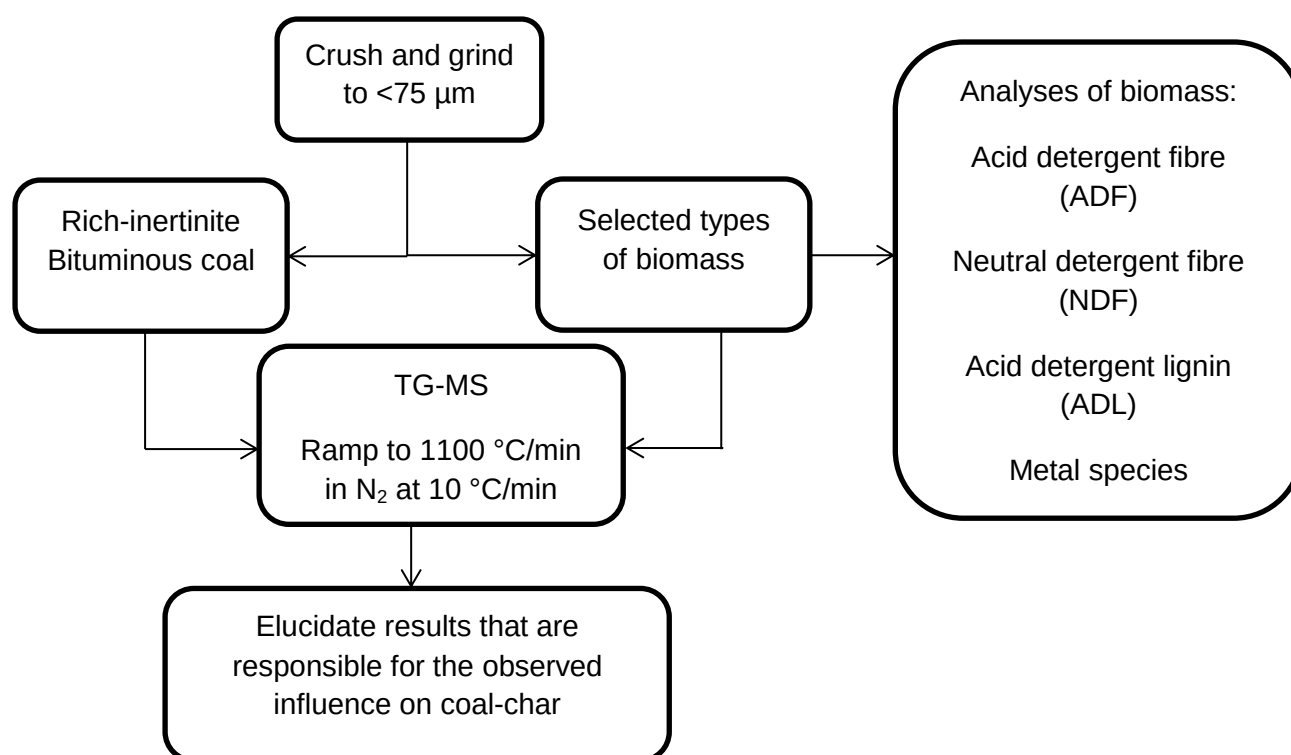


Figure 1.1: Outline of study

## 1.5 Scope of the dissertation

The dissertation is divided into seven chapters:

- ❖ Chapter 1 consists of a formulation of the problem statement and hypothesis, along with aims and objectives for this project.
- ❖ Chapter 2, the literature study, provides information from relevant publications applicable to the study. Chapter 2 also describes systems that relate to pyrolysis processes in detail, since it is the focus of this study.
- ❖ A discussion of various analytical techniques used in this project is given in Chapter 3, along with discussion on sample preparation and experimental procedures carried out to investigate and characterise the nature of the fuels.
- ❖ The chemical and physical characterisation results obtained from the methods used in Chapter 3 are broadly discussed in Chapter 4.
- ❖ Chapter 5 entails the discussion of the pyrolysis results obtained using a thermogravimetric analyser coupled to mass spectrometer (TG-MS). The chapter will be divided into two sections, namely the TG, and MS sections.
- ❖ The important conclusions derived from the experimental results are presented in Chapter 6, along with recommendations for future studies.

|                  |
|------------------|
| <b>Chapter 2</b> |
|------------------|

**Literature Study**

This section of the work will provide an introduction to coal and biomass, and focus on recent relevant investigations regarding the use of biomass and coal. It will be discussed within the following subsections: coal/biomass classification, fuel characterisation, methods used to convert biomass, reactions and thermal degradation processes involved.

**2.1 Introduction**

Biomass offers 14% of the world's available energy sources and it is ranked fourth worldwide [Hall *et al.*, 1992; McGowan; 1991; McKendry 2002]. There is a rising concern for limited resources of non-renewable fossil fuels (natural gas, oil and coal). Biomass can be used as an alternative energy source because of the fact that it is renewable. Biomass is mostly used by households in South Africa because it is an important source of domestic energy in rural areas. In the industry, the use of biomass is minor but important, i.e. biomass is mainly used for paper, pulp, and sugar refining [Haw and Hughes, 2007].

South Africa harvests 7 million tons of bagasse (husks), 20 million tons of sugar cane, and 18 million tons of timber per annum [Haw and Hughes, 2007; <http://www.saforestrymag.co.za>]. The installed electricity generation in the sugar industry has a power capacity of 245 MWe [Wrinkler *et al.*, 2006]. South Africa has small gas and oil reserves, but large coal reserves that supply the country with 70 - 79 % of primary energy [Haw and Hughes, 2007; Van Niekerk, 2008]. The other use of coal is for synthetic fuels and chemical plants [Bunt, 2006]. According to Schmidt [2012], South Africa's coal reserves consist of 55,000 million tons of recoverable hard coal and the most extracted coal type is bituminous coal with low sulphur and high ash contents [Winkler *et al.*, 2006]. These coals are from the carboniferous and Permian age, and the most important deposits are found in the Great Karoo basin [Thomas, 2002]. Prevost & Msibi [2005] stated that 11 % of coal production in South Africa is derived from the Limpopo Province, 1 % from KwaZulu-Natal, 7 % from the Free State, and nearly 80 % from Mpumalanga.

**2.2 Energy source**

The demand for energy is increasing worldwide and fossil fuels still dominate in the world energy market [Goldemberg, 2006; Shafiee and Topal, 2009]. Fossil fuels are non-renewable and there are no exact predictions with regard to when the depletion of fossil fuel reserves will occur [Shafiee and Topal, 2009]. A study conducted by Shafiee and Topal [2009] calculates the depletion duration of fossil fuels using a model modified from the Klass

model [1998]. The model approximates the time for oil, coal and gas to be 35, 107 and 37 years, respectively, before depletion. Coal, compared to oil and gas, has the largest worldwide usage and reserves [Berkowitz, 1979; Shafiee and Topal, 2009]. An alternative renewable energy resource should be considered, in order to maintain long-term energy sustainability. Some researchers believe that biomass has been a main source of energy in the past before fossil fuels became dominant in the industry, and it has a great potential for securing both domestic and industrial energy [Haw and Hughes, 2007; Demirbas, 2008; Shafiee and Topal, 2009]. Biomass, compared to coal, has environmental advantages such as reduction of CO<sub>2</sub> emissions [Mohan *et al.*, 2006]. However, there is an overlooked factor, which is the time lag between the release of CO<sub>2</sub> from thermo-chemical conversion and an uptake as biomass [McKendry, 2002].

### **2.3 The nature of Coal**

Coal is the most fundamental resource that is classified under fossil fuels. It has a wide range of chemical compositions and physical properties [Falcon and Snyman, 1986]. The deposits where coals are found are called seams and originated through the build-up of vegetation [Miller, 2005]. Falcon and Snyman [1986] defined coal as the fundamental material (non-homogeneous) composed of the fossilised remains of plant debris, which have undergone progressive physical and chemical alteration through geological time.

### **2.4 Mineral matter present in coal**

In short, coal is a sedimentary rock that consists of organic carbonaceous matter (macerals), inorganic (mainly crystalline) minerals, and fluids [Harvey and Ruch, 1986; Miller, 2005]. The organic constituents consist primarily of carbon, hydrogen, and oxygen, with smaller amounts of sulphur. The inorganic constituents contain various ranges of ash-forming compounds distributed throughout the coal [Miller, 2005]. Harvey and Ruch [1986] stated that the fluids in coal prior to mining are mainly moisture and methane. Table 2.1 summarises most of common minerals found in US coals. This highlights a need for a detailed database for South African coal properties. There are various types of minerals found in most South African coals, namely clays, carbonates, sulphides, quartz and glauconite [Falcon and Snyman, 1986].

Table 2.1: Common minerals found in U.S coals adapted from Harvey and Ruch [1984]

| Mineral                                                                    | Composition                       | Chief occurrences |           | Abundance in mineral matter |
|----------------------------------------------------------------------------|-----------------------------------|-------------------|-----------|-----------------------------|
|                                                                            |                                   | Physical*         | Genetic** |                             |
| <b>Clay minerals</b>                                                       |                                   |                   |           |                             |
| illite (sericite, K-mica)                                                  | $KAl_2(AlSi_3O_{10})(OH)_2$       | D,L               | d,s (?)   | common                      |
| smectite (mixed layered)                                                   | $Al_2Si_4O_{10}(OH)_2 \cdot H_2O$ | D,L               | d,s (?)   | common                      |
| <b>Sulphides</b>                                                           |                                   |                   |           |                             |
| pyrite                                                                     | $FeS_2$ (isometric)               | D,N,F             | s,e       | variable                    |
| marcasite                                                                  | $FeS_2$ (orthorhombic)            | D (?)             | s (?)     | rare                        |
| sphalerite                                                                 | $ZnS$                             | F                 | e         | rare                        |
| others (e.g. greigite, galena, chalcopyrite and pyrrhotite)                |                                   |                   |           | very rare                   |
| <b>Carbonates</b>                                                          |                                   |                   |           |                             |
| calcite                                                                    | $CaCO_3$                          | N,F               | e,s       | variable                    |
| dolomite, incl. ankerite (Fe)                                              | $Ca (Mg, Fe)(CO_3)_2$             | N                 | s,e       | variable                    |
| siderite                                                                   | $FeCO_3$                          | N                 | s,e       | variable                    |
| <b>Oxides</b>                                                              |                                   |                   |           |                             |
| hematite                                                                   | $Fe_2O_3$                         | N                 | s         | rare                        |
| quartz                                                                     | $SiO_2$                           | D,L,N             | d         | common                      |
| others (e.g. magnetite & rutile)                                           |                                   |                   |           | very rare                   |
| <b>Others</b>                                                              |                                   |                   |           |                             |
| limonite-goethite                                                          | $FeOOH$                           | N                 | e         | rare                        |
| apatite, incl. sulfates, mainly gypsum, barite, and several iron-rich ones | $Ca_5(PO_4)_3(F, Cl, OH)$         | D                 | d,s (?)   | rare                        |
| feldspars                                                                  | $K(Na)AlSi_3O_8$                  | D,L               | d         | rare                        |
| zircon                                                                     | $ZrSiO_4$                         | D,L               | d         | rare                        |
| others                                                                     |                                   |                   |           | very rare                   |

\* D = disseminated; L = layers (partings); N = nodules; F = fissures (cleat). Each mineral listed may often occur in rock fragments inside beds.

\*\* d = detrital; e = epigenetic, second stage of coalification (mostly along joints (cleats) in coal beds); S = syngenetic, first stage of coalification (disseminated, intimately inter-grown with macerals).

### 2.4.1 The organic carbonaceous matter (macerals)

Macerals are formed during coalification, and they represent different organic plant tissues from which the coal originates [Bunt, 2006; Skhonde, 2009]. Macerals can be identified on the basis of morphology, relief, size, shape, colour, origin and reflectance under an optical microscope (Figure 2.1) [Falcon and Snyman, 1986; Wagner and Joubert, 2005]. Four main types of macerals are found in South African coals, i.e. vitrinite, inertinite, liptinite and reactive semi-fusinite. Relatively oxygen-rich vitrinite is derived from the cell wall materials, and possess intermediate amounts of hydrogen and volatiles. Inertinite is a carbon-rich maceral found in bituminous coals and it originates from plants that had been oxidised. Inertinites are more aromatic in structure and they have the lowest hydrogen and volatile content. During carbonization, inertinite macerals are relatively inert and they are not preferred for hydrogenation and liquefaction processes. Hydrogen-rich liptinite contains the lowest oxygen content and oxidises more rapidly than inertinite and vitrinite. The liptinite is aliphatic in structure and originates from pollen, spores, algae and decayed leaf matter [Meyers, 1982; Falcon and Snyman, 1986; Falcon and Falcon, 1987].

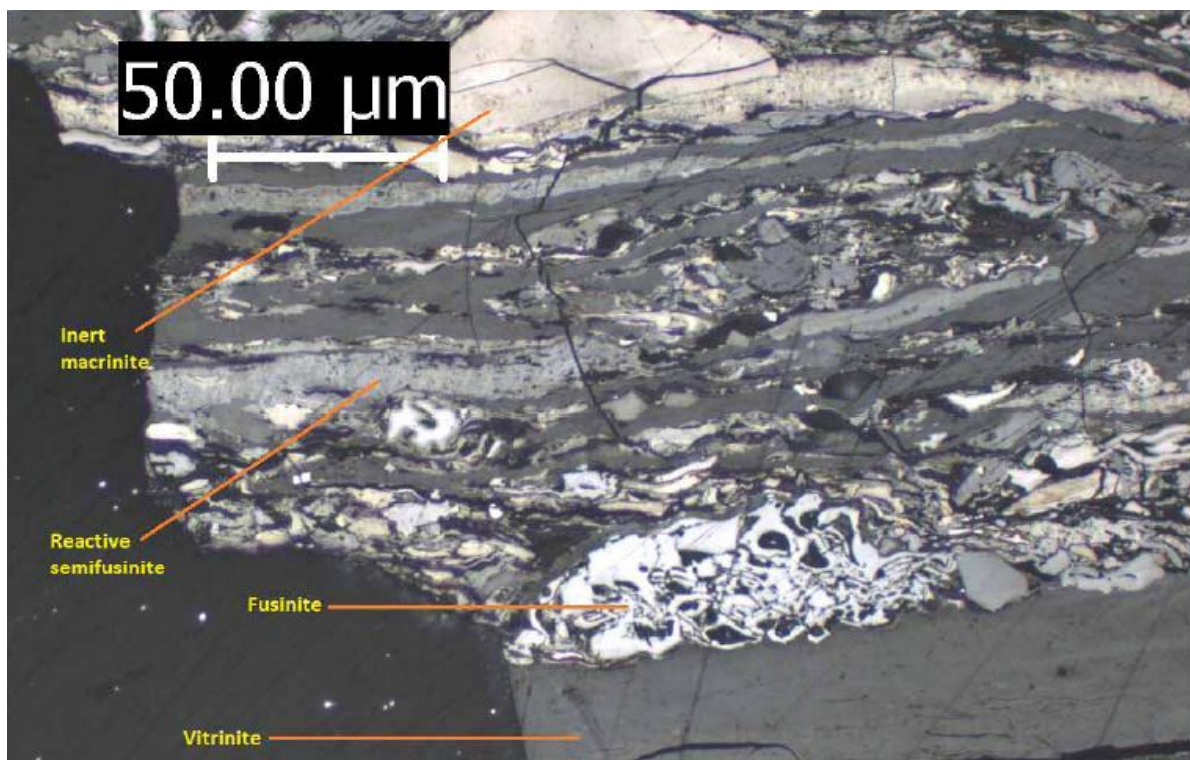


Figure 2.1: Petrographic image adapted from Singh [2011]

Heap *et al.* [1986] found a correlation between volatile matter of a black hard coal and carbon content (Figure 2.2). During carbonisation, liptinite produces high yields of tar and gas. Heap *et al.* [1986] concluded that maceral content can be used as a promising parameter to correlate coal properties and performance.

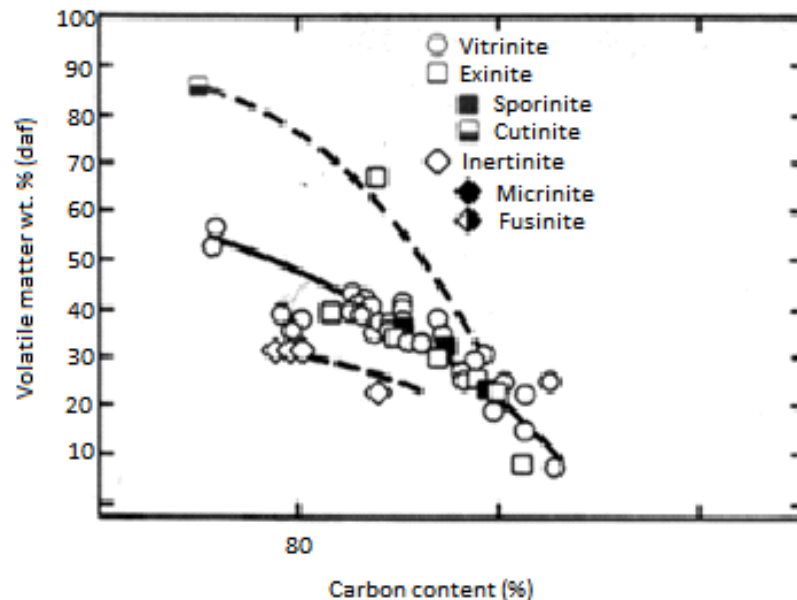


Figure 2.2: Volatile matter correlation with carbon content adapted from Heap *et al.* [1986]

#### 2.4.2 Inorganic minerals

Minerals found in coal can occur as discrete flakes or grains in one of the following physical modes: disseminated tiny inclusions within macerals; layers or partings where fine grained minerals predominate; nodules, lenticular or spherical concretions; fissures (cleat, fracture fillings and small void fillings); and rock fragments, megascopic masses of rock replacements of coal due to faulting, slumping, or related structures [Speight, 2005; Harvey and Ruch, 1986]. The type of occurrence of minerals found in coal (Figure 2.3) can be classified under three groups based on their origin, i.e. detrital, syngenetic (primary) and epigenetic (secondary) [Mackowsky and Stach, 1982; Horsfall, 1993; Falcon and Falcon, 1983]. Detrital minerals were deposited in a coal-forming peat swamp by moving water or wind currents. The deposits of detrital minerals include flakes of illite clay and microscopic grains of quartz, feldspars, zircon, apatite and rutile [Mackowsky and Stach, 1982; Horsfall, 1993; Falcon and Falcon 1983].

Syngenetic minerals (includes various carbonates, nodules of microcrystalline quartz and hematite) were formed within the peat during the early stages of coalification and are intimately inter-grown with the coal [Mackowsky and Stach, 1982; Horsfall, 1993; Falcon and Falcon, 1983]. Epigenetic minerals were deposited into the structure through cavities and cleats after the peat was consolidated and coalified [Mackowsky and Stach, 1982; Horsfall, 1993; Falcon and Falcon, 1983].

The removal of syngenetic minerals from the coal is more difficult than epigenetic minerals [Horsfall, 1993; Falcon and Falcon 1983]. The most recognised epigenetic minerals found in coals are calcite, pyrite and kaolinite [Mackowsky and Stach, 1982].

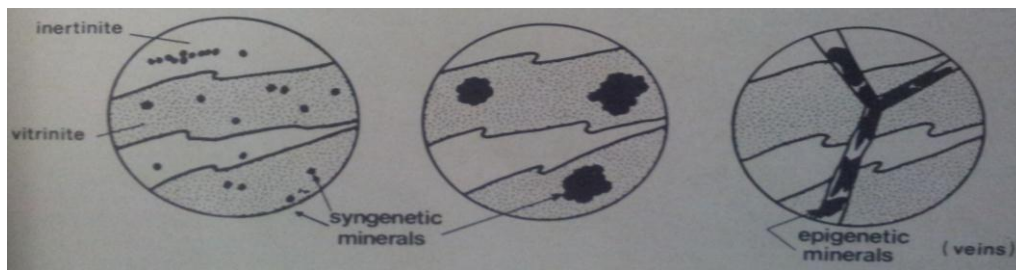


Figure 2.3: The types of occurrence of mineral matter in coal adapted from Falcon and Snyman [1986]

### 2.4.3 Ash

When a coal mass is subjected to a thermal treatment (i.e. combustion), the remaining non-combustible residue is called ash. The ash represents the bulk mineral matter left after inorganic dehydration, decomposition and oxidation processes have occurred. However, there is a difference in chemical properties and composition of ash and mineral matter [Bunt, 2006; Choudry *et al.*, 2010].

### 2.5 Coal formation

The physical and chemical alteration of coal includes the decaying of the vegetation, deposition and burying by sedimentation, compaction, and transformation of the plant remains into the black/brown rock found today [Miller, 2005]. The coalification process initiated in swamps and great river deltas [Horsfall, 1993]. Coalification is a process that took place over time, at higher temperature and pressure, and at a certain depth [Miller, 2005].

Coalification is a process that resulted in the transformation of the original peat swamp through the progressive stages of lignite, sub-bituminous coal, bituminous coal, anthracite and graphite [Miller, 2005; Bunt, 2006]. Geochemically, Tatsch [1980] describes coalification as having three processes by (Table 2.2), i.e. (1) the microbiological degradation of the

cellulose of the origin plant species, (2) the conversion of lignin into humic substances, and (3) the condensation of humic substances into larger coal structures.

Table 2.2: The coalification process adapted from Van Krevelen [1993]

| Materials                                                                                                                                                | Partial Processes                                                                                                                   | Main Chemical Reactions                                                                                                                                                                                                                                                                                                       |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Decaying<br>Vegetation<br>↓<br><i>Peat</i><br>↓<br><i>Lignite</i><br>↓<br><i>Bituminous coal</i><br>↓<br><i>Semianthracite</i><br>↓<br><i>Anthracite</i> | Peatification<br><br>Lignitification<br><br>Bituminization<br><br>Preanthracitization<br><br>Anthracitization<br><br>Graphitization | Bacterial and fungal life cycles<br><br>Air oxidation, followed by decarboxylation and dehydration<br><br>Decarboxylation and hydrogen disproportioning<br><br>Condensation to small aromatic ring systems<br><br>Condensation of small aromatic ring systems to larger ones; dehydrogenation<br><br>Complete carbonification |

## 2.6 Biomass

Literature defines biomass as an organic material derived from recent animal and plant matter [Enciner *et al.*, 1998; Usón *et al.*, 2004]. Biomass is a renewable energy source that can be reproduced or harvested over time. Coal can be regarded as a fossilised biomass that had undergone both physical and chemical alteration, but unlike biomass, it is non-renewable [McKendry, 2002]. Mohan *et al.* [2006] stated that renewable biomass can be considered an ideal source to replace coal and oil. The composition of biomass varies depending on its environmental conditions and species [McKendry, 2002]. McKendry [2002] stated that the good features of an ideal energy crop should include high yields, crops should be maintained at lowest cost, crops should require low energy to produce products, and crops should contain low amounts of contaminants.

## 2.7 Photosynthesis

During the cyclic photosynthesis process, a chlorophyll containing organism captures the energy from the sun and converts it to chemical energy, carbohydrates, and air. The photosynthesis process involves an uptake of CO<sub>2</sub> and water by the plant [McKendry, 2002].

## **2.8 Composition of biomass**

Biomass is believed to consist of high moisture, carbohydrates, alkali, ash and fibrous structures including cellulose, hemicellulose and lignin [Jenkins *et al.*, 1996; Turn, 1999; McKendry, 2002]. Biomass can be obtained from various kinds of materials such as wood, herbaceous waste, and agricultural and forestry residues [McKendry, 2002]. The herbaceous plants can be found as species that have high or low moisture content. These species, such as the perennial types, are known to have loosely bound fibres. The herbaceous biomass is different with woody species, because woody species are characterised by their slow growth and having tightly bound fibres [McKendry, 2002]. The composition of plant biomass is chemically and physically different from other types of fuels such as coal and oil [McKendry, 2002; Mohan *et al.*, 2006].

### **2.8.1 Mineral matter in Biomass**

#### **2.8.1.1 Inorganic minerals**

Thermal treatment of biomass could lead to small quantities of inorganic mineral residues in the ash. The ash residue is made up of non-biodegradable carbon that is found in biomass [McKendry 2002]. In the ash, the extraneous inorganic components (e.g. sand) can be distinguished [McKendry 2002; Mohan *et al.*, 2006; Livingston and Babcock, 2006]. For woody biomass, the most commonly found mineral constituents occur as oxides, silicates, carbonates, sulfates, chlorides and phosphates [Raveendran *et al.*, 1995].

#### **2.8.1.2 Organic Matter**

The organic components of biomass are mostly the organic extractives, which are composed of fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins and essential oils. Figure 2.4 shows the major structural chemical components in biomass containing low-molecular weight and macromolecular substances [Mohan *et al.*, 2006; Turn, 1999; McKendry, 2002].

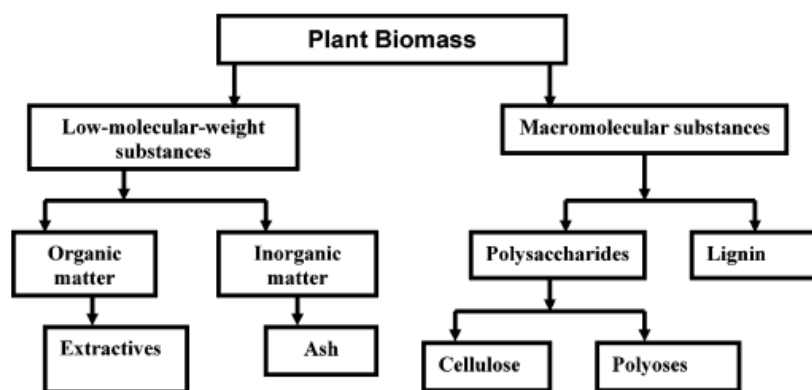


Figure 2.4: Main chemical components found in plant biomass adapted from Mohan *et al.* [2006]

### 2.8.2 Ligno-cellulosic biomass

Biomass is a renewable energy source that consists mainly of ligno-cellulosic materials (Figure 2.5) [Jenkins *et al.*, 1996; Turn, 1999; McKendry, 2002; Mohan *et al.*, 2006]. Cellulosic material, compared with coal, is mostly reported to be less homogeneous and having a lower fraction of carbon, lower hydrogen and higher oxygen content than coal [Cherubini, 2010].

An interest is shown in the thermal degradation of ligno-cellulosic materials, as it is considered a possible resource to prolong the availability of coal [Mohan *et al.*, 2006]. The chemical reactivities of various biomasses are directly influenced by the chemical differences in the ligno-cellulosic composition [Carrier *et al.*, 2011b]. Therefore, it is important to know the quantity of each component in the biomass in order to understand the reaction efficiency during thermo-chemical conversion processes [Bobleter, 1994; Ando *et al.*, 2000; Yanik *et al.*, 2008]. The reaction efficiency of biomass could help in building a better process for commercialising green fuels or producing chemicals [Carrier *et al.*, 2011a; 2011b].

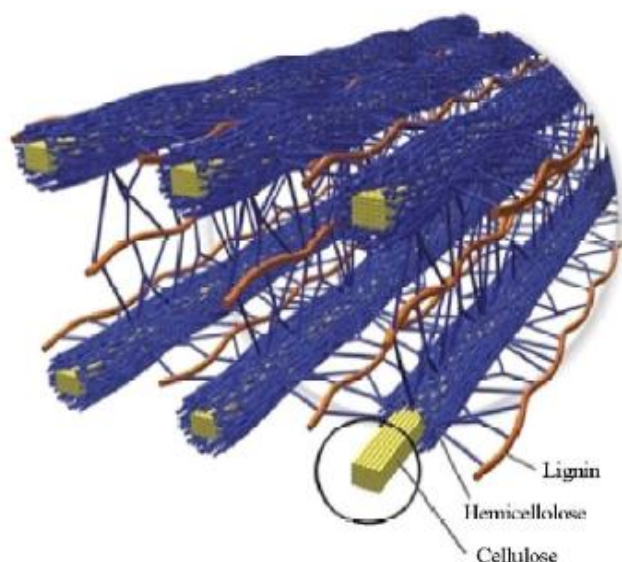


Figure 2.5: Schematic presentation of ligno-cellulosic material [Doherty, Mounsavion, and Fellows, 2010]

### 2.8.2.1 Cellulose

Cellulose is defined as a high molecular weight linear polymer of  $\beta$ -(1 $\rightarrow$ 4)-D-glucopyranose units linked by ether bonds (Figure 2.6) [McKendry, 2002; Carrier *et al.*, 2011b; Mohan *et al.*, 2006]. The equatorial conformation of  $\beta$ -linked glucopyranose residues assists in stabilising the chair structure, and minimising flexibility [Mohan *et al.*, 2006]. Cellulose is an insoluble crystalline (cellulose I<sub>a</sub>) compound that has a rigid structure [Mohan *et al.*, 2006]. Cellulose has amorphous regions which contain moisture and water of hydration. When the biomass is rapidly heated, the water within disrupts the structure “by a steam explosion-like process” prior to dehydration of the cellulose molecules [Mohan *et al.*, 2006]. The degradation of cellulose is reported to occur at 240-400 °C, and it produces levoglucosan and anhydrocellulose [Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b; Carrier *et al.*, 2012].

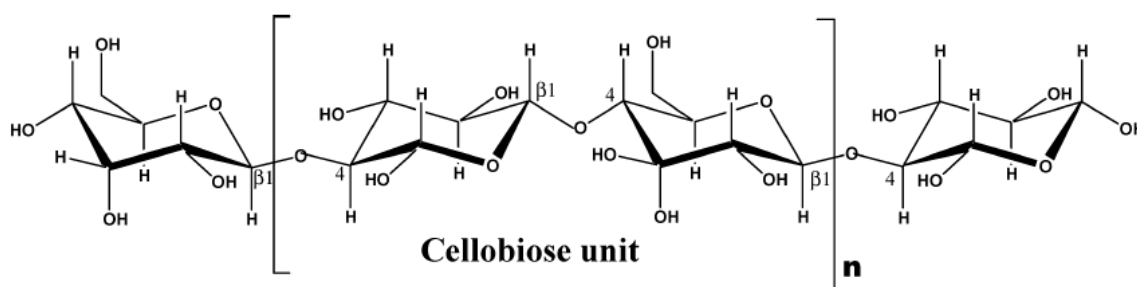


Figure 2.6: Schematic representation of the chemical structure of cellulose [Mohan *et al.*, 2006]

### 2.8.2.2 Hemicellulose

Hemicellulose is the second major chemical component of wood, also known as polyose [Mohan *et al.*, 2006]. The main components of hemicellulose are repetitive sugars such as glucose, mannose, galactose, xylose, arabinose and 4-O-methyl glucuronic acid residues (Figure 2.7) [McKendry, 2002; Mohan *et al.*, 2006; Yang *et al.*, 2007]. Hemicellulose has a random, amorphous structure with little structural strength [McKendry, 2002; Yang *et al.*, 2007]. Hemicellulose is made of heteropolysaccharide units having short side-chain branches [McKendry, 2002; Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b]. The side-chain branches are removed with ease from the main stem at low temperatures [Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b]. The hemicellulose is mostly reported to degrade at temperatures of 130-315 °C to produce less tar and chars than cellulose, and volatiles evolving CO<sub>2</sub>, CO and some light hydrocarbons [Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b].

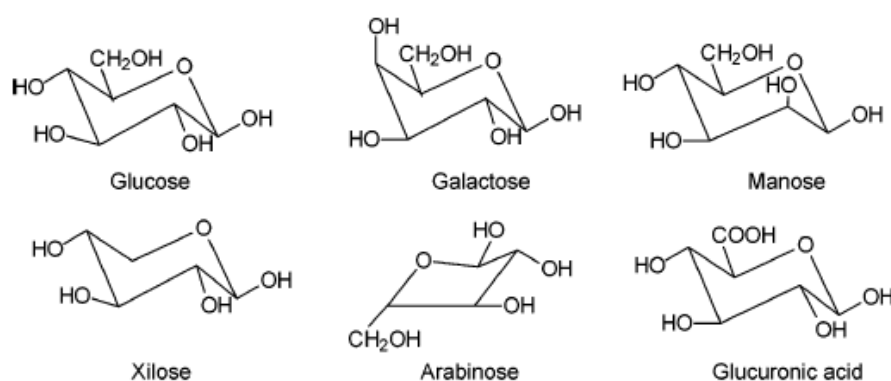


Figure 2.7: Chemical structures of main constituents of hemicellulose [Mohan *et al.*, 2006]

### 2.8.2.3 Lignin

Lignin is highly branched, full of aromatic rings and has an amorphous cross-linked, resin-like structure [McKendry, 2002; Mohan *et al.*, 2006; Yang *et al.*, 2007; Maziero *et al.*, 2012]. The main monomeric unit for lignin is phenylpropanoid, which is linked to other units mostly through ether and carbon to carbon bonds [Sharma *et al.*, 2004]. This ligno-cellulosic component has no distinct structure as its structure depends on the conditions of its extraction from the woody biomass (Figure 2.8) [Vázquez *et al.*, 1997; Sharma *et al.*, 2004; Canetti and Bertini, 2007]. Mohan *et al.* [2006] and Carrier *et al.* [2011b] describe lignin as a three-dimensional polymer formed with phenylpropane that consists of an irregular array of bonded hydroxyl- and methoxy-substituted units. Lignin is mostly reported to degrade within a wide temperature range of 300-900 °C [Sharma *et al.*, 2004; Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b].

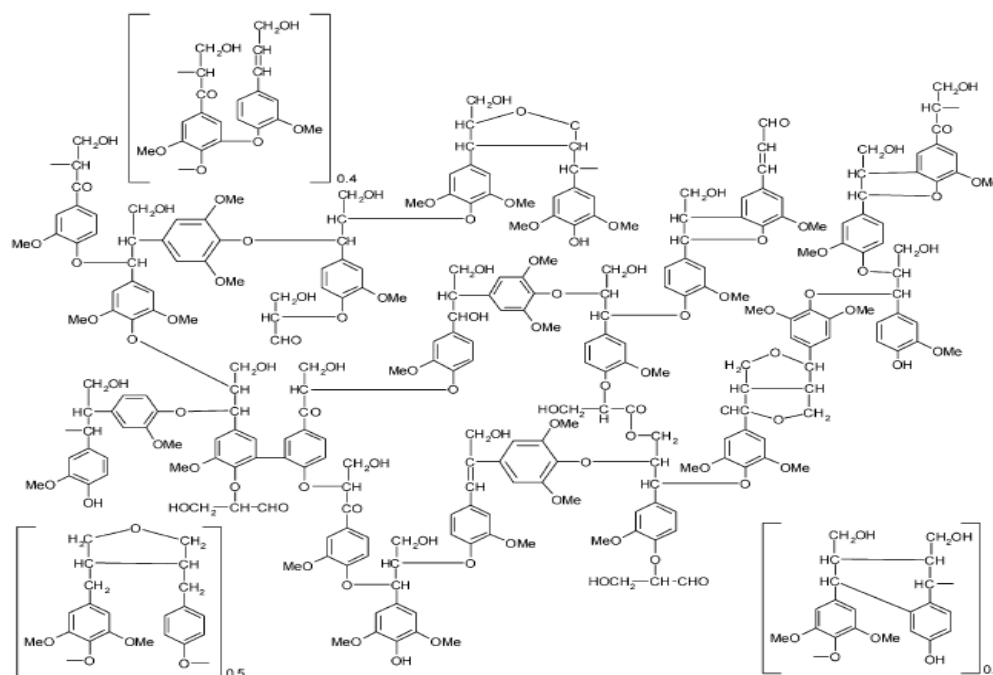


Figure 2.8: A proposed partial chemical structure for beech lignin [Nimz, 1974]

## 2.9 Biomass inherent properties

The inherent properties of woody/herbaceous biomass play a major role in determining the best suitable choice of an energy conversion process. McKendry [2002] stated that the limiting properties of interest during the thermo-chemical conversion of biomass are:

- The moisture content and calorific value (CV);
- The alkali metal content; and
- The proportions of fixed carbon and volatiles.

### 2.9.1 Biomass moisture and calorific value (CV)

Two modes of moisture are found within biomass, namely intrinsic and extrinsic moisture. Intrinsic moisture refers to the inherent moisture within the plants. Extrinsic moisture refers to the moisture caused by the surrounding atmosphere [McKendry, 2002]. Biomass with high moisture content can influence the efficiency of the heat generated under thermal treatment. The calorific value is an expression of the heat value of the material which is released when burnt in air. The energy production of each solid fuel differs in terms of atomic ratios of oxygen/carbon (O/C) and hydrogen/carbon (H/C) content [McKendry, 2002; Senneca, 2007]. The importance of O/C and H/C on the CV of each solid fuel can be illustrated using a Van Krevelen diagram (Figure 2.9) [McKendry, 20002; Biagini, 2002, Senneca, 2007].

Figure 2.9 shows that biomass feedstock are in general characterised by larger O/C and H/C ratios compared with fossil fuels such as coals. They stand, instead, close to RDFs (refuse derived fuels). As a matter of fact, it is not easy to draw a clear demarcation line between biomass and RDFs. This can be explained due to the lower energy contained in carbon-hydrogen and carbon-oxygen bonds, compared with carbon-carbon bonds. The energy density and the flame temperature are lowered by the presence of water, which may lead to ignition problems and cause pre-evaporation of the fuel (preheating problems) [Bridgewater and Peacocke, 2000]. Therefore, it is important to dry biomass (<50 %) prior to energy conversion processes that involve thermal treatment [McKendry, 2002]. Studies have shown that coal and biomass exhibit similar trends under heat treatment, but with differences in quantitative values (i.e. total yields and distribution of products) [Moghtaderi *et al.*, 2004].

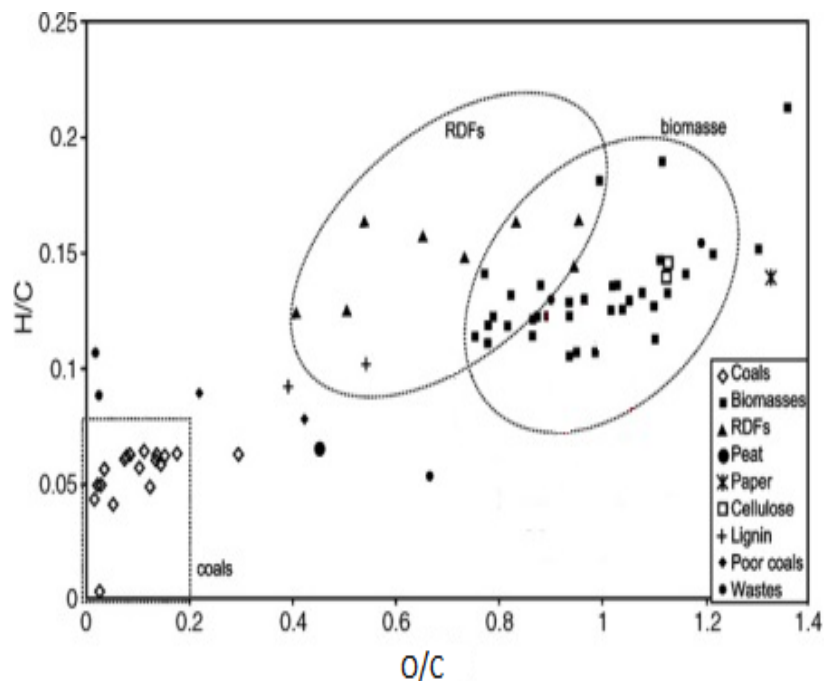


Figure 2.9: The Van Krevelen diagram for solid fuels [Senneca, 2007]

### 2.9.2 Alkali and alkaline earth metals (AAEM)

Metals are important for the growth of a plant, and an increase of metal content is a result of a decrease in lignin content due to plant biology [Kauriinoja, 2010]. Inherent alkaline compounds in biomass were found to volatilise and also influence the reactivity during thermo-chemical conversion processes [Collot *et al.*, 1999; De Jong *et al.*, 1999; McKendry, 2002; Moghtaderi *et al.*, 2004; Bi, 2005; Keown *et al.*, 2005]. The alkali metal compounds that are mostly reported as being responsible for influencing the reactivity are salts of sodium (Na), potassium (K), magnesium (Mg), phosphorus (P) and calcium (Ca) [McKendry, 2002; Keown *et al.*, 2005; Mohan *et al.*, 2006; Tao *et al.*, 2012]. Senneca [2007] stated that biomass (in general) is more reactive than coal upon thermal treatment (mostly reported for gasification processes) due to the high amount of alkaline compounds present. The high concentration of potassium and sodium metals is known to have strong catalytic effects during char gasification (interaction between volatiles and char) [Takarada *et al.*, 1986; Miura *et al.*, 1986; Hawley *et al.*, 1983; Lang and Neavel, 1982; Keown *et al.*, 2005]. The AAEM species can be found in biomass in various forms other than as chlorides, such as carboxylates [Keown *et al.*, 2005]. Raveendran *et al.* [1995], Keown *et al.* [2005] and Huang *et al.* [2011] noticed that, in the presence of potassium species, the primary products of pyrolysis (i.e. CO<sub>2</sub> and H<sub>2</sub>O) react with the char to form CO and H<sub>2</sub> and thus reduce the char's yield as a result of increasing reactivity (self-gasification in the pyrolysis stage). Figure 2.10 depicts an extension of retention of AAEM compounds in the chars after thermo-chemical conversion in argon atmosphere of sugar cane bagasse and cane trash biomass.

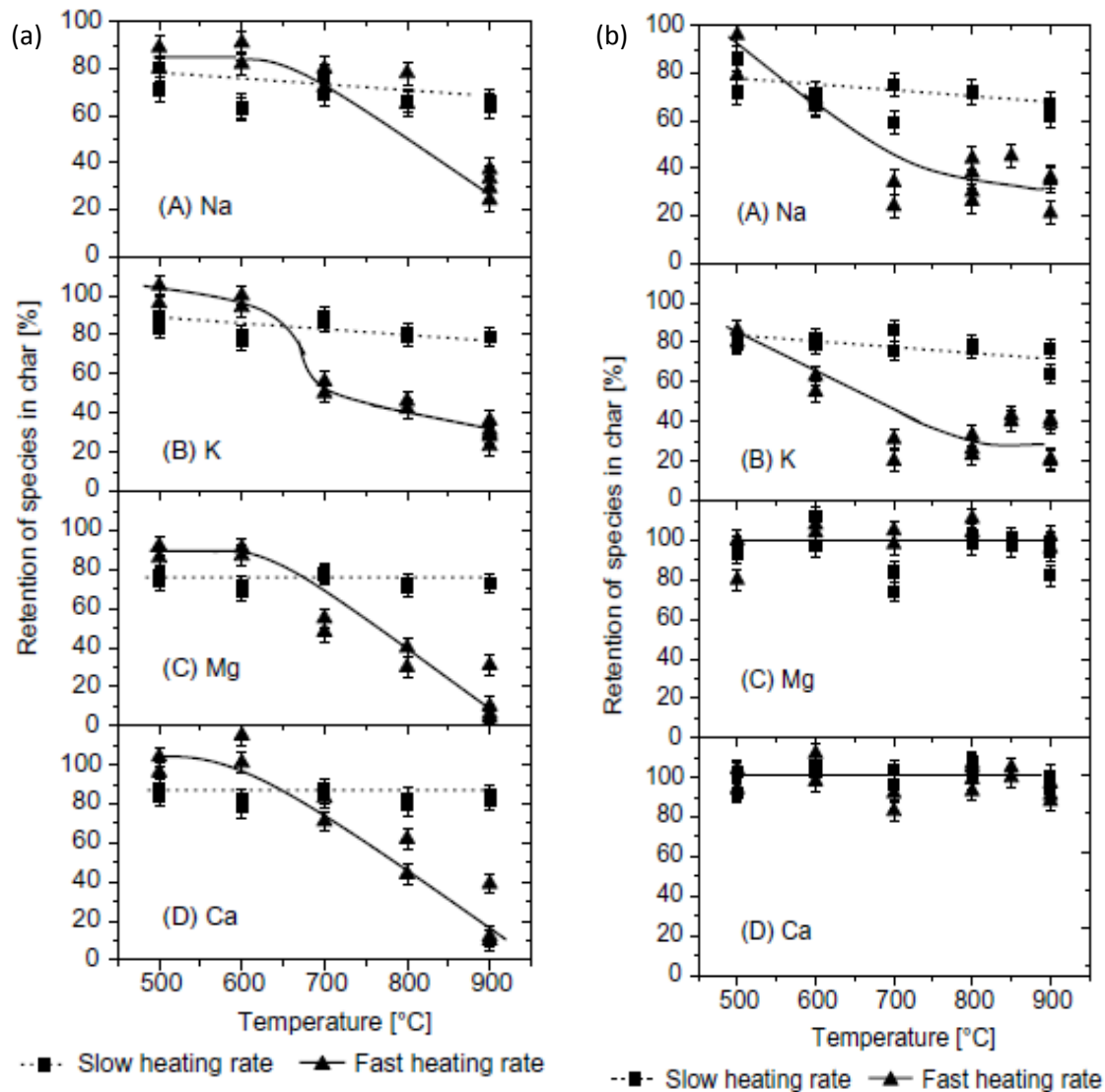


Figure 2.10: Retention of AAEM species in char after pyrolysis in a novel quartz fluidised-bed/fixed bed reactor, a) sugar cane bagasse, and b) cane trash biomass [Keown *et al.*, 2005]

The minerals in biomass could influence pyrolysis product properties and distribution [Raveendran *et al.*, 1995]. The catalytic activity of these minerals may be dependent on the interaction between the char structure and the alkali metal [Lv *et al.*, 2010]. However, it should be noted that alkali metallic compounds could also cause problems (i.e. slagging, agglomeration, fouling and corrosion) when reacting with silica (Si) present in the biomass ash due to soil contamination during harvesting [Gray *et al.*, 1996; Jenkins *et al.*, 1998; McKendry, 2002; Xiong *et al.*, 2008; Tao *et al.*, 2012].

### 2.9.3 The proportions of fixed carbon and volatiles

The chemical energy is stored in two forms in solid fuels, namely as fixed carbon and as volatiles [McKendry, 2002]. The fixed carbon content (FC) is the solid residue that remains after heat treatment and the release of volatiles, which excludes moisture and ash content, whereas the volatile matter is the portion of the mass driven off as vapours and gases during heat treatment of the solid fuel [McKendry, 2002]. The evolved gases are mostly combinations of methane ( $\text{CH}_4$ ), hydrogen ( $\text{H}_2$ ), carbon dioxide ( $\text{CO}_2$ ), water ( $\text{H}_2\text{O}$ ), carbon monoxide ( $\text{CO}$ ), carbonyl sulfide ( $\text{COS}$ ), nitrogen ( $\text{N}_2$ ), hydrogen cyanide ( $\text{HCN}$ ), hydrocarbons ( $\text{C}_2+$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ) and other low molecular mass products [Robinson *et al.*, 1998; Sami *et al.*, 2001; Ciferno and Marano, 2002; Dermibas, 2004]. The proportions of fixed carbon and volatiles may help in providing important information as to how solid fuels may be ignited during various thermo-chemical conversion processes [McKendry, 2002].

### 2.10 Coal-biomass blends

Currently, particular interest has been shown in using coal and biomass together to produce synthesis gas through various thermal processes [Brar *et al.*, 2012]. However, continuous supply of biomass can be challenging. For instance, poor weather conditions may interfere with the crop supply and delivery costs may increase, depending on how far the power plants are [Collot *et al.*, 1999; Moghtaderi *et al.*, 2004]. The situation may be fixed by blending the biomass with coal to maintain a steady supply for thermal processes [Campbell, 1983; Ravindranath and Hall, 1995; Dermibas, 2004].

Studies have shown that coal and biomass exhibit similar trends under heat treatment, but with differences in quantitative values (i.e. total yields and distribution of products) [Moghtaderi *et al.*, 2004]. There are some benefits in blending coal and biomass for thermal processes to using parent material alone [Bi, 2005]. One of the benefits is a reduction of emitted greenhouse gases and other pollutants, such as  $\text{SO}_2$  and  $\text{NO}_x$  [Robinson *et al.*, 1998; Sami *et al.*, 2001; Dermibas, 2003]. There are various ways to integrate coal and biomass within thermo-chemical conversion processes (i.e. pyrolysis and gasification) (Figure 2.11). The approach to integrate solid fuels will depend mostly on the aim of the process. Most studies investigate the influence of synergistic effects (i.e. the chemical interaction between fuels) [Pan *et al.*, 1996; Meesri and Moghtaderi, 2002; Demirbas and Arin, 2002; Moghtaderi *et al.*, 2004]. Most of the studies focus on synergistic effects during co-gasification. However, fewer reports are found that provide a detailed attention of synergistic effects on the composition of the pyrolysis process [Moghtaderi *et al.*, 2004].

Different pathways to integrating coal and biomass as shown in Figure 2.11 [Ciferno and Marano, 2002]:

1. Co-feeding biomass and coal to the gasifier as a mixture
2. Co-feeding biomass and coal to the gasifier using separate gasifier feed systems
3. Pyrolysing the biomass followed by co-feeding pyrolysis char and coal to the gasifier
4. Gasifying the biomass and coal in separate gasifiers followed by a combined fuel gas clean-up [Lau, 1997].

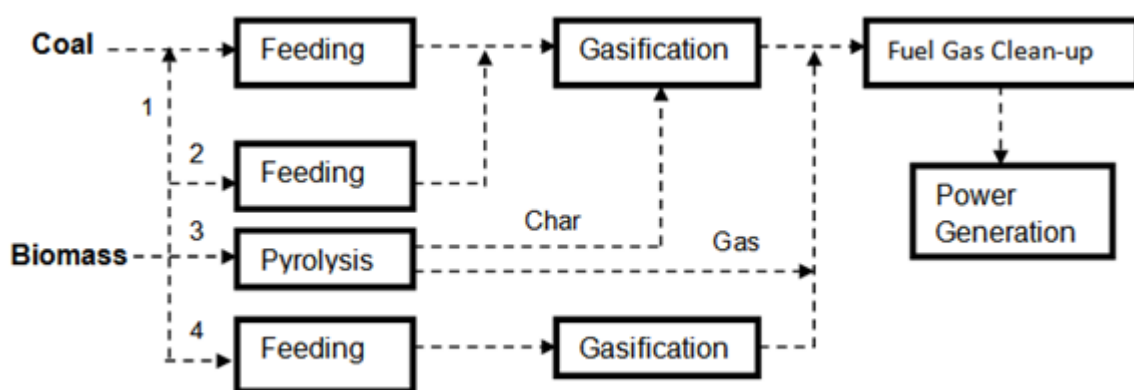


Figure 2.11: Pathway for co-utilisation of coal and biomass in a gasification process [Ciferno and Marano, 2002]

### 2.11 Thermal treatment

There are several methods to convert coal, biomass and co-blends into energy and suitable fuel products [Carrier *et al.*, 2011a]. Many studies have focused on the thermal characteristics of solid fuels with the purpose of applying that knowledge on an industrial scale [McKendry, 2002; Yang *et al.*, 2007; Munir *et al.*, 2009]. These characteristics may assist in a better understanding of the processes involved, i.e. pyrolysis, liquefaction, gasification, and combustion. The most investigated parameter is the kinetics (activation energy, reaction order and pre-exponential factor) during reactions under inert or reactive conditions. The remaining parameters (i.e. structural parameter  $\psi$ , time scale parameter  $t_p$ ) can be obtained through model-fitting analysis [Freeman and Carroll, 1958; Vyazovkin, 2000; Senneca, 2007; Munir *et al.*, 2009; Aboyade *et al.*, 2012]. The main focus of this study is the influence of biomass additions on the behaviour of an inertinite rich South African coal during the pyrolysis process only and thus only pyrolysis will be considered further. This process is important to understand, since it is the first step for most conversion processes.

### 2.11.1 Pyrolysis

Pyrolysis is defined as the thermal degradation of any material (i.e. organic and inorganic) in the absence of oxygen or when little oxygen is available [Demirbas and Arin, 2002; Mohan *et al.*, 2006; Bulmău *et al.*, 2010]. This process is important because it is the first chemical step prior to most other processes and it is also an endothermic process [Fang *et al.*, 2006; Di Blasi, 2009, Mohan *et al.*, 2006]. The major products of pyrolysis (Figure 2.12) under inert conditions are a solid residue or char (consisting of fixed carbon (FC), ash and volatile matter (VM)), condensable liquids (i.e. tar and bio-oil) and fuel gaseous components [Dermibas and Arin, 2002; Mohan *et al.*, 2006; Bulmău *et al.*, 2010].

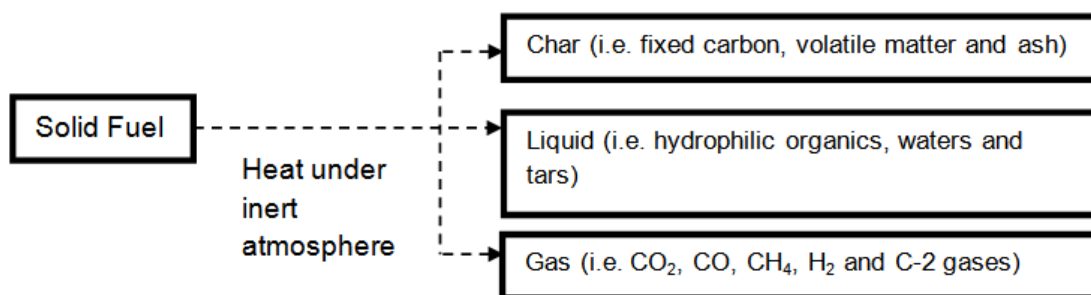


Figure 2.12: Illustration of pyrolysis process

The pyrolysis process depends on various parameters which determine the characteristics of the final products. Parameters that influence the pyrolysis process of fuels, namely the composition of the feedstock, heating rate, vapour residence time, atmosphere gas, final temperature and blending ratios, have been studied previously [Moghtaderi, 2001; Meesri and Moghtaderi, 2002; Dermibas, 2003; Moghtaderi *et al.*, 2004; Cetin *et al.*, (2004, 2005)]. Studies conducted by Yang *et al.* [2011] on high ash and low fixed-carbon coal, have shown that pyrolysis consists of two stages. During the first primary stage ( $T < 560\text{ }^{\circ}\text{C}$ ), the reaction is mostly dominated by the diffusion rate of volatile matter. The volatiles at this stage were observed to be emitted with difficulty and the process had high pyrolytic activation energy. When the temperature was increased, low pyrolysis activation energy was found. The second stage of the pyrolysis process ( $T > 560\text{ }^{\circ}\text{C}$ ) was observed to be controlled by the tar-releasing reactions and high activation energy was observed for this part of the process [Yang *et al.*, 2011].

### 2.11.2 Transformations during pyrolysis

The reaction mechanisms involved during the pyrolysis process are complex due to the chemical and physical transformations that occur, and also due to a wide product spectrum [Neves *et al.*, 2011]. Neves *et al.* [2011] stated that, to optimise pyrolysis reactions, there is a need to understand pyrolytic mechanisms by studying rates or yields and properties of the emitted volatiles. Most well-documented studies describe the use of thermogravimetric analysis to study primary and secondary pyrolytic reactions [Parihar *et al.*, 2007; Conesa and Domene, 2011; Yang *et al.*, 2011].

Figure 2.13 summarizes the changes that occur during pyrolysis. Secondary char is formed by decomposition of organic vapours (tar) on primary coal char (coking). The reaction is exothermic and most likely to be catalysed by primary coal char [Antal and Gronli, 2003]. Antal and Gronli [2003] stated that low coal char yields occur as a result of vapours and gases that are not removed from the reaction zone, resulting in a further removal from the thermodynamic equilibrium.

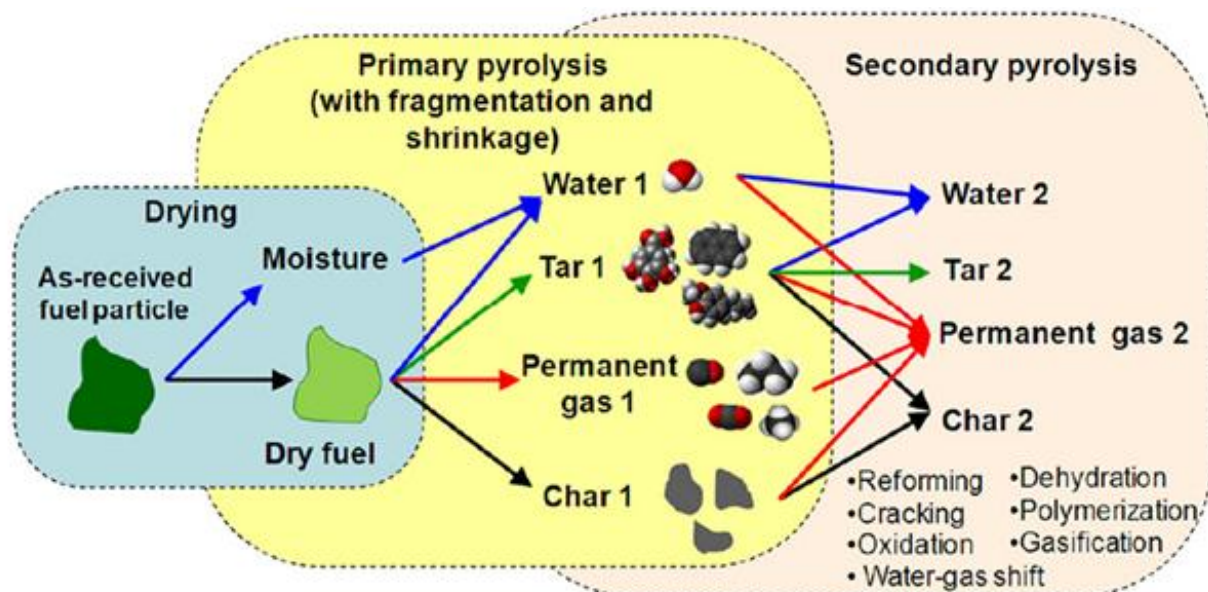


Figure 2.13: Proposed mechanism of pyrolytic reactions [Neves *et al.*, 2011]

### 2.11.3 Different processes of pyrolysis

Different pyrolysis processes are available for woody biomass. The process depends on the operating conditions (i.e. heating rates, residence time etc.) and the desired product spectra (yield of gaseous versus liquid) [Dermibas and Arin, 2002; Mohan *et al.*, 2006; Senneca, 2007; Bulmău *et al.*, 2010; Carrier *et al.*, 2011a]. The conventional pyrolysis (carbonization) and fast pyrolysis are described in the following paragraphs.

#### 2.11.3.1 Conventional pyrolysis

Conventional slow pyrolysis has been used in the past (thousand years ago) mainly for the production of coal char [Mohan *et al.*, 2006]. This process is performed using a slow heating rate (approximately from 5-29 °C/min), occurs at low to intermediate temperatures (approximately 261-570 °C), has long residence times and vapours that are not rapidly emitted [Mohan *et al.*, 2006]. As a result, components of the vapour phase continue to react with one another, forming high yields of solid chars and a small liquid fraction [Bridgewater, 2003; Mohan *et al.*, 2006; Desideri *et al.*, 2011]. The liquid fractions produced consist of two phases, namely an aqueous phase and a non-aqueous phase. An aqueous phase consists of a variety of organo-oxygen compounds of low molecular weight, while the non-aqueous phase contains water-insoluble organics of high molecular weight (mainly aromatics) [Desideri *et al.*, 2011]. Studies conducted on pyrolysis have shown that lignin provides a higher char yield compared to cellulose or hemicellulose [Antal, Jr., 1983; Shafizadez, 1985]. The stable, rich carbon bio-char produced from conventional pyrolysis can be used as soil amendment [Sohi *et al.*, 2009; Brownsort, 2009; Kameyama *et al.*, 2010].

#### 2.11.3.2 Fast pyrolysis

Fast pyrolysis entails a high temperature process whereby biomass is rapidly heated at faster heating rates, short vapour residence times and products are rapidly cooled down (< 2 seconds) [Mohan *et al.*, 2006]. Fast pyrolysis leads to minimum char formation, a high yield of bio-oil and less non-condensable gases (15-25 wt. %, 60-75 wt. % and 10-20 wt. %, respectively) [Bridgewater, 2003; Mohan *et al.*, 2006]. This bio-oil is a dark brown, organic liquid which comprises highly oxygenated compounds [Mohan *et al.*, 2006].

The liquid is formed during depolymerisation and fragmentation of the ligno-cellulosic components and it is stated to have a heating value that is half of that of conventional fuel oil [Bridgewater, 2003; <http://www.pyne.co.uk>]. Bio-oil can be stored, pumped, and transported similarly to petroleum based products and can also be fed into reactors [Czernik and Bridgewater, 2004]. Mohan *et al.* [2006] state that, during fast pyrolysis, no waste is formed,

because the products formed (char and bio-oil) can be used as fuels. The gas produced can also be recycled into the process. Table 2.3 summarises the different pyrolysis technology processes available for various products.

Table 2.3: Different processes of pyrolysis [Mohan *et al.*, 2006]

| Pyrolysis technology | Residence time | Heating rate | Temperature (°C) | Products       |
|----------------------|----------------|--------------|------------------|----------------|
| carbonization        | days           | very low     | 400              | charcoal       |
| conventional         | 5-30 min       | Low          | 600              | oil, gas, char |
| fast                 | 0.5-5 s        | very high    | 650              | bio-oil        |
| flash-liquid         | <1 s           | High         | <650             | bio-oil        |
| flash-gas            | <1 s           | High         | <650             | chemicals, gas |
| ultra                | <0.5           | very high    | 1000             | chemicals, gas |
| vacuum               | 2-30 s         | Medium       | 400              | bio-oil        |
| hydro-pyrolysis      | <10 s          | High         | <500             | bio-oil        |
| methano-pyrolysis    | <10 s          | High         | >700             | chemicals      |

## 2.12 Gaseous products formed during pyrolysis

During the pyrolysis process, there are a number of reactions occurring which directly influences the formation of gases (such as decarboxylation). The gases being formed are the result of thermal decomposition of minerals present, biomass feedstock and coal. The vapours formed during pyrolysis of solid fuel mainly consist of  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ , trace amounts of large gaseous organics, and water vapour [Klass, 1998; Robinson *et al.*, 1998; Sami *et al.*, 2001; Ciferno and Marano, 2002; Demirbas, 2004]. These vapours are evolved during thermal decomposition of a solid fuel under inert conditions. Mass spectrometry is often used to identify the pyrolytic gases evolved at certain temperatures [Várhegyi *et al.*, 1989; Yang *et al.*, 2007; Mészáros *et al.*, 2007]. Yang *et al.* [2007] and Huang *et al.* [2011] conducted studies on the characteristics of the vapours formed during pyrolysis of ligno-cellulosic biomass material. The results discuss the mass spectra of  $H_2$ ,  $CH_4$ ,  $H_2O$ ,  $C_2H_4$ ,  $CO$ ,  $C_2H_6$ ,  $O_2$ , and  $CO_2$ . The  $CO_2$  release profile during pyrolysis was observed to have displayed three peaks for hemicellulose (from 280 to 658 °C), two peaks for lignin (at 340 and 700 °C) and one peak for cellulose (380 °C) [Yang *et al.*, 2007]. The release of  $CO_2$  was mostly caused by cracking and reforming of functional groups of carboxyl ( $C=O$ ) and  $COOH$ . The release of  $CO$  was possibly caused by the cracking of carbonyl ( $C-O-C$ ) and carboxyl ( $C=O$ ) groups. The evolution of  $CO$  from lignin was observed

to increase with an increase in temperature. The release of CH<sub>4</sub> is observed to occur at lower temperatures (<600 °C). Yang *et al.* [2007] stipulated that the release of CH<sub>4</sub> was possibly caused by the cracking of the methoxyl-O-CH<sub>3</sub> group. The results from Yang *et al.* [2007] also showed a release profile of H<sub>2</sub> that increased with an increase in temperature. A prominent H<sub>2</sub> peak was observed at 600 °C. The release of H<sub>2</sub> was mainly attributed to the cracking and deformation of C=C (aromatic ring) and C-H bonds (aromatic ring) [Yang *et al.*, 2007]. The release of H<sub>2</sub> and other gases may lead to higher pyrolytic reactivity in biomass due to secondary reactions that may occur at these temperatures [Yang *et al.*, 2007; Huang *et al.*, 2011].

From literature it is clear that the characteristics of each fuel play a major role in the final product properties during thermo-chemical processes. The investigation of conditions that influence the spectrum of pyrolysis products remains important for optimising the process for a commercial scale. Therefore, it is important to understand available technological processes that may help understanding the interaction of coal-biomass, and reducing CO<sub>2</sub> emissions that impact global warming and that generate the desired product.

|                  |
|------------------|
| <b>Chapter 3</b> |
|------------------|

**Experimental methods and procedures**

This chapter provides the background of some various experimental analytical techniques used in this study. This chapter will also focus on methods and procedures used to acquire TG-MS, SEM, BET (CO<sub>2</sub> gas adsorption) and chemical-mineralogy results.

**3.1 Introduction**

Environmental investigations make use of modern analytical tools, which are applied in the industry and all branches of chemistry [Skoog *et al.*, 2004]. Analytical methods that provide reliable and comparable data are needed for important information on fuels for which the demands increase continuously [Swanson and Huffman, 1976]. These tools enable scientists to analyse and conduct research with the purpose of determining characteristics such as thermal decomposition, mass fragmentation, elemental composition, mineral structure, high magnification distribution of mineral grains and surface areas of fuels prepared at specific temperatures. The results obtained from these methods will help in the investigation to fulfil specific requirements and serve as future reference [Schweinfurth, 2003].

**3.2 Materials****3.2.1 Coal and Biomass**

Umlalazi coal (< 75 µm particle size) from the Witbank coalfield in South Africa was used in this study. This coal is characterised as a bituminous medium grade B coal. The biomass feedstock (< 75 µm particle size) used for the study was chosen based on the availability of the resource due to seasonal limitations. The Sappi Forest Division Company supplied the following biomass materials: (1) soft woodchip (SWC), (2) hard woodchip (HWC) and (3) pine wood chip (PWC). TsB Sugar Company supplied the sugar cane bagasse (SB).

**3.3 Fuel preparation****3.3.1 Sample characterisation**

The char samples (coal, biomass and their blends) obtained from the tube furnace were subjected to different analyses, which included structural, chemical and mineralogical analyses as summarised in Chapter 4. The ligno-cellulosic content analyses of the biomass samples (e.g., cellulose and metals present) are summarised in Chapter 4.

### 3.3.2 Crushing process

Coal samples (Small Nut) were pre-ground to less than 3 mm using a jaw crusher (Samuel Osborne (SA) LTD, Model: 66YROLL) and a grinder mill (Usborn Coalequip. Engineering (PTY) LTD. Speed: 425 rpm. Size: 4x6 macro crusher. Model number: 46-126) prior to ball milling. Biomass chips were chopped into smaller sizes using a hammer mill: TRF-70 (Figure 3.1. a). The laboratory ball mill with stainless steel balls (Figure 3.1.b) was used on all materials to grind samples to fine powders. The sieving instrument (Fritsch, serial: 00.6020 / 00506) in Figure 3.1.c was used to separate samples according to their particle sizes. The fraction of the samples with sizes of  $<75\ \mu\text{m}$  was used for the reported research.



a) Hammer mill

b) Ball mill

c) Sieving instrument

Figure 3.1: Illustration of crushing and separation techniques used on coal and biomass samples

### 3.4 Reactant Gas

Pyrolysis conditions require the absence of reactive gases such as oxygen. The inert gas nitrogen ( $\text{N}_2$ ), with an ultra-high purity of more than 99.999%, was chosen for preparation of the chars. For the  $\text{CO}_2$  gas adsorption (Brunauer-Emmet-Teller (BET)) analysis (using Micrometrics ASAP 2010 analyser), carbon dioxide ( $\text{CO}_2$ ) gas was used to conduct  $\text{CO}_2$  adsorption experiments on the entire parent and char samples ( $< 75\ \mu\text{m}$  particle size). Both nitrogen and carbon dioxide gas cylinders were provided by African Oxygen Limited (Afrox).

### 3.5 Reagents

Reagents used for ligno-cellulosic extraction procedure were supplied by ACE (associated chemical enterprise), which includes sodium hydroxide ( $\text{NaOH}$ ), 38% hydrochloric acid ( $\text{HCl}$ ) and ethanol ( $\text{C}_2\text{H}_6\text{O}$ ).

### 3.5.1 Ligno-cellulosic materials

The cellulose used for the study was extracted from the softwood chips and the lignin was extracted from sugarcane bagasse. The particle size of both softwood chips and the lignin used to extract cellulose and lignin was less than 75  $\mu\text{m}$ .

### 3.5.2 Ligno-cellulosic extraction procedure

The two ligno-cellulosic fractions were extracted using sodium hydroxide (NaOH) and ethanol solutions by the modified method previously described by Xue *et al.*, 2010 and Sun *et al.*, 2012. A 5 g sample (< 75  $\mu\text{m}$  particle size) was weighed using scientech model ZSP-250 balance and it was selected because the procedure from the literature also used 5 g, such the required fraction is separated successfully. The extraction was done in an Erlenmeyer flask using 1% NaOH solution with a biomass to liquid ratio of 1:25. The samples were heated in a microwave on high for 5 minutes before they were filtered. The solid residue contained the cellulose fraction. The filtrate was washed (to purify it) and neutralised to pH 5.5 (the pH meter used is the Hanna HI Model 9025, the pH meter was used to check neutralisation) with 6 M hydrochloric acid (HCl). The filtrate was concentrated to about 5 mL using a rotary evaporator (BUTCHI RII SN-1000102313, rotation 0-10 rpm and temperature of 20-100  $^{\circ}\text{C}$ ) under reduced pressure. The concentrated liquor was then precipitated in 3 volumes of 95% ethanol (15 mL) and filtered. The filtered solid residue contained the hemicellulose fraction. The filtrate containing the ethanol-soluble liquor was concentrated under reduced pressure (~4 mL) and adjusted to a pH of 1.5-2 with 6 M HCl. The solution was centrifuged at 100 rpm for 5 minutes, and afterwards washed with acidified water (pH 2.0), in order to purify it. The final precipitated residue represented the lignin fraction.

### 3.6 Sample characterisation analyses

A summary of laboratories responsible for some analyses conducted on the samples as shown in Table 3.1. Analyses of samples were at least duplicated for consistency of the produced data.

Table 3.1: Characterisation analyses conducted on coal, biomass, and their blends

| Analysis                   | Property        | Laboratory responsible              |
|----------------------------|-----------------|-------------------------------------|
| Chemical and Mineralogical | Proximate       | Inspectorate M & L (PTY) LTD        |
|                            | Ultimate        | Inspectorate M & L (PTY) LTD        |
|                            | Calorific value | Inspectorate M & L (PTY) LTD        |
|                            | Total sulphur   | Inspectorate M & L (PTY) LTD        |
|                            | Ash (XRF)       | Inspectorate M & L (PTY) LTD        |
|                            | Mineral (XRD)   | XRD Analytical and Consulting cc    |
|                            | Biomass content | Agricultural Research council (ARC) |

The description of standard methods used to conduct analyses is provided in **Appendix A.1**.

### 3.7 Characterisation techniques and apparatus

The methods used to investigate the influence of biomass additions on coal's degradation process during pyrolysis include the thermogravimetric analyses (TGA), mass spectrometer (MS), tube furnace, scanning electron microscopy (SEM), BET (Brunauer-Emmet-Teller) surface area analysis, proximate analysis, calorific value (CV) determination, ultimate analysis, x-ray fluorescence (XRF) and x-ray diffraction (XRD) analyses.

#### 3.7.1 Chemical-mineralogy analyses

A summary of standard methods used for some chemical and mineralogical analyses is shown in Table 3.2. Table 3.3 shows the specific instruments used by Inspectorate M & L (PTY) LTD to analyse the char samples.

Table 3.2: Standard methods used for chemical and mineralogical analyses conducted on samples

| Property        | Analysis                   | Standard Method |
|-----------------|----------------------------|-----------------|
| Proximate       | Inherent moisture          | SANS 5925       |
|                 | Ash                        | ISO 1171        |
|                 | Volatile matter            | ISO 562         |
|                 | Fixed carbon               | By difference   |
| Ultimate        | Carbon, Hydrogen, Nitrogen | ASTM D 5373     |
| Calorific value |                            | ISO 1928        |
| Total sulphur   |                            | ASTM D 4239     |
| Ash (XRF)       |                            | ASTM 3682       |
| Biomass content | Moisture and minerals      | ASM 013         |
|                 | Ash                        | ASM 048         |
|                 | Neutral detergent fibre    | Outsourced      |
|                 | Gross energy               | ASM 053         |

Table 3.3: Specific instruments used to analyse the char samples

| Analysis              | Instrument                               |
|-----------------------|------------------------------------------|
| Moisture              | Mermmert air oven at 105°C               |
| Ash analysis          | Lenton ISO ash furnace from 0°C TO 815°C |
| Volatile matter       | Lenton ISO volatile furnace at 900°C     |
| Total sulfur          | Eltra CS500                              |
| Ultimate analysis     | Leco truspec                             |
| Calorific value       | Parr 6300                                |
| Full ash constituents | Varian spectrometer - wet chemistry      |

### 3.7.2 Proximate analysis

The proximate analysis is one of the most important analyses in coal and biomass usage and research [Senneca, 2007; Badenhorst, 2009, Schobert *et al.*, 2011; Carrier *et al.*, 2012]. The results obtained from this technique have many uses in the characterisation of the various fuels. There is an observed mass loss in the form of water being driven off and gas evolution when a sample is heated to 950 °C. These emitted compounds are lumped together under the term volatile matter, and the remaining residue is the ash [Schobert *et al.*, 2011]. The proximate analysis is used to determine percentages of moisture, volatile matter, fixed carbon, and ash content in the material [Badenhorst, 2009]. The American Society for Testing and Materials (ASTM) governs the method used for proximate analysis [Schobert *et al.*, 2011; Badenhorst, 2009]. The proximate data can be calculated and presented according to different bases, which reflect the composition of the material ( i.e. as received (ar), air dried, moisture free, dry basis (db), ash free (daf), or dry, mineral matter free (dmmf)) [Miller, 2005; Schobert *et al.*, 2011]. The proximate and ultimate analyses were conducted according to the ASTM specified conditions listed in Table 3.2.

### 3.7.3 Ultimate analysis

The ultimate analysis is as important as the proximate analysis. The two analyses are always used for most coal related studies because they complement each other in the characterisation of the sample [Swanson and Huffman, 1976; Várhegyi *et al.*, 1998; Senneca, 2007]. The ultimate analysis is more comprehensive than the proximate analysis as it determines the elemental composition of fuels in terms of weight percentages of carbon, hydrogen, oxygen (by difference), sulphur and nitrogen [Várhegyi *et al.*, 1998; Levendis *et al.*, 2011; Schobert *et al.*, 2011; <http://www.astm.org>]. The carbon percentage determined includes the presence thereof as an organic substance and as a mineral. The hydrogen value includes the presence of hydrogen as an organic substance and in water associated with the fuel. The determination of sulfur includes the presence of sulfur in a form

as organic sulfur compounds, inorganic sulfates and as inorganic sulfides (mostly as iron sulfides; pyrite and marcasite) [Hashimoto *et al.*, 1986]. The remaining nitrogen is assumed to be part of the organic compounds found in the fuel [<http://www.astm.org>].

For proximate analysis, a sample was heated under controlled conditions while recording the mass loss as a function of temperature. Ultimate analysis was conducted by determining each element through chemical analysis and was expressed as a percentage of the total mass of the original sample [<http://www.sgs.co.za>].

#### **3.7.4 Calorific value**

The calorific value of solid fuel combustible samples is measured using an oxygen bomb calorimeter. This value serves as an indicator of the chemical energy stored in fuels and is important for assessing the efficiency of fuels [Shiraz *et al.*, 1995; Patel *et al.*, 2007]. The calorific value is defined as the amount of heat evolved when a unit weight of the fuel is burned completely and the combustion products cooled to a standard temperature of 298 K [Patel *et al.*, 2007]. The calorific value is usually expressed as gross calorific value using a bomb calorimeter.

A known weight of the sample (1.0 gram) was placed along an ignition wire inside a sealed pressurised bucket in a measured quantity of water [Hagen, 2012; <http://www.scimed.co.uk>]. To prevent loss of heat, an insulating jacket was used to cover the bucket. A thermometer was used to measure the change in temperature that arises during the combustion process. Combustion was facilitated by an electric current that passed through a fuse wire within the bomb.

#### **3.7.5 X-ray fluorescence (XRF)**

The XRF elemental analysis provides detailed information about the major and trace elemental concentration in fuels reported as their respective oxides [Nel, 2009; Skhonde, 2009]. The analysis also generates, detects, and measures X-rays simultaneously [Huggins, 2002]. The XRF, compared with SEM, is highly sensitive to the detection of major ash forming elements. The process involves bathing of a sample directly or an ash inside the radiation spectrum [Huggins, 2002]. This radiation is generated using an X-ray tube. An X-ray tube with chromium (Cr) or tungsten (W) is commonly used for analysis [Huggins, 2002]. The absorption of radiation occurs according to K-edge (excitation of 1s electron) or L-edge electron jumps [Huggins, 2002]. When excited atomic states start to decay to the ground state, it releases energy due to the change in energy between the two states. This energy is associated with characteristic X-rays for each individual element. The wavelength dispersive

(WDXRF) detector can be used to separate complex emitted x-ray spectra according to their wavelengths, and fits these spectra to known elements [Carlton, 2012a].

A char sample was calcined at 850 °C for 4 hours in an air atmosphere. The calcination was done to decompose carbonates and other compounds, and to remove all organic compounds and moisture from the sample [Matjie, 2008]. The calcined sample was converted into a solid solution by fusing it with lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) [Matjie, 2008]. A sample was placed in the XRF spectrometer to obtain the intensity of characteristic lines of each element. This test method instruction specifies the procedure for the determination of eleven major and minor constituents in coal ash by flame atomic absorption spectrometry.

### 3.7.6 X-ray diffraction (XRD)

The X-ray diffraction analysis makes it possible to determine crystalline mineral abundance, distribution, amorphous materials, and mineral associations [Quanta 250 manual, 2012]. X-ray crystalline powder diffraction (Figure 3.2) is an analytical tool used to determine mineral phases (crystalline material and amorphous carbon) present in a bulk sample using qualitative and quantitative analysis [Huggins, 2002; Matjie, 2008; Hattingh, 2009; Skhonde 2009; Carlton, 2012b]. For example, phase identification is achieved through comparison of peaks and relative intensities of specimen and standard data. This data is acquired from the International Center for Diffraction Data (ICDD) [Connolly, 2007]. The X-rays are generated in the cathode ray tube of the instrument, where the specimen is bombarded with electrons. A known wavelength of coherent beam of monochromatic X-rays is required for the analysis [Connolly, 2007]. Copper (Cu) is the most commonly used anode for characterisation of specific wavelengths of the specimen. Other commonly used X-ray generating tubes include cobalt (Co), Iron (Fe), chromium (Cr) and molybdenum (Mo) [Connolly, 2007].

Three types of radiation are produced in the tube, namely  $K_{\alpha 1}$ ,  $K_{\alpha 2}$  and  $K_{\beta}$  radiation [Connolly, 2007]. The mostly used radiation is  $K_{\alpha 1}$ . Connolly [2007] stated that  $K_{\beta}$  radiation is removed with a filter, monochromator or an energy-selective detector. During the data processing the  $K_{\alpha 2}$  radiation is electronically removed from the X-ray data [Connolly, 2007]. The X-ray scans are normally recorded at angles of 2-theta degrees, while rotating the sample [Huggins, 2002; Matjie, 2008; Hattingh, 2009; Skhonde 2009; Carlton, 2012b]. When the X-rays satisfy the Bragg equation, constructive peaks arise from the mineral matter associated with the sample [Carlton, 2012b]. The detector will process the incoming X-ray signals into a meaningful count rate and display the results in a meaningful way [Carlton, 2012b].

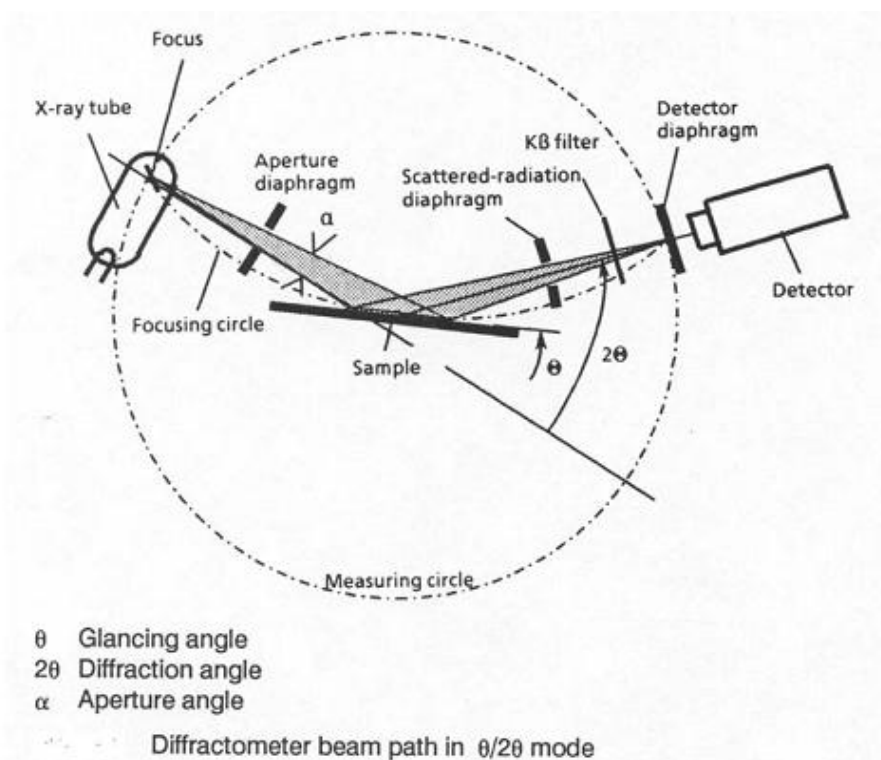


Figure 3.2 Schematic diagram of a diffractometer, adapted from Connolly [2007]

The fine powder char samples were transferred into sample holders made of aluminium alloy. The surplus sample was sliced off with a glass slide to approximately 50x70 mm and 5 mm thick, while simultaneously compressing the sample in the holder [Matjie, 2008]. The prepared sample was then loaded into the PANalytical X'Pert Pro diffractometer (Philips). The diffraction spectrum of each sample was measured. PANalytical Highscore plus analytical software and the Rietveld method were used for quantification of the relative phase amounts (wt. %) [Matjie, 2008; Hattingh, 2009]. The experimental parameters used for the analysis are shown in Table 3.4.

Table 3.4: The analysis settings and parameters used for XRD system

|                       |                                                                                                                |
|-----------------------|----------------------------------------------------------------------------------------------------------------|
| Goniometer            | PW3050/60 ( $\Theta/\Theta$ configuration)                                                                     |
| X-ray detector        | X'Celerator (Solid State, RTMS)                                                                                |
| X-ray tube            | Copper target, ceramics, LFF-type; $\lambda$ Cu $K\alpha$ = 1.5418 Å, $Kc(002)$ = 0.89 and $Ka$ (10/11) = 1.84 |
| Voltage               | 40 KV                                                                                                          |
| Amperage              | 40 mA                                                                                                          |
| Prog. Divergence Slit | 1.0° (fixed)                                                                                                   |
| Anti-scatter Slit     | 2.0°                                                                                                           |
| Scan from             | 5° 2 $\Theta$                                                                                                  |
| Scan to               | 135° 2 $\Theta$                                                                                                |
| Soller slits          | 0.02 Rad                                                                                                       |
| Scanning              | Continuous                                                                                                     |
| Duration of scan      | 6 - 14 hours                                                                                                   |

The aromaticity ( $f_a$ ) values were determined using the areas of the  $\gamma$ -side band ( $A_{002}$  and  $A_\gamma$ ) and  $d_{002}$  band [Lu *et al.*, 2001; Lu *et al.*, 2002; Okolo, 2010]. OriginPlus 8 data analysis software was used to calculate the aromaticity ( $f_a$ ) of chars under the areas of the bands, as shown in Figure 3.3. This was done by assuming  $A_{002}$  and  $A_\gamma$  to be equivalent to the number of aliphatic and aromatic carbon atoms [Lu *et al.*, 2001; 2002; Trejo *et al.*, 2007; Van Niekerk, 2008], where:

$$f_a = \frac{A_{d002}}{A_{d002} + A_\gamma} \quad 5.1$$

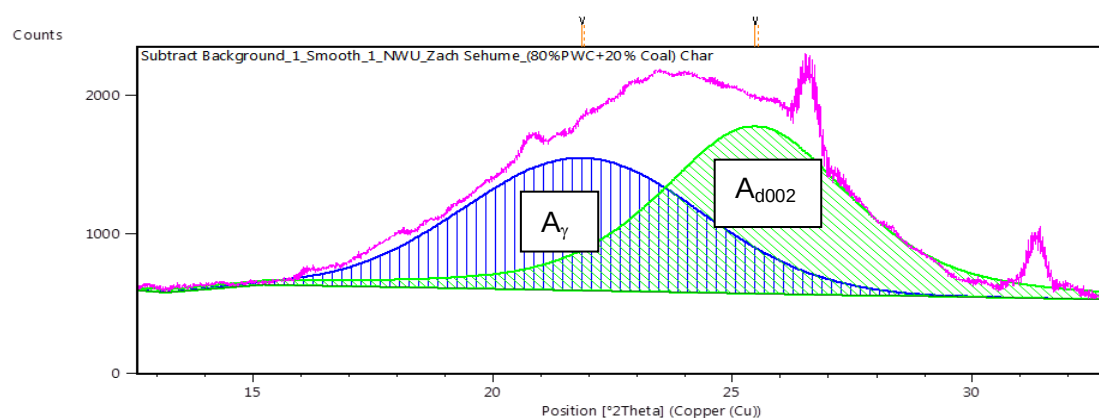


Figure 3.3: Determination of the areas under the  $\gamma$ -side band and  $d_{002}$  band using OriginPlus 8 data analysis software (i.e. 80% PWC + 20% Coal)

The average carbon crystallite factors for all of the char samples, such as interlayer distance between aromatic sheets ( $d_{002}$ ), crystallite height ( $L_c$ ), average crystallite diameter ( $L_a$ ), average number of aromatic layers per carbon crystallite ( $N_{ave}$ ), amorphous carbon ( $X_A$ ) and the degree of disorder index (DOI) were determined according to the following equations:

The interlayer spacing,  $d_{002}$ , was calculated from the maximum value of the (002) band according to Bragg's equation [Lu *et al.*, 2001; Van Niekerk, 2008]:

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad 5.1$$

The crystallite height ( $L_c$ ) and average crystallite diameter ( $L_a$ ), were determined using maximum peak value and full width at maximum (FWHM) of the (002) and (10) bands, however, the (11) band was not used due to its diffuse and obscure nature [Davis *et al.*, 1995; Lu *et al.*, 2001; Trejo *et al.*, 2007; Van Niekerk, 2008; Okolo, 2010]:

$$L_c = \frac{K\lambda}{\beta_{002} \cdot \cos \theta_{002}} \quad 5.2$$

$$L_c = \frac{K\lambda}{\beta_{10} \cdot \cos \theta_{10}} \quad 5.3$$

The average number of aromatic layers per carbon crystallite,  $N_{ave}$  [Trejo *et al.*, 2007; Van Niekerk, 2008]:

$$N_{ave} = \frac{L_c}{d_{002}} + 1 \quad 5.4$$

The fraction of amorphous carbon,  $X_A$ , was calculated from the areas under the Gaussian curves. It is assumed that  $X_A$  does not contribute to the X-ray intensity of the  $d_{002}$  band, but is only reflected in the reduced background [Franklin, 1951; Ergun and Tiensuu, 1959; Wu *et al.*, 2008; Lu *et al.*, 2001; Hattingh, 2012]:

$$X_A = \frac{S_A}{S_A + S_G} \quad 5.5$$

The degree of disorder index of the samples was calculated using the relation between the aromaticity and amorphous carbon [Lu *et al.*, 2002]:

$$DOI = X_A + (1 - X_A)(1 - f_a) \quad 5.6$$

### 3.7.7 Fractionation of biomass

The following methods were used by Agricultural Research council (ARC) laboratory in order to analyse the composition of the raw biomass feedstock. Standard methods were described in Section 3.7.1. Samples were heated at 550 °C overnight to determine the residue left (ash). The metallic element concentrations were determined as follows:

#### 3.7.7.1 Method for perchloric acid + nitric acid sample digestion:

0.5 g of freeze-dried and milled sample was digested with HNO<sub>3</sub> (conc. nitric acid) and HClO<sub>4</sub> (perchloric acid) at temperatures up to 200°C. All samples digested were in duplicate. (Adapted from Zasoski and Burau [1997]).

#### 3.7.7.2 Method for nitric acid only digestion:

HNO<sub>3</sub> (conc. nitric acid) was added to a freeze-dried and milled sample and heated (in an open glass digestion tube in a heating block) to 120°C (block temperature). After addition of 30% H<sub>2</sub>O<sub>2</sub> and distilled water, the samples were digested at this temperature for another 20 minutes before cooling. All samples digested were in duplicate. (Adapted from Huang and Schulte [1985]).

#### 3.7.7.3 ICP-OES Determination of magnesium (Mg), calcium (Ca), phosphorus (P), potassium (K), sodium (Na), and iron (Fe):

An aliquot of the digested solution was used for the ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) determination of these elements. The ICP-OES is a multi-element instrument that can determine all these elements effectively at the same time. The instrument used (Varian Liberty 200) is a sequential instrument, so the elements are not quite determined simultaneously, but almost so, with only a few seconds between each element, so that the sample may be analysed for all six elements in around two and a half minutes. Each element was measured at an appropriate emission wavelength, chosen for high sensitivity and lack of spectral interferences. The wavelengths used included: Mg: 383.826 nm; Ca: 422.673 & 317.933 nm; P: 213.618 nm; K: 769.896 nm; Na: 589.592 nm and Fe: 259.940 nm. (Adapted from Zasoski and Burau [1977]; Huang and Schulte [1985]).

### 3.7.8 Thermogravimetric analysis (TGA)

A SDTQ600 thermogravimetric analyser was used as an investigating tool as it provides information on the decomposition of the material (moisture and volatiles released), derivative mass loss (DTG), thermal degradation (during pyrolysis process), and the effect of purge gas used on the reactivity of the sample [Mohan *et al.*, 2006]. The thermogravimetric balance used, is a simultaneous differential thermal analyser (SDTA). The TG and differential scanning calorimetry (DSC) signals allow simultaneous determination of mass loss and calorimetric effects (e.g. melting point of a sample). Thermogravimetric analysis is a method that monitors the changes in the mass of a material as a function of temperature or time [Skoog *et al.*, 1999]. The TGA consists of a thermo balance, furnace, purge-gas inlet for controlled inert or reactive gas, and output system such as a computer for data acquisition [Skoog *et al.*, 1999]. The TGA can be used for both isothermal and non-isothermal studies.

#### 3.7.8.1 Thermo-balance

A very sensitive microbalance provides quantitative mass data in the TGA. The TGA uses alumina sample pans (ceramic cups) that can accommodate sample masses ranging from less than 1 mg to 200 mg (350 mg including sample holder). The mass balance (Figure 3.4) is able to detect changes in mass as little as 0.1  $\mu\text{g}$  (balance sensitivity) and the DTA sensitivity of 0.001  $^{\circ}\text{C}$ . The DSC noise level is below 4 mW and the calorimetric precision  $\pm 2\%$  (based on metal standards). The change in mass is observed due to a deflection of the beam, which generates current in a coil, and then restores the beam to its original position [Skoog *et al.*, 1999]. The mass loss curve of a sample occurs as the result of the water and volatile matter released by the sample [Rawson, 2012].

#### 3.7.8.2 Furnace

The SDTQ600 SDTA furnace is a bifilar wound type, which also accommodates a temperature range from ambient temperature up to 1500  $^{\circ}\text{C}$ . The certified calibration standards are based on curie point (curie temperature) or metal standards (1 to 5 points). The TGA also has heating rate of 0.1 to 100  $^{\circ}\text{C}/\text{min}$  (ambient to 1000  $^{\circ}\text{C}$ ) and 0.1 to 25  $^{\circ}\text{C}/\text{min}$  (ambient to 1500  $^{\circ}\text{C}$ ). The furnace requires insulation to prevent heat transfer to the balance, and nitrogen or argon gas is commonly used to prevent oxidation of the sample, where needed. Reactive gases (i.e.  $\text{CO}_2$ ) can also be introduced into the furnace as required during the thermal treatment of the sample [Skoog *et al.*, 1999]. The purge gas system provides better baselines with minimum buoyancy effects [<http://www.perkinelmer.com>].

### 3.7.8.3 Data acquisition

The experimental data recorded by the TGA reflects the actual temperature reading of the sample inside the furnace in real time, having a 0.5 second per point (sec/pt) data sampling interval. A computerised data acquisition and process control system generates electronic files and presents the results visually on the monitor.

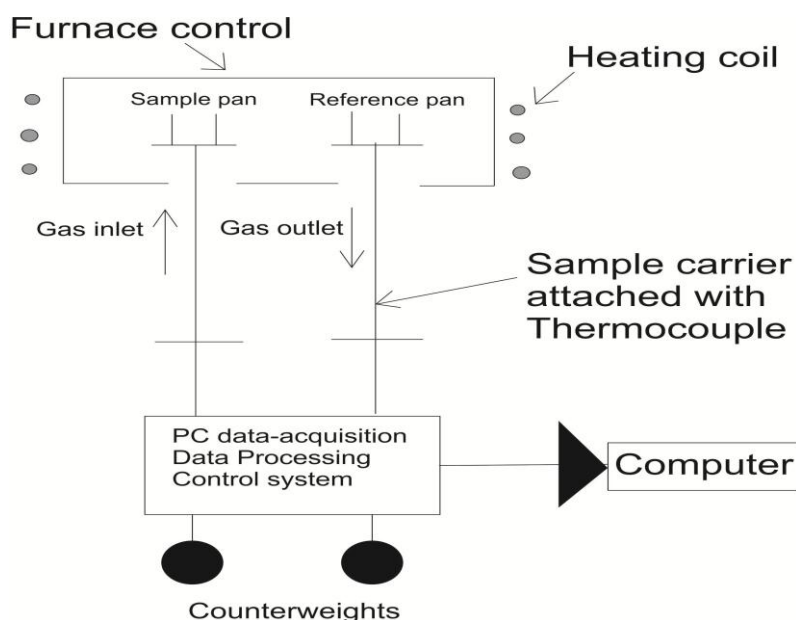


Figure 3.4: The thermo balance diagram [Skoog *et al.*, 1999; Rawson, 2012]

### 3.7.9 Mass spectrometer (MS)

An MKS Cirrus quadrupole mass spectrometer was coupled to the output of the TGA (TG-MS). The TG-MS analysis can be used to identify emitted gas species that are responsible for specific mass losses. The MS data can also be used to help interpret possible mechanisms of thermally induced reactions at various temperatures [Skoog *et al.*, 1999, Várhegyi *et al.*, 1998; Rubel *et al.*, 1992; Huggins, 2002; <http://www.henniker-scientific.com>]. The quadrupole MS can detect evolved gases in real time. However, it can be challenging to identify the gaseous species evolved, because the mass spectrum displays the fragmentation as a sum of all the emitted gas profiles [Rubel *et al.*, 1992]. The evolved gases were transferred from the TGA furnace to the MS through a heated inert silica capillary. The capillary temperature is set at  $\pm 200$  °C to prevent condensation of products that can result in blockage of the capillary line [Várhegyi *et al.*, 1998; <http://www.henniker-scientific.com>]. The rotary pump provides first-stage and second-stage pressure reduction. During the first stage, a desired viscous flow is attained for a faster transfer. For the second stage of pressure reduction, a clean sample entry and low operating pressure was reached

through the molecular leak valve [Raj *et al.*, 2003]. The MS consists of three main components, which are the ionization source, the analyser and the detector [Ashcroft, 1998].

### 3.7.9.1 Ionization source

Nearly simultaneous analyses of the TG and MS data are made possible through gases being transferred through a very short heated capillary line (200 °C). To prevent blockage of the capillary line, small sample size of approximately 25 mg with high flow rate 100 ml/min of nitrogen gas (easily flush sample molecules from the TG outlet into the MS instrument) was used. Sample molecules are ionised in the ion source to form ions [McLafferty and Tureček, 1993; Bottom, 2008]. The MKS Cirrus quadrupole mass spectrometer has a hard ionisation mode for complex molecules. The hard ionisation mode refers to a process where chemical bonds are broken and formation of ions occurs. Components of a sample are bombarded with electrons, photons, ions, or molecules to produce gaseous ions [Skoog *et al.*, 1999; Henniker-scientific, 2012]. The ions formed (positive, molecular and fragmented) are then distinguished according to their different mass-to-charge ratios ( $m/z$ ) through a combination of magnetic and electrostatic fields [Bottom, 2008]. Most quadrupole mass spectrometers use a default electron energy set to 70 eV, because this value is close to the maximum value needed to ionise most gaseous species. However, interference of multiple ionisation and dissociative ionisation can occur, in addition to direct ionisation [<http://www.henniker-scientific.com>]. The measured gaseous species consist of streams of positive ions that are accelerated into the mass analyser [Skoog *et al.*, 1999].

Direct ionisation:  $AB + e^- \rightarrow AB^+ + 2e^-$

Multiple ionisation:  $A + e^- \rightarrow A^{2+} + 3e^-$

Dissociative ionisation:  $AB + e^- \rightarrow A + B^+ + 2e^-$  or  $A^+ + B + 2e^-$

### 3.7.9.2 Analyser

The evolved gases from the TG outlet enter the MS through a heated (200 °C) stainless steel capillary line, after which the molecules are ionised to form fragmented ions. The fragmented ions are collected in the analyser (Figure 3.5), where separation occurs according to their mass ( $m$ ) to charge ( $z$ ) ratios ( $m/z$ ) [Ashcroft, 1998]. The MKS Cirrus MS has a triple mass filter that can detect atomic mass in the range of 1 to 200 amu [Cirrus-manual, 2011]. The MS quadrupole analyser is very sensitive and reliable, and it can manage high amounts of gaseous evolved species [Ashcroft, 1998]. The quadrupole MS has pairs of opposite rods that are driven by a combination of direct current (DC) and radio frequency. This combination enables the separation of relatively low energy ions with

different polarities [McLafferty and Tureček, 1993; Ashcroft, 1998]. Molecular ions will experience an electric field as they enter through the quadrupole assembly. This field will cause the ions to oscillate at a certain radio frequency [Ashcroft, 1998]. Only stable oscillations will proceed straight inside the quadrupole assembly and reach the highly sensitive dual (Faraday and secondary electron multiplier) detector system. The current Faraday sensitivity for the MS configuration (high electron energy) was  $1.50 \times 10^{-6}$  A/mbar. All of the other masses will be filtered out for successful separation of low masses [Ashcroft, 1998]. The recordings are displayed as spectra of the relative ion current or partial pressure of the detected ions per scan (1-50). The atoms or molecules in the sample can be identified by correlating known masses to the identified masses or through a characteristic fragmentation pattern.

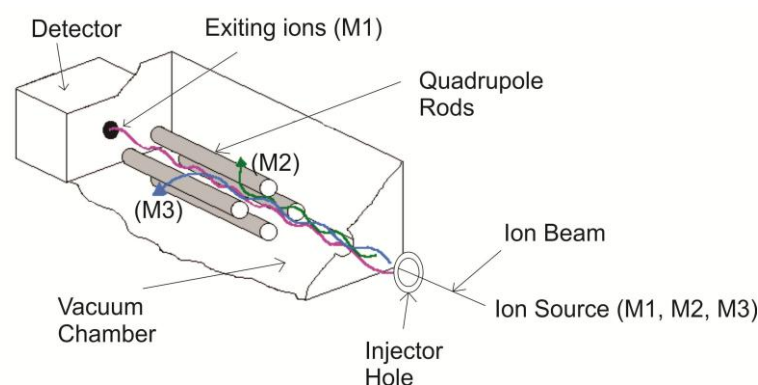


Figure 3.5: The quadrupole analyser adapted from the Cirrus-manual [2011]

### 3.7.9.3 Detector and data acquisition

The sole purpose of the detector (Figure 3.5) is to capture the filtered ion beams and convert them into small electrical currents. The electrical signals are then amplified by the electronics, and a process control system that displays the data as a trend line and/or bar chart view on the monitor [Cirrus-manual, 2011]. For data accuracy, the duration of each specific measurement was set to 1.9 seconds.

### 3.7.10 Sample preparation for experiments

The prepared biomass samples ( $<75 \mu\text{m}$ ) were dried in an oven at  $80^\circ\text{C}$  for a day to remove the moisture present in samples and stored in a desiccator flushed with nitrogen gas, in order to control the moisture content. A known weight percentage of oven-dried biomass (20%, 40%, 60% and 80%) based on mass was added to the air-dried coal ( $<75 \mu\text{m}$ ). For TG-MS experiments, the samples (coal and biomass) were blended together using a Wig-I-Bug as shown in Figure 3.6. The samples were mixed for 5 minutes to achieve good mixture. For further analysis which requires large sample (i.e. proximate analysis), the coal and

biomass feedstock were blended together in different ratios for five minutes using ball mill, as described in Section 3.3.2.



Figure 3.6: Wig-I-Bug grinding mill

#### **3.7.10.1 Thermogravimetric analysis coupled to mass spectrometer (TG-MS) experiments**

$\text{Al}_2\text{O}_3$  ceramic pans were used to load small masses of coal, biomass and blends ( $\pm 25$  mg) into the thermogravimetric analyser, in order to prevent blockage of capillary line to the MS. Small sample masses were also used to reduce the limiting effects of mass and heat transfer [Bliek *et al.*, 1985; Munir *et al.*, 2009]. TG runs were repeated to ensure reproducibility and to ensure good reliability of the results. The mass loss curves were recorded as a function of temperature and time during the thermal treatment of each sample run. A heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  was chosen for the study to allow even distribution of heat by means of conduction. Mass loss and derivative thermogravimetric curve (DTG) data of the samples was acquired while heating the samples from ambient temperature to  $1100\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  in a  $\text{N}_2$  atmosphere (carrier gas) with a flow rate of  $100\text{ ml}/\text{min}$  to prevent samples from oxidizing during the experiment.

The MKS quadrupole MS was coupled to the TGA (shown in Figure 3.7) to monitor gas evolution ( $\text{H}_2$  or  $2\text{ m/z}$ ,  $\text{CH}_3^+$  or  $15\text{ m/z}$ ,  $\text{H}_2\text{O}$  or  $18\text{ m/z}$  and  $\text{CO}_2$  or  $44\text{ m/z}$ ) while the sample undergoes thermal treatment. The evolution of the gas species were recorded in real time. The TG-MS coupling system was optimised by the supplier of these instruments. The MS utilizes standard electron energy with a dual Faraday and multiplier detector to detect maximum peak heights of  $4.4\text{e}+002$  pressure mbar. The data acquisition property of the MS was set to scan all masses from a first mass of 1 up to 50 atomic mass unit (amu). The results of the TG-MS (time, temperature, DTG and  $\text{m/z}$  of gas species) were transferred to

an Excel® file for data processing. The MS results could not be compared quantitatively due to varying intensities during pyrolysis as no internal standard was used. Semi-quantitative analysis of MS signals have been described by Arenillas *et al.* [1999] which describes the normalisation procedure. However, for this study only the shape and peak temperatures were used to give indications of which of the chosen gases form in specific temperature ranges [Arenillas *et al.*, 2003].



Figure 3.7: SDTQ 600 TGA coupled to MKS quadrupole MS

### 3.7.11 Tube furnace

The tube furnace was used to prepare chars from parent and blended materials, and to obtain enough of the chars to be sent for product characterisation [Senneca, 2007]. The furnace (model TSH12/75/610) has a maximum operating temperature of 1200 °C [Elite-user manual, 2011]. The tube furnace uses a single-zone wire wound type element, attached to a thermocouple. The thermocouple is located between the heating element and the outside of the work tube [Elite-user manual, 2011]. This allows the furnace to be efficient in heating the samples to the pre-determined temperatures. The ceramic pans (150 mm x 45 mm x 12 mm) were used to load a known sample mass into the centre of a tube furnace (Figure 3.8). The samples were then first flushed with N<sub>2</sub> for 10 minutes prior to heat treatment. The heating programme used to prepare chars was similar to the treatment of the samples in the TGA. A sample was heated to 1100 °C at 10 °C/min with a flow rate of 100 ml/min under N<sub>2</sub> atmosphere. After reaching the target temperature of 1100 °C, the furnace was programmed to cool stepwise to 25 °C and under nitrogen environment (duration of cooling time was ±6 hours).



Figure 3.8: The tube furnace used to collect larger volumes of products

### 3.7.12 Scanning electron microscopy (SEM)

Sample materials were analysed with SEM to study the external morphology of the surface. The SEM is often used in coal and biomass studies by numerous authors to obtain microstructural details [Senneca, 2007; Levendis *et al.*, 2011]. The name of the instrument used for SEM analysis is Quanta 250 field emission gun (FEG) scanning electron microscope with environmental scanning electron microscope (ESEM) capabilities. This analytical tool is able to characterise conductive and non-conductive samples with the optional beam deceleration mode. The Quanta series can produce a fast and accurate analysis due to stable high beam currents (up to 2  $\mu\text{A}$ ). The SEM is equipped with an energy dispersive X-ray spectrometer (EDS) accessory to provide elemental composition of samples. SEM images can also be used to determine particle shape, grain size distributions (densities and shape factors), and surface morphology (e.g., texture) [Quanta 250 manual, 2012]. Images of SEM are acquired through focusing a beam of electrons at an accelerating voltage of 30 kV. The beam of electrons causes an impact on the surface of the solid specimen and renders high-resolution pictures approaching one nanometre [Skoog *et al.*, 1999]. For simple measures, an analog scanning system (Figure 3.9) was used to provide a description of how the SEM acquires data. An analog scanning instrument uses scan coils that are able to scan across the sample in a raster scan [Skoog *et al.*, 1999]. The raster-scanner uses similar principles used in the cathode-ray tube (CRT) of a television set [Skoog *et al.*, 1999; Egerton, 2005]. The coils create a magnetic field in the y-direction, which creates a force on an electron (moving in the z-direction) and deflects it in the x-direction [Egerton, 2005]. Scanning systems generate signals using backscattered electrons, for which the signals are received above the surface (the z-direction). The signals are stored in the computer where they are converted into an image. The magnification (M) of the images

in SEM are obtained by making the x- and y-scan distances on the sample a small fraction of the size of the displayed image, where:  $M = (\text{scan distance in the image}) / (\text{scan distance on the sample})$  [Egerton, 2005].

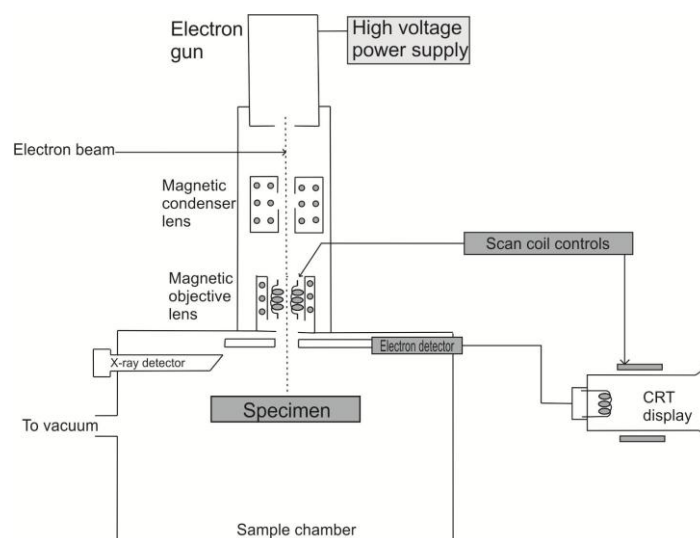


Figure 3.9: Schematic representation of an analog scanning system (SEM) adapted from Zubritsky [2002]

Carbon tape was used to mount samples on SEM pin stubs/holders. The carbon tape can distribute electrons and prevent reflection of electrons under the beam. The samples were kept as thin as possible on the carbon tape to avoid uneven distribution. Biomass samples were coated with a gold-palladium mixture (Au/Pd). The Au/Pd mixture increases the sample conductivity and prevents charging. Better images were also recorded in this case.

### 3.7.13 BET (Brunauer-Emmet-Teller) surface area analyser

A Micromeritics ASAP 2010 analyser (Figure 3.10) can provide adequate information about the surface areas and pore sizes of a sample. Physical characteristics, such as surface area and the porosity of samples, are important key parameters. These parameters are very helpful in determining the properties, behaviour, and performance of solid powder materials [Gregg and Sing, 1982]. The extent and rate of reactions are, among other factors, also controlled by the surface areas of the reactants [Senneca, 2007; Carrier *et al.*, 2012]. The surface analyser uses the BET theory to determine a specific surface area, expressed in units of area per mass of sample ( $\text{m}^2/\text{g}$ ), and micro pore volume ( $\text{cm}^3$ ) [Carrier *et al.*, 2012]. Gas adsorption refers to the ability of gas molecules to adhere/accumulate onto the surface of a solid material [Gregg and Sing, 1982]. Cracks or fissures that may be present deep within the specimen influence the internal surface of most solid structures. Indentation and superficial cracks can also influence the external surface [Malumbazo, 2011].



Figure 3.10: Surface area and porosity analyser

Figure 3.11 shows the schematic representation of the surface area analyser, which the BET theory is based upon. The BET theory is an extended and modified model for the Langmuir model. The Langmuir model provides an assumption that, on the surface of the solid, there exists fixed adsorption sites and only one gas molecule can be adsorbed at a single adsorption site [Brunauer *et al.*, 1938]. The model also assumes that the solid material's surface is energetically homogeneous, and that the adsorption energy is constant for all sites with no lateral interactions [Adiraju, 2010]. The use of the Langmuir model is limited for complex material (e.g. coal) where multilayer adsorption occurs. The surface of coal or char is not energetically homogeneous and it can lead to limited application with regard to determining the surface area using CO<sub>2</sub> adsorption [Adiraju, 2010]. The BET model assumes that the surface of the adsorbent is homogenous, and there are no interactions between molecules. The number of layers turn out to be infinite at saturation pressure and the heat of adsorption at the first layer is not the same at higher layers where heat of condensation can occur [Adiraju, 2010; Malumbazo, 2011]. The derived BET equations are given as [Brunauer *et al.*, 1938]:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0} \quad 3.1$$

Where,  $p_0$  and  $p$  are the initial and final saturation vapour pressures,  $v_m$  and  $v$  are the monolayer and final volumes, and  $c$  is a constant.

The specific surface area at lower relative pressures (from 0 to 0.35) is given as [Gregg and Sing, 1982]:

$$S = n_m A_m N \quad 3.2$$

Where,  $n_m$  is the monolayer capacity (mol/g),  $A_m$  is the monolayer area (m<sup>2</sup>/molecule) and  $N$  is Avogadro's number (molecules/mol).

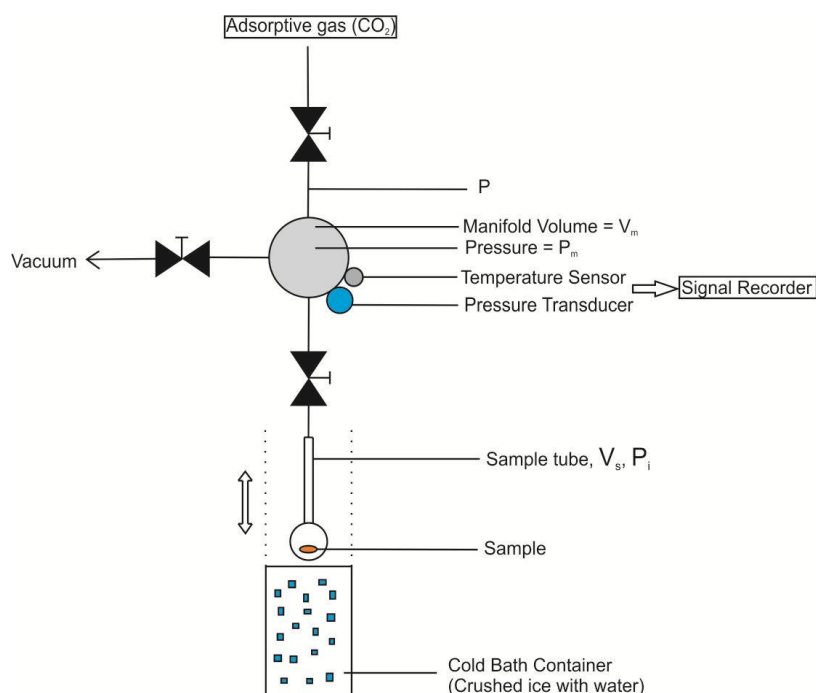


Figure 3.11: Schematic representation of the surface area analyser

### 3.7.13.1 Degassing of samples

A sample tube was filled with approximately 0.2 g of sample and securely fitted on the programmable station degas port. A thermal jacket was attached to the bottom of the sample tube to maintain a constant holding temperature. Raw samples were degassed at 30 °C, while char samples were degassed at 380 °C. As the char samples were prepared at 1100 °C, the structure of the samples will not change at 380 °C. All of the samples were degassed at a pressure of  $5.333\text{e-}1 \text{ N/m}^2$  for 48 hours.

### 3.7.13.2 Analysis of samples

For analysis conditions, carbon dioxide ( $\text{CO}_2$ ) was used as an adsorbent gas operated at 273.15 K, and crushed ice with water was used as cooling medium. The results (BET surface area determined from isotherm data and micropore surface area) were transferred to an Excel® file for data processing.

### 3.7.14 Experimental outline

The experiments and analyses (as summarised in Figure 3.12) were conducted in order to investigate the chemical and physical changes involved during heat treatment of the samples. The experiments and analyses were designed in such a way that they would comply with the aims and objectives of the study. Coal was mixed with selected biomass feedstock at various ratios. The representative sample was loaded into the TG-MS and tube furnace. The sample was subjected to a heat treatment under nitrogen atmosphere. The resulting char obtained from the tube furnace was further characterised using the analytical techniques discussed in this chapter.

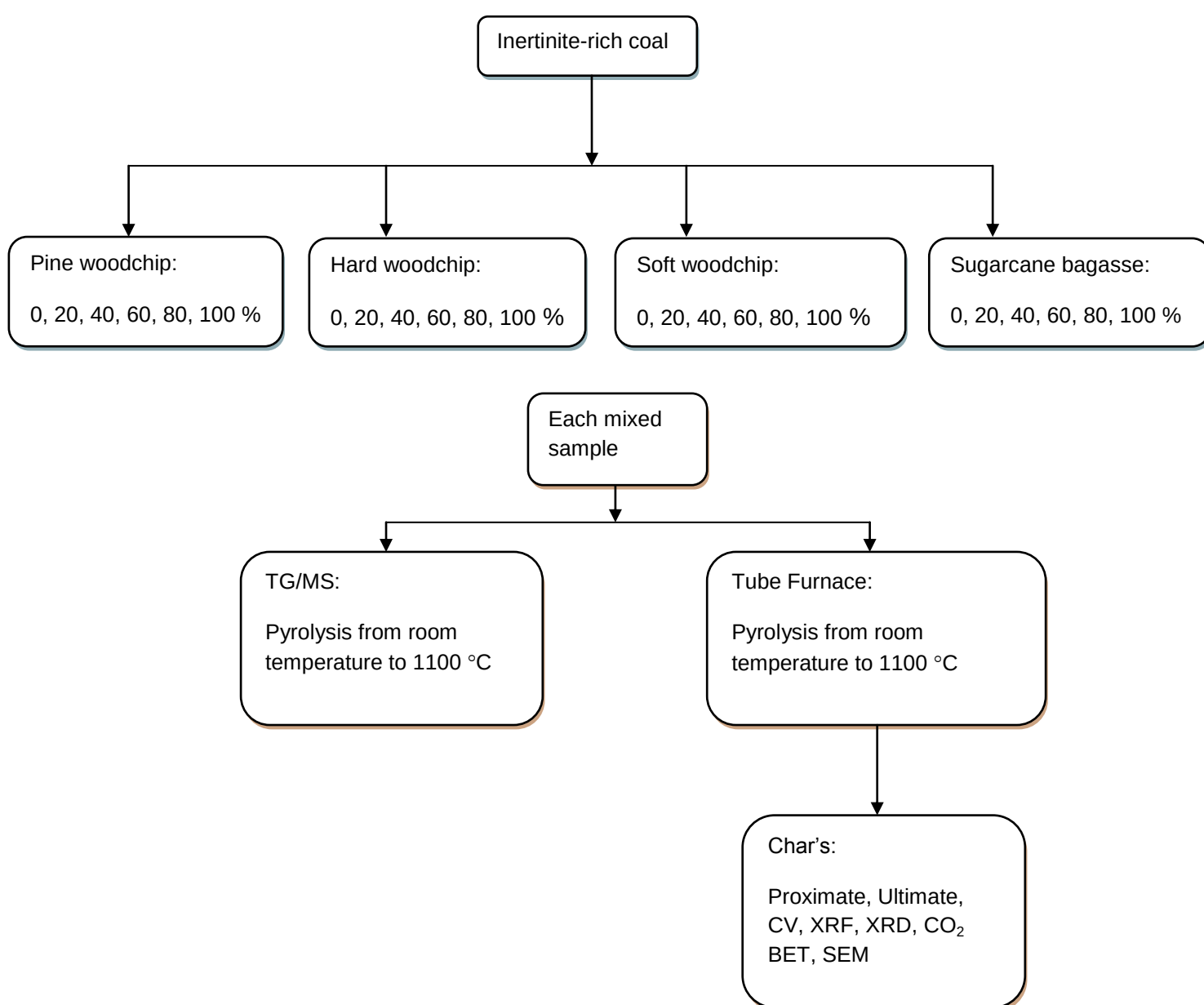


Figure 3.12: Experimental procedures outline diagram

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| <b>Chapter 4</b> |
|------------------|

**Characterisation of solid fuels: Results and Discussion**

The characterisation of coal, biomass, and coal-biomass blends were conducted in order to relate the state of these solid fuels with the fundamental coal/biomass properties. The conventional techniques described in Chapter 3 were used to perform both the chemical and physical analyses (proximate and ultimate analysis, biomass composition, XRD, XRF and CO<sub>2</sub> BET adsorption) of the samples.

**4.1 Results and Discussion****4.1.1 Blends of biomass and coal**

The samples of coal and biomass feedstock were pulverised as described in Section 3.3.2. Each sample was mixed with biomass to coal blending ratios in different batches of 0:100, 20:80, 40:60, 60:40, 80:20, and 100:20 (wt. %: wt. %) prior to charring. All of the characterisations were conducted on samples with a blending ratio of 80% biomass + 20% coal.

**4.1.2 Biomass composition**

A summary of the ligno-cellulosic compositions of the selected raw biomass feedstock used is given in Table 4.1. The analyses were done by ARC laboratories. The values obtained were determined as described in Section 3.7.7. SB contained a significantly larger content of ash (31.7 wt. %) in comparison to results reported by Bonelli *et al.* [2007] and Levendis *et al.* [2011] (3.1 and 4.0 wt. %, respectively). This value may be attributed to the inclusion of soil in the initial biomass samples based on the environmental conditions as well differences between species. The ash contents of HWC, SWC and PWC, were in the range of 0.2-0.5 wt. %, with PWC having the lowest ash content (0.2 wt. %). All of the values for woody biomass feedstock are within the general reported ash content value of below 1% for these types of biomass material [McKendry, 2002; Varol *et al.*, 2010; Nordgren *et al.*, 2013]. The differences in the chemical structures of cellulose, hemicellulose, and lignin have been reported to influence the chemical reactions [Carrier *et al.*, 2011b]. The cellulose content ranged between 27.8-39.9 wt. %, whilst the content for hemicellulose was in the range of 17.4-21.1 wt. %. The results are in agreement with the reported values for cellulose and hemicellulose, i.e. 40.0-60.0 wt. % and 20.0-40.0 wt. %, respectively [McKendry, 2002; Mohan *et al.*, 2006]. PWC contained the largest amount of lignin (32.4 wt. %) in comparison to the other biomass feedstock. Reeves *et al.*, [2002] observed that the ash can interfere with fibre composition of dried dairy manures, suggesting a relation between the lignin and

ash contents. If a biomass has a high lignin content, it is generally expected to find a high ash content when combusted or gasified, hence the drive to remove lignin prior to gasification. The dry matter and moisture contents of the biomass feedstock were: 42.7 wt. % for HWC; 18.6 wt. % for SWC; 10.7 wt. % for PWC and 11.3 wt. % for SB. The ASM 013 method described in the Appendix A.1 was used to measure dry matter and moisture content of biomass feedstock. The dry matter refers to the material remaining after removal of water, and the moisture content reflects the amount of water present in the feed ingredient. The dry matter (DM) content of a feed is determined by weighing a sample before and after complete drying. Since most of the weight lost during drying is water, the original sample contained certain amount of moisture (%).

Table 4.1: Ligno-cellulosic composition of biomass feedstock (before charring)

| Parameters (wt. %) - air dry basis* | HWC (hard woodchip) | SWC (soft woodchip) | PWC (pine woodchip) | SB (sugar cane bagasse) |
|-------------------------------------|---------------------|---------------------|---------------------|-------------------------|
| Ash                                 | 0.3                 | 0.5                 | 0.2                 | 31.7                    |
| Cellulose                           | 27.8                | 39.9                | 39.3                | 27.9                    |
| Hemicellulose                       | 21.1                | 20.5                | 17.4                | 21.1                    |
| Lignin                              | 8.1                 | 20.5                | 32.4                | 8.0                     |
| Dry matter and moisture             | 42.7                | 18.6                | 10.7                | 11.3                    |
| Total                               | 100.0               | 100.0               | 100.0               | 100.0                   |

\* Results were normalised

Table 4.2 lists the amounts of inorganic compounds found in the raw biomass feedstock as percentages of the metals present within the sample. This ICP analyses (in comparison to the XRF analysis (in Section 4.1.4)) were done in order to obtain the amounts of inorganic species present in the biomass prior to addition to coal. The values in Table 4.2 were determined as described in Section 3.7.7.3. These metallic compounds determine the ash characteristics (e.g. ash melting behaviour) in some thermo-chemical conversion processes [McKendry, 2002]. The Mg (8.8 wt. %), Ca (30.9 wt. %), P (9.4 wt. %), and K (20.0 wt. %) concentrations were higher in SWC than in the other biomass feedstock. These metallic compounds are considered essential plant macronutrients, as opposed to sodium [Carrier *et al.*, 2012]. From Table 4.2 it can be observed that HWC and PWC had very high Na contents, i.e. 64.2 wt. % and 41.3 wt. %, respectively. SB had the highest content of Fe (93.7 wt. %), followed by SWC, PWC and HWC with 20.4 wt. %, 9.0 wt. % and 0.9 wt. %, respectively. The four selected biomass feedstock differed in their levels of Na, Ca or Fe (wt. %). These inorganic matters present in biomass have been known to influence or catalyse gasification processes of coal [Brar *et al.*, 2012].

Table 4.2: Element concentration in the biomass feedstock (values are expressed as the percentage of the metal within the total sample, although the metals are present in inorganic combinations as well)

| Parameters (wt. %) - air dry basis | HWC         | SWC         | PWC         | SB          |
|------------------------------------|-------------|-------------|-------------|-------------|
| Magnesium (Mg)                     | 2.6         | 8.8         | 3.5         | 0.8         |
| <b>Calcium (Ca)</b>                | <b>17.1</b> | <b>30.9</b> | <b>11.7</b> | <b>1.4</b>  |
| Phosphorus (P)                     | 3.2         | 9.4         | 3.6         | 0.5         |
| Potassium (K)                      | 11.4        | 20.0        | 9.2         | 0.4         |
| <b>Sodium (Na)</b>                 | <b>64.2</b> | <b>4.7</b>  | <b>41.3</b> | <b>1.2</b>  |
| Manganese (Mn)                     | 0.4         | 5.0         | 19.3        | 1.5         |
| <b>Iron (Fe)</b>                   | <b>0.9</b>  | <b>20.4</b> | <b>9.0</b>  | <b>93.7</b> |
| Zinc (Zn)                          | 0.2         | 0.8         | 2.1         | 0.3         |
| Copper (Cu)                        | 0.0         | 0.2         | 0.3         | 0.2         |
| Total                              | 100.0       | 100.0       | 100.0       | 100.0       |

\* The high iron content in the SB sample probably due to inclusion of soil in initial sample

#### 4.1.3 Chemical analyses – proximate and ultimate analyses

The results of the chemical analyses conducted on the char samples prepared at 1100 °C, as well as the atomic ratios of hydrogen-carbon (H/C) and oxygen-carbon (O/C) are summarised in Table 4.3. From the results it can be seen that the inherent moisture content of the samples ranged between 2.4 to 3.4 wt. %. The coal, sugarcane bagasse and blend chars were characterised as having high ash contents of 18.3 wt. %, 45.8 and 50.8 wt. %, respectively. The ash content of the coal char was within reported values of 19.0-35.0 wt. % [Hattingh, 2009; Okolo, 2010; Aboyade *et al.*, 2012], while the ash content of the sugarcane bagasse chars was much higher than the values reported in literature to be in the range of 4-12.6 wt. % [Munir *et al.*, 2009; Levendis *et al.*, 2011; Aboyade *et al.*, 2012]. The high ash content value observed for the sugarcane bagasse char and 80% SB + 20% Coal char could be the inclusion of soil particles present during harvesting and environmental conditions [McKendry, 2002]. This increased ash value of the SB char sample tends to correspond to the elevated value observed in Table 4.1 for the SB sample (31.7 wt. %). The ash content of the other biomass chars are well within reported ranges, varying from 0.9-2.0 wt. % [Sami *et al.*, 2001; Senneca, 2007; Varol *et al.*, 2010]. The ash content values for 80 % biomass to 20 % coal char blends with HWC, SWC, PWC and SB were 10.7%, 9.5%, 9.0% and 50.8 wt. %, respectively. As expected, the chars prepared from the parent and blended materials were observed to have low volatile matter contents in the range of 0.7-2.4 wt. %. The volatiles of the coal char was comparable with all the biomass and coal-biomass chars except for 80%

SB + 20% Coal char. The low volatile matter content found for coal char was similar to that reported to be in the range of 0.8-3.2 wt. % by Hattingh [2009] and Okolo [2010]. The volatile matter content of coal char compared with the parent biomass chars was in the same range, with the exception of HWC and PWC chars which contained more volatiles. The residual volatile content has been stated to make biomass chars more reactive than lignite and hard coal for gasification purposes [Smolinski *et al.*, 2011]. The reported fixed carbon content in Table 4.3 was observed to be rather high for biomass chars (93.5-94.5 wt. % a.d.b) and coal-biomass chars (84.7-86.3 wt. % a.d.b) compared to the coal char (77.5 wt. % a.d.b) as general literature places the fixed carbon content of raw biomass around 15-20% [Sadhukhan *et al.*, 2008]. The 80% SB + 20% Coal and sugarcane chars had the lowest calorific values on an air dry basis of 16.0 MJ/kg and 17.4 MJ/kg, respectively. Channiwala and Parikh [2002] observed raw sugarcane bagasse to have a calorific value of 18.73 MJ/kg, which was comparable to that found for the biomass chars (16.0 MJ/kg and 17.4 MJ/kg). The high mineral matter content (reflected in the high ash content) of the SB biomass must have contributed to the observed lower calorific value for the SB containing samples and blends [Bonelli *et al.*, 2007]. The other chars had comparable higher calorific values in the range of 26.5-30.8 MJ/kg. Similar results were obtained by Hattingh [2009] and Varol *et al.* [2010] for coal and biomass. One of the possible reasons for the difference in the calorific values is that the higher the ash content, the lower the calorific value would be [Ebeling and Jenkins, 1985]. Ultimate analysis (daf) results showed that the samples were rich in carbon, with values in the range of 79.4-94.2 wt. %. Parent biomass chars and blended chars are richer in carbon than coal char. Sugarcane bagasse and 80% SB+ 20% Coal chars were observed to have the lowest carbon content of 48.3 and 45.7 wt. %, respectively. As expected, all of the char samples have low hydrogen contents in the range of 0.0-0.2 wt. % (daf). This can be attributed to organics rich in hydrogen that are released during the volatilisation and activation stages [Carrier *et al.*, 2012]. The nitrogen value decreased accordingly from coal to blend chars, with 1.1 wt. % (daf) for coal char, and HWC char having the lowest value of 0.4 wt. % (daf). Studies conducted by Hashimoto *et al.* [1986] and Senneca *et al.* [2001] stated that the oxygen content serves as an important factor in indicating the number of available free sites after devolatilisation. The oxygenated species that were considered as oxygen carriers are known to influence the devolatilisation process through secondary reactions [Senneca *et al.*, 2001]. The oxygen content of samples ranged from 19.0 wt. % for coal char, 50.9 wt. % for sugarcane bagasse char, 5.2-6.9 wt. % for woody chars and 11.9-53.2 wt. % for blends, with 80% SB + 20% Coal char having the highest oxygen content. These results suggest the char of 80% SB added to 20% coal was the most reactive blend compared with the other blends.

Table 4.3: Chemical analyses of coal, biomass and coal-biomass chars

| <b>Proximate analysis (Air dry basis)</b>  | Standard method | Coal char    | HWC char     | SWC char     | PWC char     | SB char      | (80% HWC + 20% Coal) char | (80% SWC + 20% Coal) char | (80% PWC + 20% Coal) char | (80% SB + 20% Coal) char |
|--------------------------------------------|-----------------|--------------|--------------|--------------|--------------|--------------|---------------------------|---------------------------|---------------------------|--------------------------|
| Inherent moisture (wt. %)                  | SANS 5925       | 2.4          | 2.9          | 2.8          | 3.1          | 2.9          | 3.4                       | 3.1                       | 2.8                       | 2.6                      |
| Ash (wt. %)                                | ISO 562         | 18.3         | 0.9          | 0.9          | 1.0          | 45.8         | 10.7                      | 9.5                       | 9.0                       | 50.8                     |
| Volatiles (wt. %)                          | ISO 1171        | 1.8          | 2.4          | 1.8          | 2.4          | 1.9          | 1.2                       | 1.3                       | 1.9                       | 0.7                      |
| Fixed Carbon (wt. %)                       | By difference   | 77.5         | 93.8         | 94.5         | 93.5         | 49.4         | 84.7                      | 86.1                      | 86.3                      | 45.9                     |
| <b>Total (wt. %)</b>                       |                 | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b>              | <b>100.0</b>              | <b>100.0</b>              | <b>100.0</b>             |
| <b>Gross Calorific Value (MJ/kg)</b>       | ISO 1928        | <b>26.5</b>  | <b>28.6</b>  | <b>30.8</b>  | <b>28.6</b>  | <b>17.4</b>  | <b>28.9</b>               | <b>28.5</b>               | <b>29.1</b>               | <b>16.0</b>              |
| <b>Ultimate analysis (daf)</b>             | ASTM D5373      |              |              |              |              |              |                           |                           |                           |                          |
| Carbon (wt. %)                             |                 | 79.4         | 93.6         | 92.4         | 94.2         | 48.3         | 86.8                      | 86.6                      | 84.8                      | 45.7                     |
| Hydrogen (wt. %)                           |                 | 0.1          | 0.1          | 0.2          | 0.1          | 0.2          | 0.2                       | 0.0                       | 0.2                       | 0.2                      |
| Nitrogen                                   |                 | 1.1          | 0.4          | 0.6          | 0.5          | 0.3          | 0.7                       | 0.7                       | 0.8                       | 0.7                      |
| Total Sulfur (wt. %)                       | ASTM D4239      | 0.4          | 0.0          | B.D.L        | 0.0          | 0.3          | 0.4                       | 0.2                       | 0.2                       | 0.2                      |
| Oxygen (wt. %)                             | By difference   | 19.0         | 6.0          | 6.9          | 5.2          | 50.9         | 11.9                      | 12.5                      | 14.0                      | 53.2                     |
| <b>Total (wt. %)</b>                       |                 | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b> | <b>100.0</b>              | <b>100.0</b>              | <b>100.0</b>              | <b>100.00</b>            |
| <b>Hydrogen / Carbon Ratio</b>             |                 | <b>0.02</b>  | <b>0.01</b>  | <b>0.02</b>  | <b>0.01</b>  | <b>0.05</b>  | <b>0.02</b>               | <b>0.00</b>               | <b>0.03</b>               | <b>0.06</b>              |
| <b>Oxygen / Carbon Ratio</b>               |                 | <b>0.18</b>  | <b>0.05</b>  | <b>0.06</b>  | <b>0.04</b>  | <b>0.79</b>  | <b>0.10</b>               | <b>0.11</b>               | <b>0.12</b>               | <b>0.87</b>              |
| <b>Fuel Ratio (Volatiles/Fixed Carbon)</b> |                 | <b>0.02</b>  | <b>0.03</b>  | <b>0.02</b>  | <b>0.03</b>  | <b>0.04</b>  | <b>0.01</b>               | <b>0.02</b>               | <b>0.02</b>               | <b>0.02</b>              |

The total sulfur of all samples were within reported values in the range of 0.0-0.4 wt. %, with the exception of SWC char for which the sulfur content was below detection limits [Hattingh, 2009; Biagini *et al.*, 2002; Varol *et al.*, 2010]. The low amounts of sulfur and nitrogen in solid fuels are desirable to reduce evolution of  $\text{SO}_x$  and  $\text{NO}_x$  gases during conversion processes [Pedersen *et al.*, 1996]. The efficiency of solid fuels depends on the fuel's atomic ratios [Lu *et al.*, 2001]. For instance, the aromaticity and the H/C and O/C ratios are major factors indicating the energy obtained from the fuels [Lu *et al.*, 2001]. The fuel ratios calculated from both proximate and ultimate analyses of the raw char materials were in the range of 0.02-0.04, more than blended samples (0.01-0.02), indicating high energy efficiency (and a similar trend was observed for calorific values of the samples). The H/C atomic ratios ranged from less than 0.01 to 0.06. The O/C atomic ratios of all samples were in the range between 0.04-0.79, with PWC char having the lowest value. From these results, it is evident that the SB and 80% SB + 20% coal samples showed the lowest energy efficiency compared to the other blended samples.

#### 4.1.4 Ash analysis of coal, biomass and coal–biomass blend chars (XRF)

The amounts of inorganic components expressed as oxides in the ash of various chars are given in Table 4.4. The ash composition of samples has been found to vary considerably [Christian *et al.*, 2006]. The samples of coal and biomass were analysed as described in Section 3.7.5. All the ash formed from coal, biomass, and blended chars were observed to contain an abundance of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , in the ranges of 49.0-58.0 wt. % and 25.4-32.5 wt. %, respectively. These oxides confirm the presence of clay minerals in the form of kaolinite and quartz in the samples [Hattingh, 2009; Okolo, 2010].

The SB char ash contained a high amount of 10.1 wt. %  $\text{Fe}_2\text{O}_3$ , with the PWC char containing the lowest amount of  $\text{Fe}_2\text{O}_3$  (1.3 wt. %). From these results, the presence of  $\text{Fe}_2\text{O}_3$  could be possibly due to pyrite, siderite, troilite and alpha iron identified in the samples. SWC char contained the highest amount of CaO (1.9 wt. %), MgO (1.1 wt. %),  $\text{Na}_2\text{O}$  (0.9 wt. %) and  $\text{K}_2\text{O}$  (1.22 wt. %) in comparison to other char samples of coal and biomass. CaO and MgO seem to be found in larger proportions in the ashes of the 80% HWC + 20% Coal and 80% SWC + 20% Coal chars, 5.28 wt. % and 2.5 wt. %, respectively. The 80% SWC + 20% Coal char contained large amounts of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  (1.0 wt. % and 1.1 wt. %, respectively) compared with other blended char samples. The alkali elemental compounds (reported as CaO, MgO,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$ ) have been found to have a catalytic effect on the coal's degradation during gasification [McKendry, 2002].

Table 4.4: Chemical composition of char samples expressed as oxides (XRF analyses)  
(Values are given as percentages of oxides in the total inorganic matter left)

|                                                    | Coal<br>char    | HWC<br>char     | SWC<br>char     | PWC<br>char     | SB<br>char      | (80%<br>HWC<br>+ 20%<br>Coal)<br>char | (80%<br>SWC<br>+ 20%<br>Coal)<br>char | (80%<br>PWC<br>+ 20%<br>Coal)<br>char | (80%<br>SB +<br>20%<br>Coal)<br>char |
|----------------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------------------------------|---------------------------------------|---------------------------------------|--------------------------------------|
| Inorganic<br>Species                               | Wt.%<br>(a.d.b) | Wt.%<br>(a.d.b) | Wt.%<br>(a.d.b) | Wt.%<br>(a.d.b) | Wt.%<br>(a.d.b) | Wt.%<br>(a.d.b)                       | Wt.%<br>(a.d.b)                       | Wt.%<br>(a.d.b)                       | Wt.%<br>(a.d.b)                      |
| <b>Silica<br/>(SiO<sub>2</sub>)</b>                | <b>54.2</b>     | <b>58.0</b>     | <b>54.5</b>     | <b>53.7</b>     | <b>56.2</b>     | <b>49.0</b>                           | <b>52.2</b>                           | <b>50.2</b>                           | <b>49.9</b>                          |
| <b>Aluminium<br/>(Al<sub>2</sub>O<sub>3</sub>)</b> | <b>28.2</b>     | <b>29.1</b>     | <b>30.6</b>     | <b>30.2</b>     | <b>25.4</b>     | <b>29.6</b>                           | <b>29.5</b>                           | <b>32.5</b>                           | <b>29.5</b>                          |
| Iron (Fe <sub>2</sub> O <sub>3</sub> )             | 1.8             | 2.3             | 2.5             | 1.3             | 10.1            | 5.2                                   | 7.3                                   | 1.5                                   | 2.2                                  |
| Titanium<br>(TiO <sub>2</sub> )                    | 1.4             | 1.3             | 1.2             | 1.3             | 1.2             | 1.5                                   | 1.9                                   | 1.3                                   | 2.1                                  |
| Phosphorus<br>(P <sub>2</sub> O <sub>5</sub> )     | 1.5             | 0.3             | 0.3             | 0.4             | 1.3             | 1.5                                   | 0.5                                   | 1.6                                   | 1.4                                  |
| Calcium<br>(CaO)                                   | 4.3             | 1.9             | 1.1             | 2.5             | 0.9             | 5.3                                   | 1.2                                   | 3.4                                   | 7.6                                  |
| Magnesium<br>(MgO)                                 | 1.0             | 1.1             | 1.1             | 1.0             | 1.1             | 0.9                                   | 2.5                                   | 2.4                                   | 1.9                                  |
| Sodium<br>(Na <sub>2</sub> O)                      | 0.1             | 0.2             | 0.9             | 0.2             | 0.9             | 0.1                                   | 1.0                                   | 0.2                                   | 0.5                                  |
| Potassium<br>(K <sub>2</sub> O)                    | 0.6             | 1.0             | 1.2             | 0.9             | 1.6             | 1.1                                   | 1.1                                   | 1.0                                   | 0.9                                  |
| Sulfur<br>(SO <sub>3</sub> )                       | 6.2             | 3.0             | 5.8             | 6.9             | 0.2             | 6.8                                   | 1.0                                   | 4.6                                   | 3.7                                  |
| Un-<br>identified                                  | 0.8             | 1.8             | 0.9             | 1.6             | 1.1             | 0.9                                   | 1.9                                   | 1.3                                   | 0.5                                  |
| <b>Total</b>                                       | <b>100.0</b>    | <b>100.0</b>    | <b>100.0</b>    | <b>100.0</b>    | <b>100.0</b>    | <b>101.8</b>                          | <b>100.0</b>                          | <b>100.0</b>                          | <b>100.0</b>                         |

#### 4.1.5 X-Ray diffraction (carbon crystallite) analysis

Figure 4.1 and Figure 4.2 show the raw X-ray diffractograms (corrected for geometrical effects and polarisation) obtained for the various chars (described in Section 3.7.6). The analysis was conducted in order to acquire structural information on the crystalline part of the samples. The high background intensity may have been caused by the fact that samples were not demineralised and not all the carbon present is in aromatic form, but also found in amorphous form [Hattingh, 2009]. The observed baseline of the graphs was due to the sample pan and had to be corrected using the OriginPro 8 peak analysis tool.

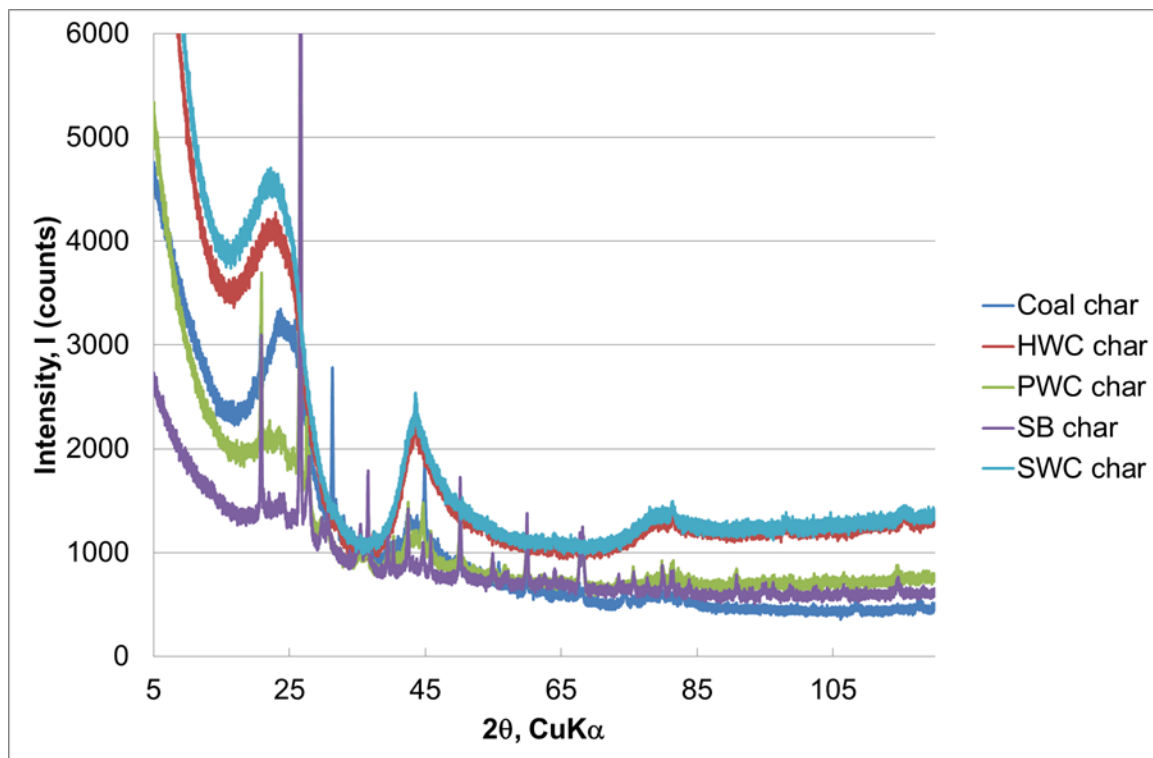


Figure 4.1 Diffractograms of coal and biomass chars

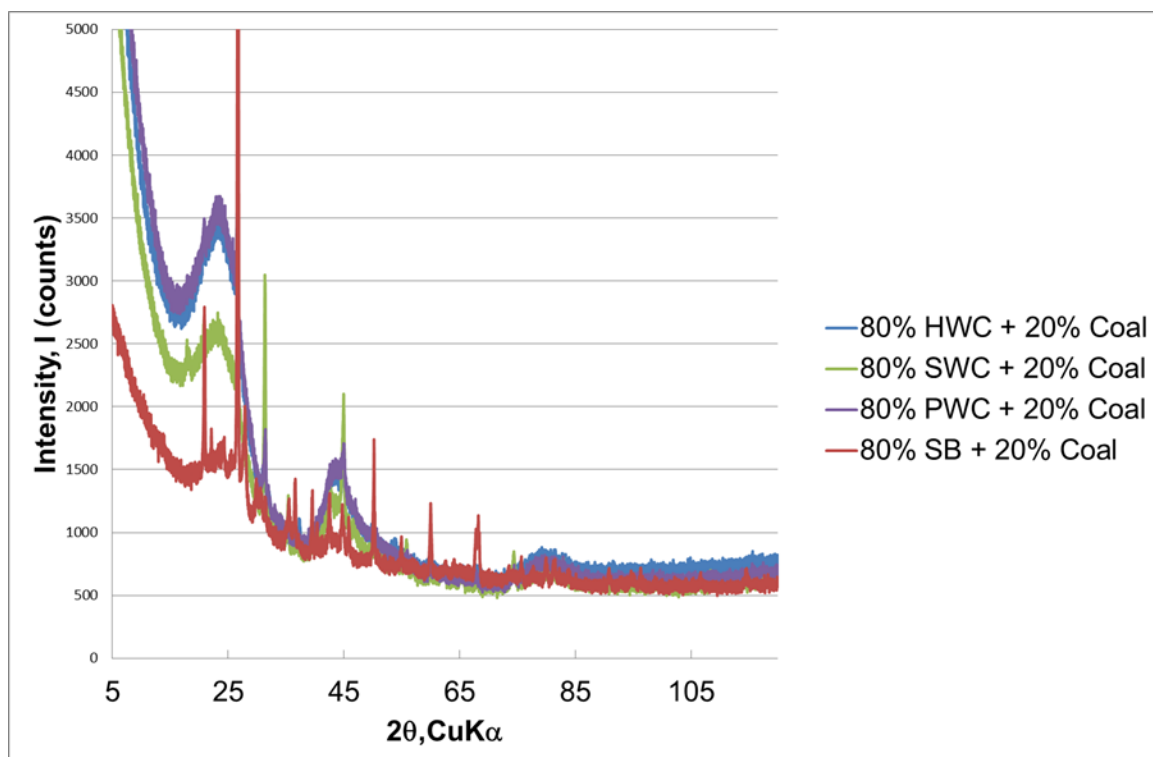
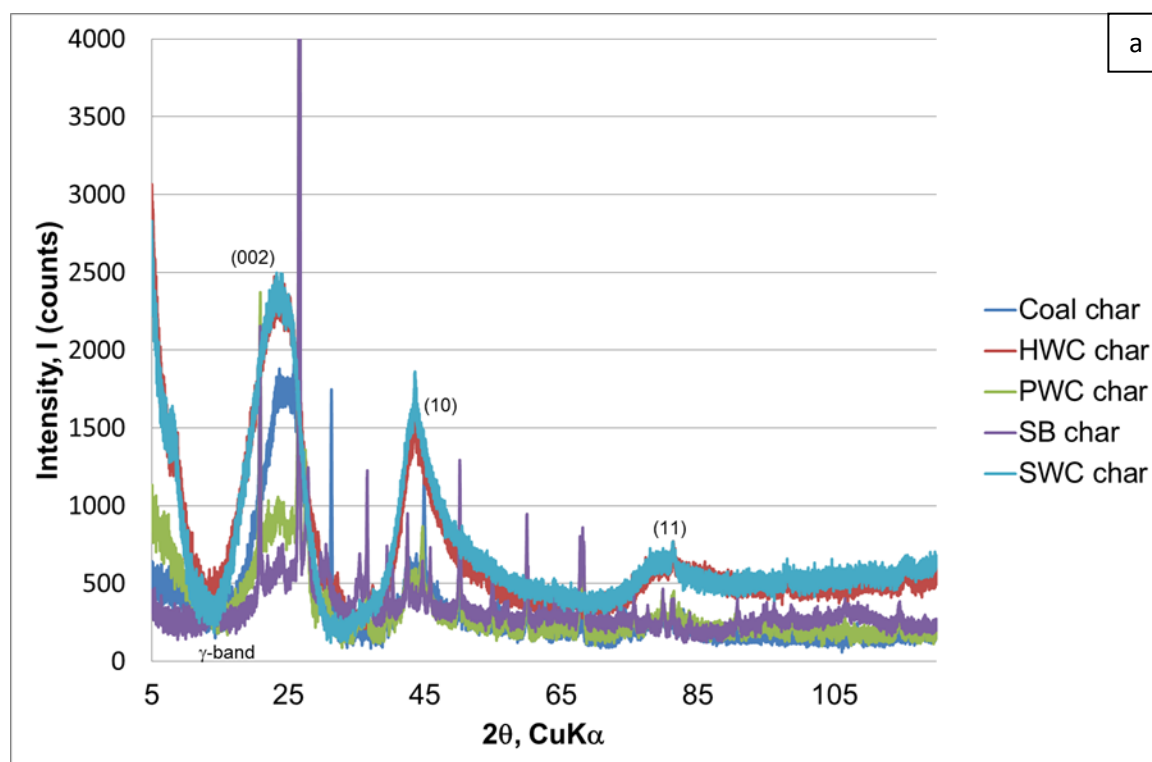


Figure 4.2 Raw diffractogram of coal-biomass blend chars

It can be seen from Figure 4.3 that the small peaks (noise) observed for SB char and 80% SB + 20% Coal char throughout the  $2\theta$  axis are more likely to be caused by the inorganic matter (i.e. quartz) present in the biomass.

Figure 4.3 shows broad, diffused peaks observed at  $2\theta$  between  $23^\circ$  and  $80^\circ$  for both parent chars and blend chars [Sharma *et al.*, 2000]. The broad peaks between  $23^\circ$  and  $38^\circ$  show graphitic properties established by the presence of  $d_{002}$  peaks, indicating graphite presence in the sample. This graphite band may be due to the structural re-ordering, re-orientation and closed stacking of the aromatic carbon layers [Sharma *et al.*, 2000; Okolo, 2010]. The sharp peak positions that relate to (10) and (11) peaks possibly indicate the presence of crystalline features. The intensity of HWC and SWC chars seem to be higher than that of the coal char and blended char in terms of the (002), (10) and (11) bands, this high intensity may suggest that HWC and SWC chars were more graphitic than coal at high temperatures. SB and 80% SB + 20% Coal chars showed the lowest intensity of the bands (002) and (11).



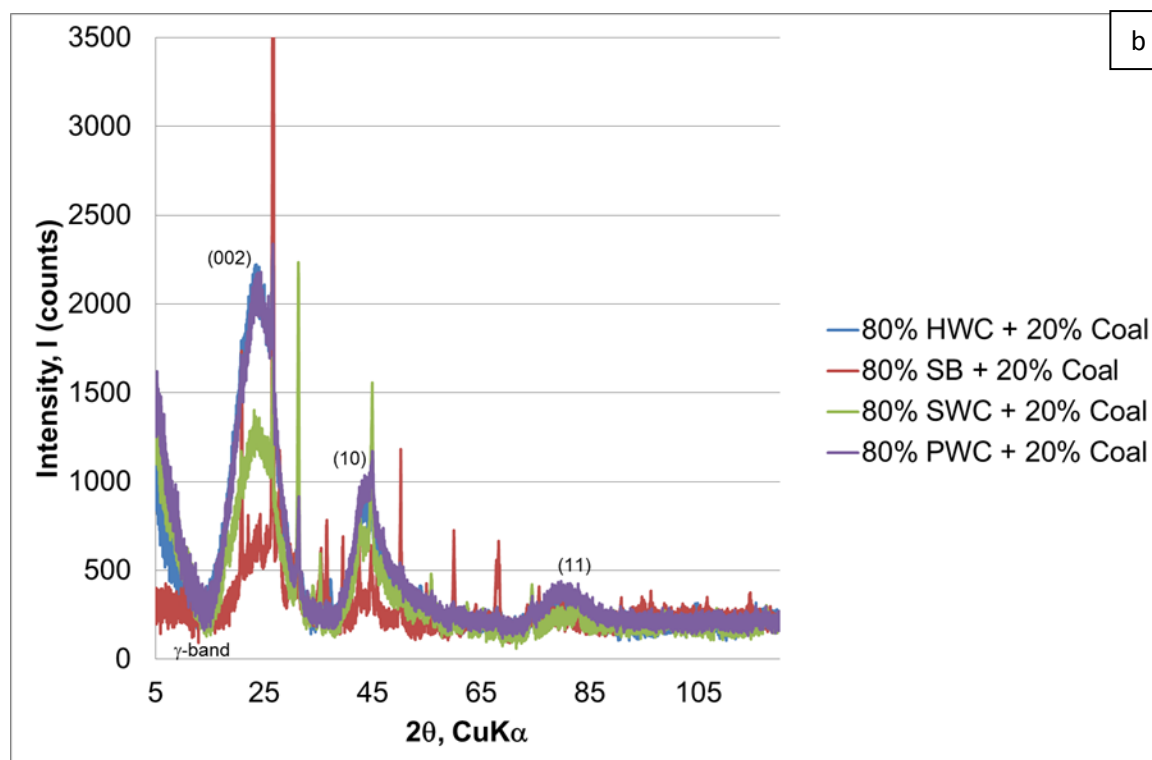


Figure 4.3: Diffractograms of corrected baseline of (a) coal, biomasses and (b) coal – biomass blend chars

Table 4.5 shows a summary of the XRD characteristic values calculated for the chars. The areas of the  $\gamma$ -side band and  $d_{002}$  band were too small to calculate the aromaticity and other parameters for the SB and 80% SB + 20% Coal chars, possibly due to the high ash content in the samples, as observed in Section 4.1.3. Literature suggests that chars prepared at higher temperatures during devolatilisation are known to show lower gasification reactivity [Okolo, 2010]. From Table 4.5, the coal char had the highest aromaticity value of 0.83; biomass and blended chars ranged from 0.74-0.79. It is known that the lower the aromaticity values of a sample, the higher the reactivity [Okolo, 2010].

Table 4.5: XRD characteristics values of the chars

| Parameters        | Coal char   | HWC char    | SWC char    | PWC char    | SB char | (80% HWC + 20% Coal) char | (80% SWC + 20% Coal) char | (80% PWC + 20% Coal) char | (80% SB + 20% Coal) char |
|-------------------|-------------|-------------|-------------|-------------|---------|---------------------------|---------------------------|---------------------------|--------------------------|
| $f_a$ (-)         | <b>0.83</b> | <b>0.74</b> | <b>0.75</b> | <b>0.69</b> | -       | <b>0.77</b>               | <b>0.79</b>               | <b>0.78</b>               | -                        |
| $d_{002}$ (Å)     | 3.64        | 3.71        | 3.78        | 3.75        | -       | 3.78                      | 3.77                      | 3.71                      | -                        |
| $L_c$ (Å)         | 11.69       | 9.63        | 9.99        | 10.98       | -       | 10.22                     | 10.05                     | 10.20                     | -                        |
| $L_{a, (10)}$ (Å) | 31.10       | 38.47       | 29.05       | 40.24       | -       | 32.00                     | 35.60                     | 30.67                     | -                        |
| $N_{ave}$ (-)     | 4.21        | 3.59        | 3.64        | 3.93        | -       | 3.70                      | 3.67                      | 3.75                      | -                        |
| $X_A$ (-)         | 0.64        | 0.60        | 0.74        | 0.75        | -       | 0.48                      | 0.40                      | 0.33                      | -                        |
| DOI (-)           | 0.70        | 0.70        | 0.81        | 0.83        | -       | 0.68                      | 0.53                      | 0.48                      | -                        |

The interplanar distances for all of the chars were comparable to graphite, with  $d_{002}$  that was in the range of 3.64-3.78. This increase of  $d_{002}$  is proposed to be due to the removal of moisture and volatiles, and annealing of the carbon crystallites, which causes the disordered carbons of the samples to be more oriented and structurally ordered [Okolo, 2010]. The  $L_c$  and  $N_{ave}$  of the chars were in the ranges of 11.69-10.05 and 4.21-3.59, respectively. This decrease could be caused by more compact, oriented and ordered structure conveyed to the chars due to thermal treatment, which hardens the chars and may influence its skeletal and bulk density [Okolo, 2010]. However, significant differences could be observed for the  $L_{a, (10)}$  of the chars (29.05-30.67 Å). The  $X_A$  and DOI of the chars were between the range of 0.33-0.74 and 0.48-0.81, respectively. From these results, it can be observed that, at high temperatures, properties of the chars tend to be similar.

The quantitative XRD results shown in Table 4.6 are based on the total amounts of the crystalline phases present in the char samples. It should be noticed that mineral names may not reflect the actual compositions of minerals identified, but rather the mineral group. The experimental error for the phases detected was found to be less than 1.6 wt. %. The XRD results of the 80% HWC + 20% Coal char show that the mineral CaO (lime) is the most abundant species (0.1 wt. %), whilst CaO was not detected in the other char samples. The organic carbon is represented by the mineral “graphite” and quantification may not be accurate. All of the chars were observed to be rich in graphitic material, where the SB char had the lowest value of 55.3 wt. %. This corresponds with the 80% SB + 20% Coal char having the lowest value of graphitic material (73.6 wt. %) among the blends. The XRD analyses showed that some of the chars contained small amounts of diopside, alpha iron, oldhamite (halite may be present), microcline and plagioclase. The SB char contained the

highest amount of quartz (31.2 wt. %), followed by the blend D char, possibly due the soil particles present in the material.

Table 4.6: XRD analyses of char samples (Percentages of crystalline phases only)

|                                                                                                            | Coal<br>char | HWC<br>char  | SWC<br>char   | PWC<br>char  | SB<br>char   | (80%<br>HWC<br>+ 20%<br>Coal)<br>char | (80%<br>SWC +<br>20%<br>Coal)<br>char | (80%<br>PWC +<br>20%<br>Coal)<br>char | (80%<br>SB +<br>20%<br>Coal)<br>char |
|------------------------------------------------------------------------------------------------------------|--------------|--------------|---------------|--------------|--------------|---------------------------------------|---------------------------------------|---------------------------------------|--------------------------------------|
| Mineral Species                                                                                            | Wt.%         | Wt.%         | Wt.%          | Wt.%         | Wt.%         | Wt.%                                  | Wt.%                                  | Wt.%                                  | Wt.%                                 |
| <b>CaO lime</b>                                                                                            | -            | -            | -             | -            | -            | <b>0.1</b>                            | -                                     | -                                     | -                                    |
| Diopside<br>(MgCaSi <sub>2</sub> O <sub>6</sub> )                                                          | -            | -            | -             | -            | 5.5          | -                                     | -                                     | -                                     | 3.3                                  |
| <b>Graphite (C)</b>                                                                                        | <b>97.3</b>  | <b>100.0</b> | <b>mainly</b> | <b>84.6</b>  | <b>55.3</b>  | <b>98.5</b>                           | <b>96.7</b>                           | <b>99.0</b>                           | <b>73.6</b>                          |
| <b>Alpha iron (<math>\alpha</math>-Fe)</b>                                                                 | -            | <b>0.0</b>   | <b>traces</b> | <b>0.5</b>   | <b>0.4</b>   | <b>0.0</b>                            | <b>0.1</b>                            | -                                     | <b>0.4</b>                           |
| Magnetite (Iron<br>(II,III) oxide)                                                                         | -            | -            | -             | -            | -            | -                                     | 0.3                                   | -                                     | -                                    |
| Microcline<br>(KAlSi <sub>3</sub> O <sub>8</sub> )                                                         | -            | -            | -             | 2.9          | -            | -                                     | -                                     | -                                     | -                                    |
| <b>Oldhamite<br/>(Ca<sub>0.9</sub>Mg<sub>0.05</sub>Fe<sub>0.05</sub>S)</b>                                 | <b>0.7</b>   | -            | -             | -            | -            | <b>0.2</b>                            | <b>1.5</b>                            | <b>0.2</b>                            | -                                    |
| Plagioclase<br>(NaAlSi <sub>3</sub> O <sub>8</sub> -<br>CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ) | -            | -            | -             | 2.1          | 7.6          | -                                     | -                                     | -                                     | 4.4                                  |
| <b>Quartz (SiO<sub>2</sub>)</b>                                                                            | <b>2.1</b>   | -            | -             | <b>10.0</b>  | <b>31.2</b>  | <b>1.3</b>                            | <b>1.4</b>                            | <b>0.8</b>                            | <b>18.4</b>                          |
| <b>Total</b>                                                                                               | <b>100.0</b> | <b>100.0</b> | -             | <b>100.0</b> | <b>100.0</b> | <b>100.0</b>                          | <b>100.0</b>                          | <b>100.0</b>                          | <b>100.0</b>                         |

#### 4.1.6 Physical structural analyses- CO<sub>2</sub> BET analysis

Table 4.7 gives a summary of results obtained for the surface areas, micropore surface areas, average micro diameters and the porosities of raw material and the chars. The surface areas of solid fuels upon devolatilisation may strongly influence the physical properties of samples [Apaydin-Varol and Pütün, 2012]. The repeatability was within 1 m<sup>2</sup>/g and accuracy of the BET technique is given within 7.0 m<sup>2</sup>/g. The CO<sub>2</sub> BET measurements are usually confined to the micropore range (for coal analysis) [Hattingh, 2009]. Table 4.7 shows a reference to range of pore sizes found for micro-, meso- and macropores [Hattingh, 2009].

Table 4.7: Pore sizes of coal

| Pores      | Size Range (Å)     |
|------------|--------------------|
| Micropores | < 4; 4-12          |
| Mesopores  | 12-300             |
| Macropores | 300-29600, > 29600 |

It can be seen from Table 4.8 that there was an increase in the surface area as the fuels were charred [Carrier *et al.*, 2012]. This increase in the BET surface area of raw and char samples may be due to the opening and development of the structure [Salatino *et al.*, 1998; Guerrero *et al.*, 2008; Carrier *et al.*, 2011a]. The surface areas of the blended chars were observed to be close to or less than the values obtained for biomass chars, except for the 80% SB + 20% Coal char. This shows that the pores of biomass chars, or entry to the biomass chars, were not blocked by carbonaceous deposits in the sample [Darmstadt *et al.*, 2001]. There was not much variation between the surface area and the micropore surface area for coal and coal char. The surface area values differ between 91.5 m<sup>2</sup>/g for coal and 94.2 m<sup>2</sup>/g for coal char. The micropore surface area has the value of 139.0 m<sup>2</sup>/g for coal and 146.7 m<sup>2</sup>/g for coal char. This slight variation may be caused by the presence of inorganic matter in the coal, especially silica components due to their high thermal resistance [Raveendran and Ganesh, 1998]. The rest of the reported values for the biomass and blended chars show an increase in surface area values of 5 – 8 times over the values of raw samples. The HWC char and SWC char were observed to have the highest porosities of 23.5% and 22.8%, respectively, compared with the rest of the chars. The 80% HWC + 20% Coal char and the 80% PWC + 20% Coal char had the highest porosities of 18.3% and 15.6%, respectively, and raw PWC were observed to have the lowest porosity value of 1.4%. The results determined from the CO<sub>2</sub> adsorption are generally accepted to provide better characterisation of micropores of less than 20.0-25.0 Å, compared to nitrogen adsorption [Walker *et al.*, 1988; Kajitani *et al.*, 2006].

Table 4.8: CO<sub>2</sub> BET adsorption results

| Material                  | BET surface area (m <sup>2</sup> /g) | Micropore surface area (m <sup>2</sup> /g) (D-R) | Monolayer capacity (cm <sup>3</sup> /g) (D-R) | Average micropore diameter (Å) (H-K) | Porosity (%) (Dr ≤ 5 Å) (AD) |
|---------------------------|--------------------------------------|--------------------------------------------------|-----------------------------------------------|--------------------------------------|------------------------------|
| Coal                      | 91.5                                 | 139.0                                            | 139.0                                         | 3.8                                  | 5.7                          |
| Coal char                 | 94.2                                 | 146.7                                            | 32.1                                          | 4.0                                  | 4.8                          |
| HWC                       | 56.5                                 | 82.0                                             | 18.0                                          | 4.1                                  | 2.4                          |
| HWC char                  | 328.1                                | 476                                              | 104.2                                         | 3.6                                  | 23.5                         |
| SWC                       | 50.4                                 | 62.9                                             | 13.8                                          | 4.0                                  | 1.5                          |
| SWC char                  | 332.4                                | 527.3                                            | 115.4                                         | 3.7                                  | 22.8                         |
| PWC                       | 51.2                                 | 59.6                                             | 13.0                                          | 4.0                                  | 1.4                          |
| PWC char                  | 329.4                                | 504.9                                            | 110.5                                         | 3.7                                  | 23                           |
| SB                        | 42.5                                 | 59.5                                             | 13.0                                          | 4.2                                  | 1.6                          |
| SB char                   | 100.5                                | 156.6                                            | 34.3                                          | 3.8                                  | 6.4                          |
| (80% HWC + 20% Coal) char | 271.5                                | 434.6                                            | 95.1                                          | 3.7                                  | 18.3                         |
| (80% SWC + 20% Coal) char | 256.5                                | 436.4                                            | 95.5                                          | 3.7                                  | 17.0                         |
| (80% PWC + 20% Coal) char | 238.5                                | 380.1                                            | 83.2                                          | 3.8                                  | 15.6                         |
| (80% SB + 20% Coal) char  | 107.3                                | 167.2                                            | 36.6                                          | 3.9                                  | 6.4                          |

Nomenclature:

D-R: Dubini-Radushkevich method

H-K: Horvath-Kawazoe method

AD: CO<sub>2</sub> BET method

#### 4.1.7 Physical structural analyses- SEM images

Figures 4.4 – 4.7 show the physical structures of the various raw and charred samples that were taken at various magnifications using SEM. The images were taken in order to understand some of the textural properties and morphology changes occurring during pyrolysis. The highly fibrillar raw biomass samples exhibited regular and compact surface structures that were influenced by the crushing methods used to obtain a powder size sample [Xiao *et al.*, 2011]. From the SEM images of raw and charred biomass feedstock, and blended coal-biomass chars, the original structure of the biomass can be clearly seen, along with structural components in the biomass (longitudinal tracheids, vessel elements and cell walls) [Jansen, 2011]. The SEM images of coal char, biomass chars and blended chars (as in Figure 4.4.b) show open structures that can be related to the high surface areas, reported in Table 4.8. Kannan and Richards [1990] and Vanvuka *et al.* [2011] reported that the high surface areas observed for the biomass chars could be correlated to a high concentration of carbon active sites in the biomass feedstock, which are directly influenced by increasing temperature.

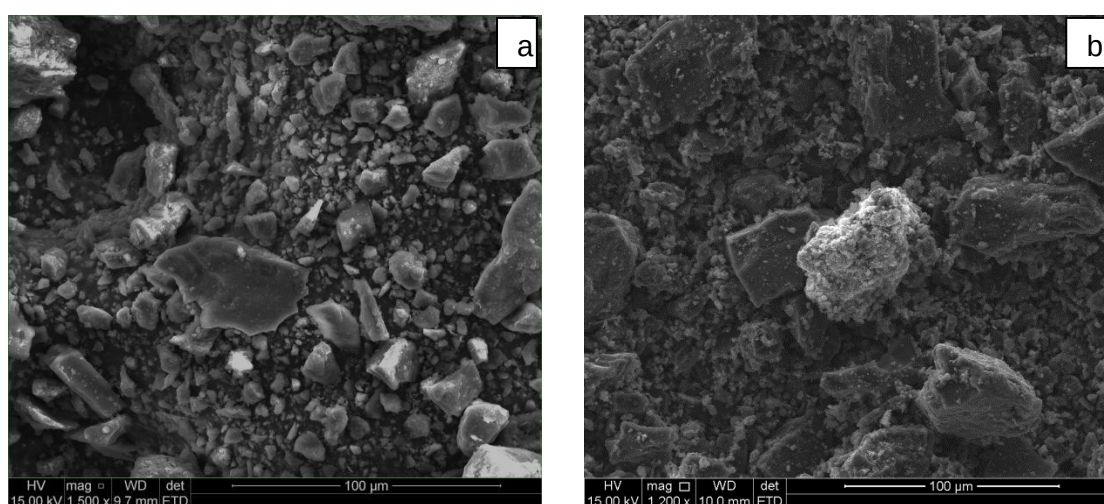


Figure 4.4: SEM micrographs of (a) raw coal and (b) coal char

Electron microscopy of the coal char particles that were prepared at 1100 °C under nitrogen atmosphere revealed that it is not as sharp-edged as the raw coal particles after devolatilisation. The surface of the coal char particles seemed to be less smooth or glassy and the structure was less clustered. The coal char particle appeared to have increased slightly in particle size, suggesting that upon pyrolysis, there was perhaps a limited swelling. This observation is in agreement with the BET surface of the coal char result obtained, as mentioned in Section 4.1.6, (i.e. an increase of surface area from raw coal (91.5 m<sup>2</sup>/g) to coal char (94.2 m<sup>2</sup>/g).

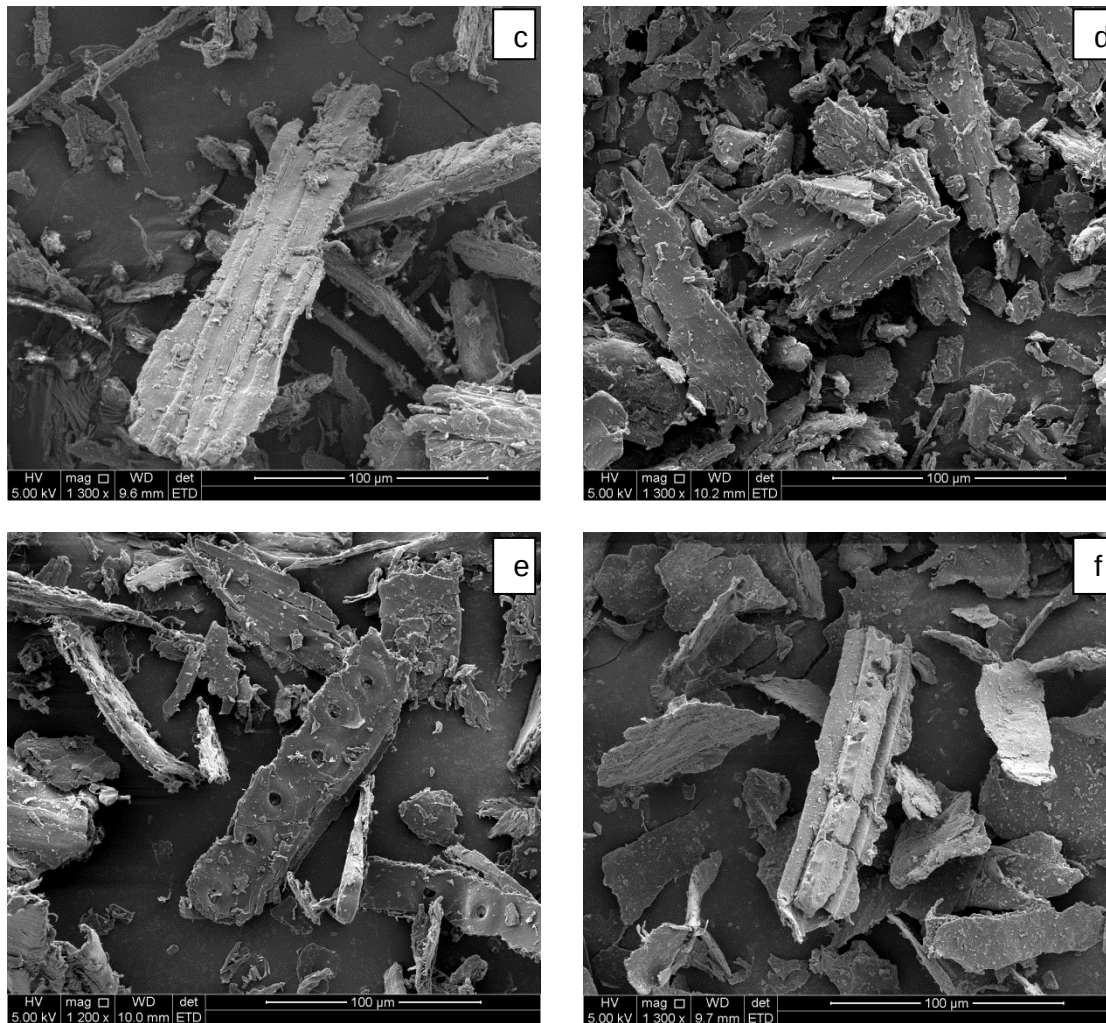


Figure 4.5: SEM micrographs of (c) raw HWC, (d) SWC, (e) PWC and (f) SB

From the SEM results, Figure 4.5 (c-f) revealed the elongated heterogeneous particles of biomasses that are fibrous and loose in structure. Figure 4.5 (e-f) shows flattened tracheids with pores, used to supply the plant with water. The surface of SB seems to be smoother compared with the other samples, possibly due to the softness of the biomass under the mechanical strain experienced during the crushing process. The surface morphology of raw materials revealed the presence of heterogeneous particles that were uneven in shape.

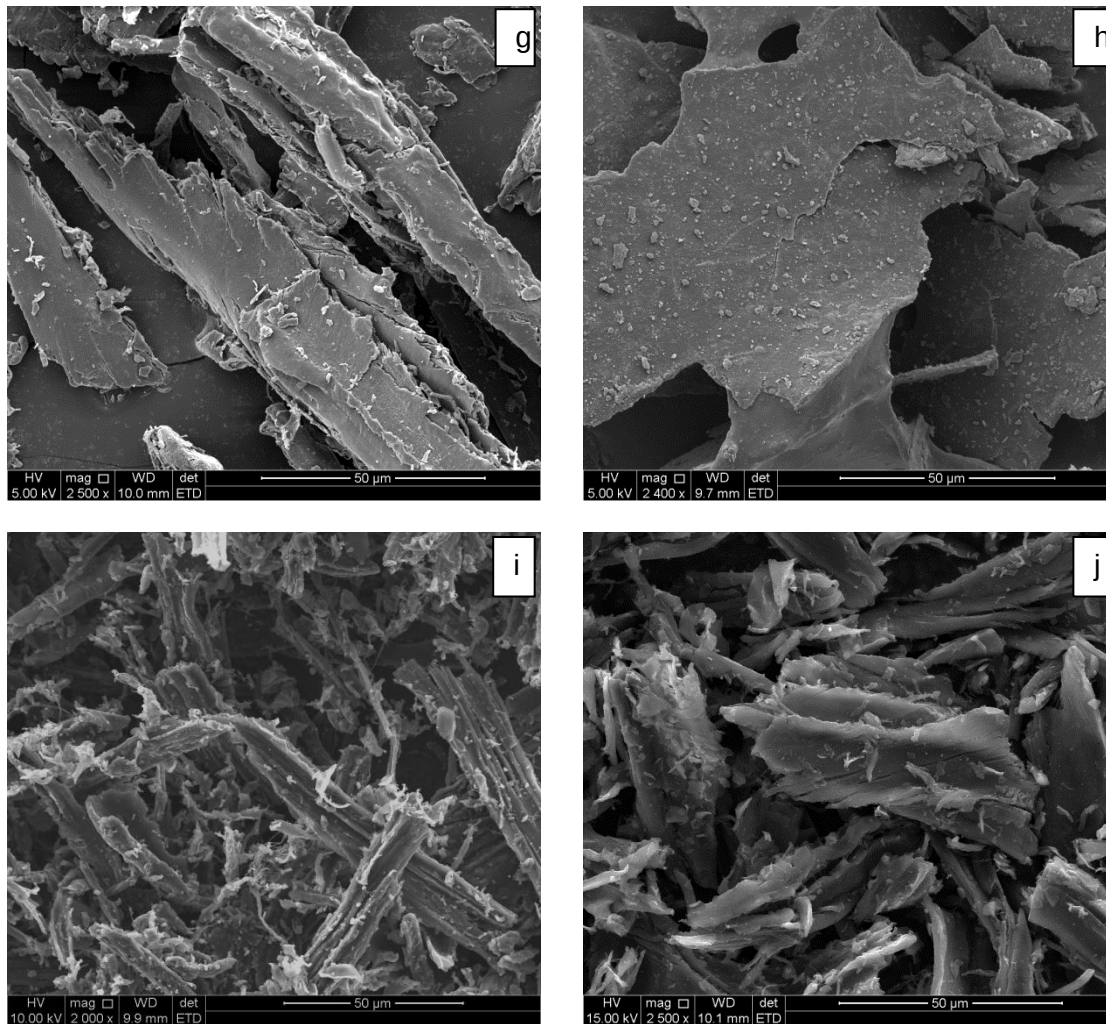


Figure 4.6: SEM micrographs of (g) PWC char, (h) SB char, (i) HWC char and (j) SWC char

Figure 4.6 shows SEM images of biomass chars produced by pyrolysis at a final temperature of 1100 °C under a nitrogen atmosphere. In order to observe a morphological structural change from raw precursors to chars, Figure 4.6 showed the biomass char particles to have a glassy and fibrous morphology. The SB char particle revealed that the surface and morphology remained similar; this may be due to the high ash content in the starting raw material, i.e. silica components that have high thermal resistance [Guerrero *et al.*, 2008; Apaydin-Varol and Pütün, 2012]. Figure 4.6 (i-j) clearly shows open structures, which may be caused by the volatile components being released.

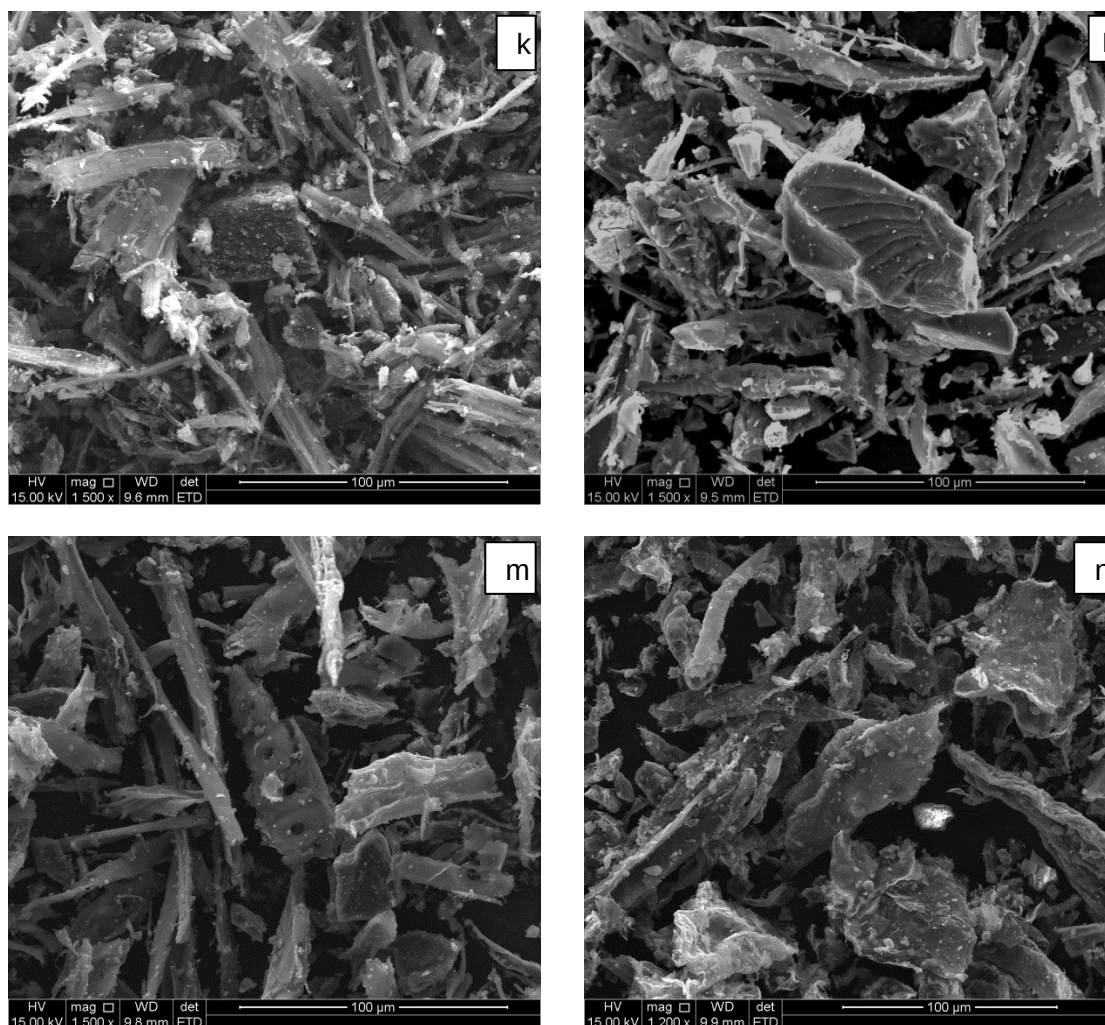


Figure 4.7: SEM micrographs of (k) 80% HWC + 20% Coal char, (l) 80% SWC + 20% Coal char, (m) 80% PWC + 20% Coal char, and (n) 80% SB + 20% Coal char

Figure 4.7 (k-n) shows SEM micrographs of blended chars prepared at 1100 °C under a nitrogen environment. The images revealed glassy heterogeneous particles that mainly consisted of coal char and plant components (tracheid, and fibrous and non-fibrous components). The blended char particles had porous and close packed structures, which is mostly likely caused by volatiles being emitted [Zhu *et al.*, 2008]. The 80% HWC + 20% Coal char seemed to be more compact in structure when compared with the other chars, because of the small space between the particles. The coal char particle distribution in the blends appeared to be uneven. From Figure 4.7 (n), a shiny inorganic component was seen (possibly silica which comes from the raw SB material) in the 80% SB + 20% Coal char, which could be responsible for the high ash content observed in the proximate results in Section 4.1.3. The presence of inorganic matter may influence the interaction of the biomass with the coal, making active carbon sites less easily accessible. This postulation might help explain the low BET surface area value observed for the blend D char (see Section 4.1.6).

#### 4.1.8 Summary

Table 4.9: Summary of some of the important characteristic properties obtained through various techniques applied on coal, biomass feedstock and their blends

| Properties                          | Coal<br>char | HWC<br>char | SWC<br>char | PWC<br>char | SB<br>char | (80%<br>HWC<br>+<br>20%<br>Coal)<br>char | (80%<br>SWC<br>+<br>20%<br>Coal)<br>char | (80%<br>PWC<br>+<br>20%<br>Coal)<br>char | (80%<br>SB +<br>20%<br>Coal)<br>char |
|-------------------------------------|--------------|-------------|-------------|-------------|------------|------------------------------------------|------------------------------------------|------------------------------------------|--------------------------------------|
| Ash (wt. % a.d.b)                   | 18.3         | 0.9         | 0.9         | 1.0         | 45.8       | 10.7                                     | 9.5                                      | 9.0                                      | 50.8                                 |
| Volatiles (wt. % a.d.b)             | 1.8          | 2.4         | 1.8         | 2.4         | 1.9        | 1.2                                      | 1.3                                      | 1.9                                      | 0.7                                  |
| Fixed Carbon (wt. % a.d.b)          | 77.5         | 93.8        | 94.5        | 93.5        | 49.4       | 84.7                                     | 86.1                                     | 86.3                                     | 45.9                                 |
| Gross Calorific Value (MJ/kg a.d.b) | 26.5         | 28.6        | 30.8        | 28.6        | 17.4       | 28.9                                     | 28.5                                     | 29.1                                     | 16.0                                 |
| Aromaticity values                  | 0.83         | 0.74        | 0.75        | 0.69        | -          | 0.77                                     | 0.79                                     | 0.78                                     | -                                    |
| BET analysis (m <sup>2</sup> /g)    | 94.2         | 328.1       | 332.4       | 329.4       | 100.5      | 271.5                                    | 256.5                                    | 238.5                                    | 107.3                                |

From Table 4.9, the proximate analysis showed the ash content of the blends to have increased more than the parent chars. It is expected to observe a linear relationship between the evolution of the volatiles and an increase of the biomass addition (wt. %) in the blends. Structural and physical analyses of the blends showed that an increase in the surface area was ascribed to the opening and development of the structures at high temperature. The aromaticity values of the blends were in between the ranges of the parent materials. This is as expected and indicates that the different processes by which coal and biomass is decomposed during pyrolysis, occur similarly to that in the parent material.

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| <b>Chapter 5</b> |
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**Results and Discussion****Thermogravimetric analysis - Mass Spectrometry (TG-MS) on co-pyrolysis process**

In this chapter, results obtained from the TG-MS analyses of the coal, biomass and coal-biomass samples under nitrogen atmosphere are presented. The chapter contains the discussion of synergistic effects from the co-pyrolysis of biomass with coal. The experimental conditions used for the TG-MS was described in Section 3.7.10.1. The influence of the biomass on some of the gaseous products formed during co-utilization with coal is also discussed in this chapter.

**5.1 Introduction**

The thermal behaviour of blends of four biomasses (HWC, SWC, PWC, and SB) and inertinite-rich bituminous coal was investigated using the TG-MS technique. The samples were pulverised to less than 75  $\mu\text{m}$  (as described in Section 3.3.2). The blends were prepared in ratios of 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0 (wt. %: wt. %) prior to charring. The samples were subjected to heat treatment from ambient temperature to 1100 °C at a heating rate of 10 °C/min under inert gas ( $\text{N}_2$ ) (as described in Section 3.7.10.1). The mass losses were recorded as a function of temperature [Yang *et al.*, 2007; Carrier *et al.*, 2011b]. The mass to charge ratio ( $m/z$ ) of the evolved gases were correlated with the DTG (derivative thermogravimetric) curves of the 80% biomass to 20% coal sample for comparison.

**5.2 TGA results****5.2.1 Reproducibility of TG results**

The consistency of the produced data of each experiment was examined. The TGA run of each starting material was repeated three times to investigate the reproducibility as shown in Figure 5.1. The rest of the plots are presented in the Appendix A.2. The average TG curves were used to represent the experimental results of each sample. From Figure 5.1 it is clear that the TG results are reproducible.

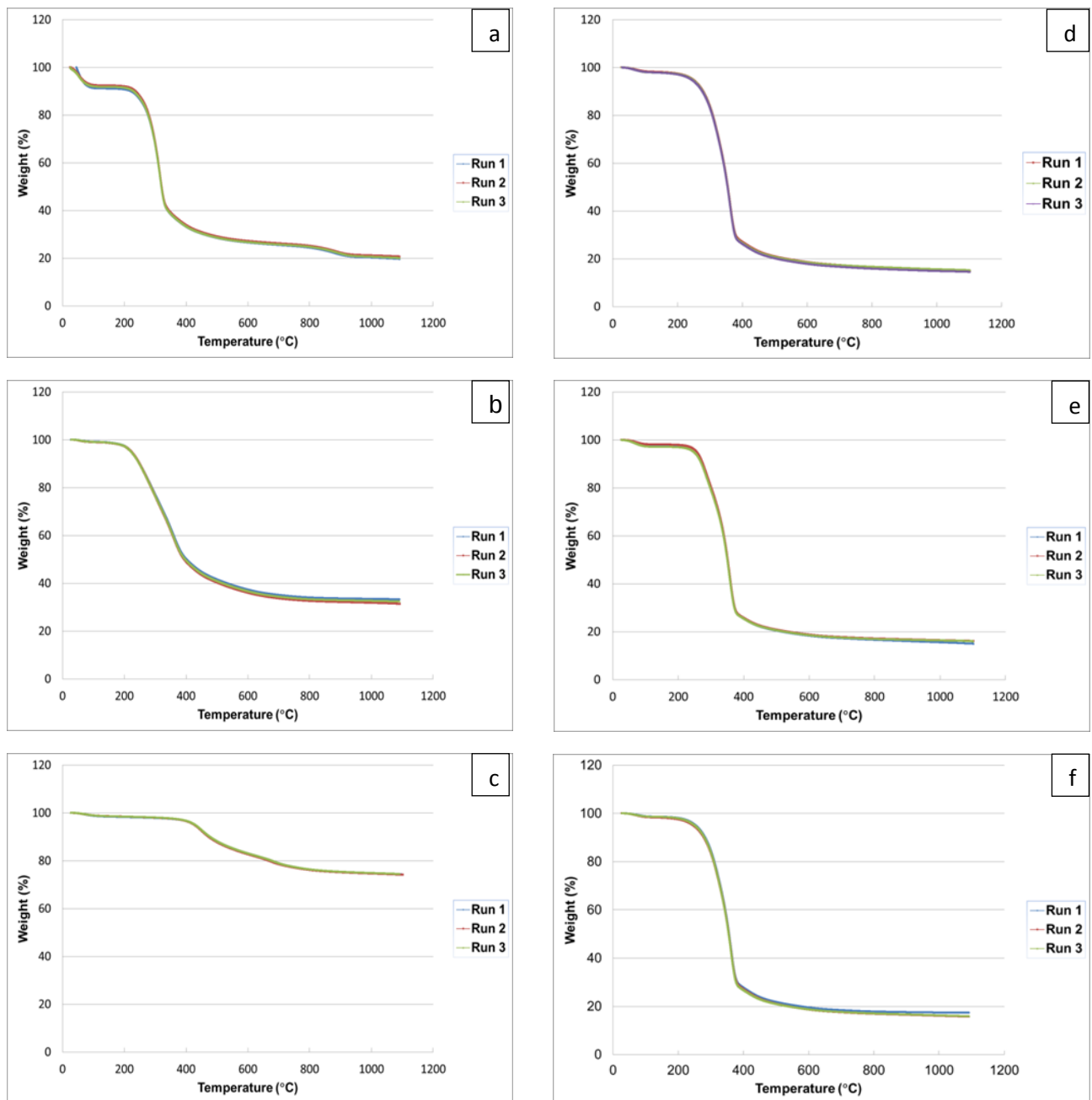


Figure 5.1: Repeated TG curves of (a) cellulose, (b) lignin, and (c) coal, (d) HWC, (e) SWC and (f) PWC during pyrolysis

### 5.2.1.1 Thermograms of ligno-cellulosic materials

Figures 5.2 present the thermal degradation curves (TG and DTG) of cellulose and lignin. The TG/DTG results of xylan used in this work was obtained from a paper published by Yang *et al.* [2007], since the hemicellulose was difficult to extract. Xylan is widely used as a representative of hemicellulose in the pyrolysis process [Arfao *et al.*, 1999; Rao and Sharma, 1998; Koufopoulos *et al.*, 1989]. The weight loss and DTG curves are plotted as a function of temperature. The breakdown of ligno-cellulosic materials in a  $N_2$  atmosphere produced volatiles. The DTG curve shows three peaks of weight loss for cellulose and two peaks for lignin. The DTG was used to determine temperature at maximum rate of reaction only (where  $dm/dT = 0$ ). From Figure 5.2 (a), cellulose heated in an inert environment has a mass loss of 80 wt. % when heated up to 1000 °C. The initial weight loss was observed at around 100 °C from the TG/DTG curves of cellulose and lignin, and is associated with the mass loss due to moisture and light volatiles [Yang *et al.*, 2007; Munir *et al.*, 2009]. The second weight loss peak started at approximately 160 °C. This is ascribed to the structural changes associated with the breakdown of cellulose or glucose polymers to produce anhydrocellulose and levoglucosan [Mohan *et al.*, 2006]. The third stage of decomposition started at higher temperatures of approximately 750 °C, and appeared as a small peak. This small peak may be due to the presence of inorganic components or the secondary pyrolysis of residual lignin [Ferdous *et al.*, 2001; Biagini *et al.*, 2002; Bonelli *et al.*, 2007; Yang *et al.*, 2007].

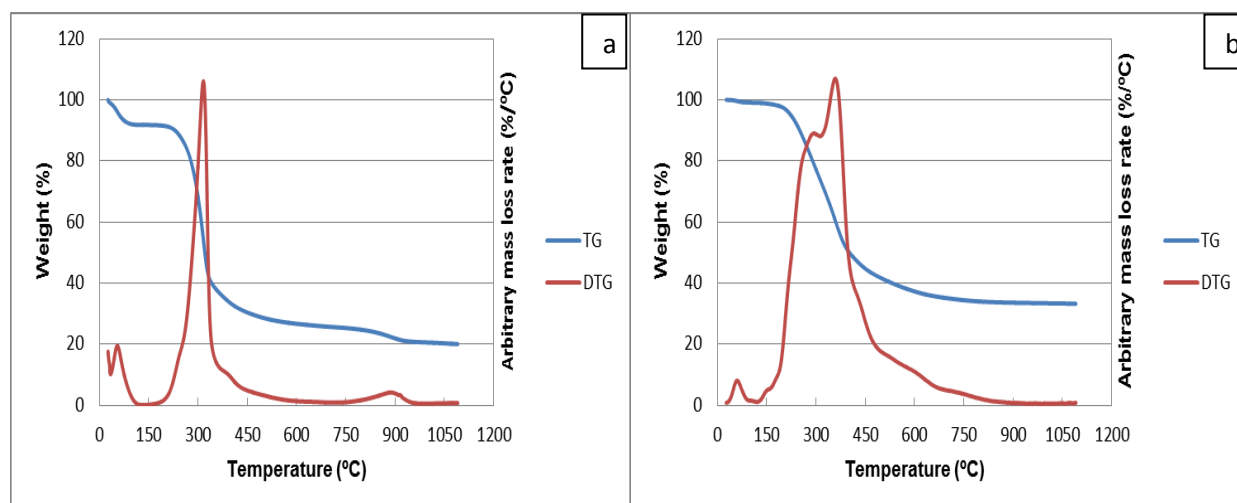


Figure 5.2: TG/DTG curves of (a) cellulose and (b) lignin

Figure 5.2 (b) presents the thermal degradation of lignin under an inert atmosphere (nitrogen) at a heating rate of 10 °C/min. The first stage of decomposition is ascribed to entrapped water, and was observed at approximately 100 °C for all samples. The second stage of mass loss of lignin started at approximately 140 °C. The total mass loss of lignin at

the final temperature was 68 wt. %. The char residue of lignin (32 wt. %) was found to be higher than that of cellulose (20 wt. %). From the DTG curve, lignin degradation showed two distinctive peaks which are overlapping. This could be due to some of the hemicellulose that sticks to the ligno-sulfonate in the lignin. The first part of the distinctive second peak (overlapped) was a pronounced shoulder which started at 290 °C, which may be the result of the degradation of the residual hemicellulose or polyose. It correlated with the decomposition range of 220-315 °C for hemicellulose in literature [Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b]. The second part of the second peak started at a higher temperature of 357 °C. The second part of the second peak was in the range of 315-400 °C (from overlapping peaks) which could be assigned to the thermal decomposition of cellulose [Yang *et al.*, 2007]. The degradation of lignin was completed at approximately 900 °C. This result is in agreement with the decomposition of lignin reported in literature to be within a temperature range of 300-900 °C [Sharma *et al.*, 2004; Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b]. This decomposition temperature range could be due to the structure of lignin which is full of aromatic rings with various branches [Yang *et al.*, 2007].

Table 5.1 shows the thermogravimetric data obtained from the temperatures observed in Figures 5.2. The thermal characteristics of the three components showed wide differences. The temperatures of interest are the initial ( $T_i$ ), terminal ( $T_f$ ) and maximum mass loss rate ( $T_{max}$ ) temperatures. The decomposition temperature range,  $\Delta T$ , for lignin indicates degradation within a wide temperature range of 786 °C, followed by cellulose and hemicellulose with 507 °C and 95 °C, respectively. The lignin degradation showed  $T_{max}$  at 357 °C and this could be associated with traces of cellulose, since the value is close to that reported in literature (315-400 °C) by Yang *et al.* [2007].

Table 5.1: The characteristic temperatures (°C) of ligno-cellulosic materials

| Ligno-cellulosic material  | $T_i$ | $T_f$ | $\Delta T = T_f - T_i$ | $T_{max}$ |
|----------------------------|-------|-------|------------------------|-----------|
| Cellulose                  | 160   | 660   | 507                    | 315       |
|                            | 750   | 965   | 215                    | 890       |
| Hemicellulose <sup>a</sup> | 220   | 315   | 95                     | 268       |
| Lignin                     | 140   | 900   | 786                    | 290, 357  |

<sup>a</sup> denotes values obtained from Yang *et al.* [2007] for xylan used as hemicellulose

### 5.2.1.2 Thermograms of biomass samples

Figure 5.3 shows the TG curves of the four biomass feedstock heated at 10 °C/min under a nitrogen atmosphere. As mentioned in Section 3.7.10.1  $\pm 25$  mg of sample mass was used for all TGA experiments. The TG system was flushed with carrier gas (N<sub>2</sub>) at a high flow rate (100 ml/min). This was done to decrease vapour residence time, and thus to limit secondary reactions within the system. The TG curve showed that SB had more char residue (39 wt. %) than the other biomass samples, and this could be due to the high ash and lignin contents in this material, as observed in Section 4.1.3. The char residue value of PWC and HWC were 17.1 wt. % and 14.6 wt. %, respectively. The SWC had the lowest char residue (8.7 wt. %), which may be due to the highly fibrous structure with low thermal resistance. In addition, the differences in char residues may also be due to the low heating rate applied and differences in the chemical composition of each biomass [Meesri and Moghtaderi, 2002; Carrier *et al.*, 2011b].

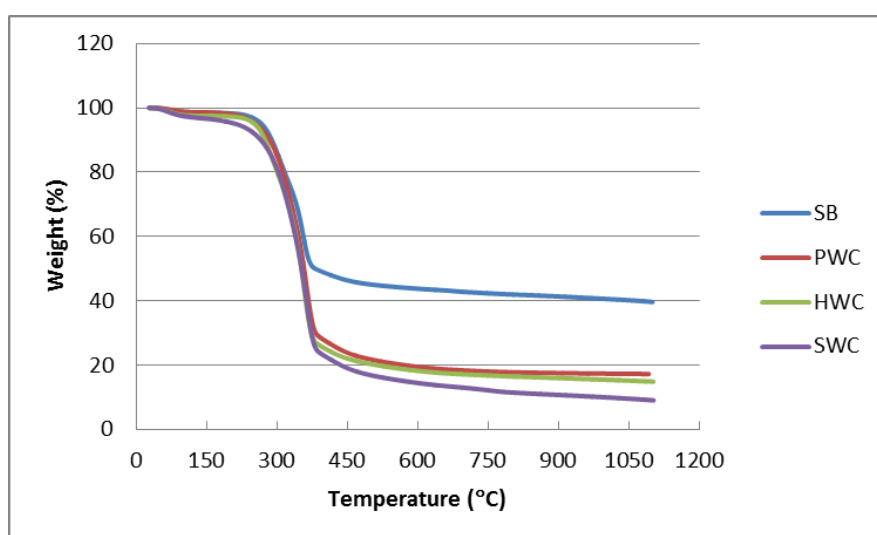


Figure 5.3: TG curves of biomass feedstock

Figure 5.4 presents the DTG curves of the biomass feedstock. The curves showed that the degradation range is approximately 180-525 °C. The PWC and SWC samples showed a single peak with a maximum mass loss rate at approximately 360 °C for both samples. The SB and HWC exhibit two overlapping major peaks and had maximum mass loss rates at 308 and 353 °C, and 289 and 357 °C, respectively [Ouensanga and Picard, 1988; Aiman and Stubington, 1993; Manya and Arauzo, 2008; Shanmukharadhya and Ramachandran, 2009; Munir *et al.*, 2009; Mothé and de Miranda, 2009]. The first peak is associated with the decomposition of hemicellulose [Griffin, 2011]. The second peak (at the higher temperature) is associated with the decomposition of cellulose [Mohan *et al.*, 2006]. This overlap is

reported to be the result of the increased heat stability of the residual hemicellulose [Oudia *et al.*, 2007]. The four biomass feedstock exhibited a shoulder on the DTG curves at approximately 440 °C. This shoulder peak could be ascribed to the degradation of lignin, which occurs at higher temperatures [Yang *et al.*, 2007]. The result corroborates the observation in Section 5.2.1.1, where the amount of lignin was observed to decrease at a higher temperature range. The very small peak at approximately 750 °C could be attributed to secondary reactions caused by devolatilisation of oxygenated species from the biomass [Biagini *et al.*, 2002]. Gašparovic *et al.* [2010] reported that the decomposition of biomass depends mainly on the concentration and composition of ligno-cellulosic compounds.

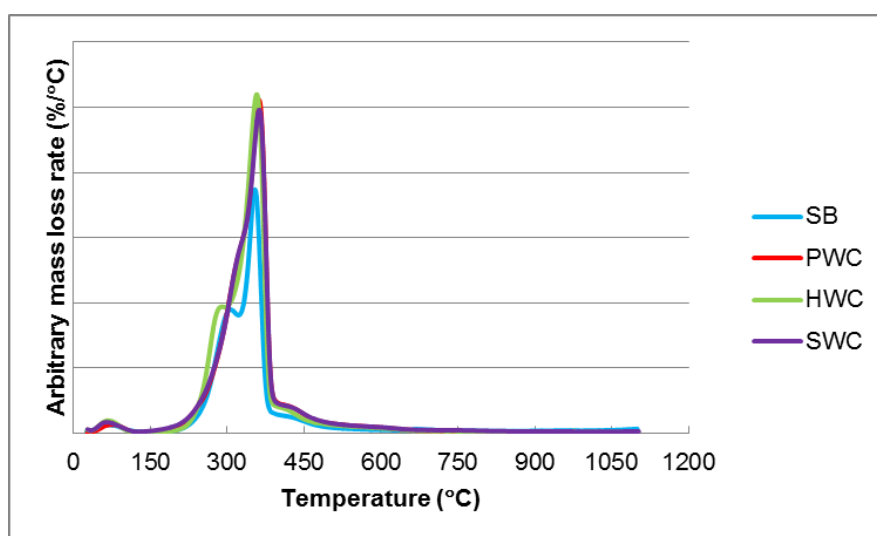


Figure 5.4: DTG curves of biomass feedstock

Table 5.2 shows the characteristic temperatures ( $T_i$  and  $T_{max}$ ) of each biomass. The temperatures at maximum rate of thermal degradation ( $T_{max}$ ) are within the range reported in literature for cellulose, hemicellulose and lignin [Sharma *et al.*, 2004; Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011b].

Table 5.2: The characteristic temperatures (°C) of biomass feedstock

| Biomass materials | $T_i$ | $T_{max}$ |
|-------------------|-------|-----------|
| HWC               | 174   | 289       |
|                   |       | 357       |
| SB                | 158   | 308       |
|                   |       | 353       |
| PWC               | 135   | 360       |
| SWC               | 124   | 362       |

### 5.2.1.3 Thermograms of blended coal-biomass samples

Figures 5.5 show the TG/DTG curves of blended samples of coal/biomass during co-pyrolysis under nitrogen atmosphere at a heating rate of 10 °C/min. The decomposition of coal-biomass (blended at different blending ratios of 20:80, 40:60, 60:40 and 80:20 (wt. %: wt. %)) samples were shown to be more reactive than coal (alone), decompose at lower temperatures than observed for coal. This observation may be due to the limiting amount of the biomass in the mixture. The ligno-cellulosic materials in the biomass have weak bonds (bonding energies of 380-420 kJ/mol), which do not withstand high heating treatment, even at low temperatures [Vuthaluru, 2003].

The devolatilisation process of the blended samples started at approximately 160 °C and was completed at around 900 °C. The breakdown of the biomass started at lower temperatures, which accounts for the easy degradation of ligno-cellulosic materials as observed in Section 5.2.1.1. The bonds of ligno-cellulosic materials are considered to be weak and connected through ether bonds which have low thermal stability [Hykiri-Acma and Yaman, 2010]. For coal (alone), the devolatilisation started at a higher temperature than the blended samples (at approximately 300 °C and the pyrolysis process was completed at 1000 °C). This observation can be attributed to the bond strength in the coal structure, and the functional groups within the coal which have higher thermal stability compared with biomass [Arenillas *et al.*, 1999; Hykiri-Acma and Yaman, 2010].

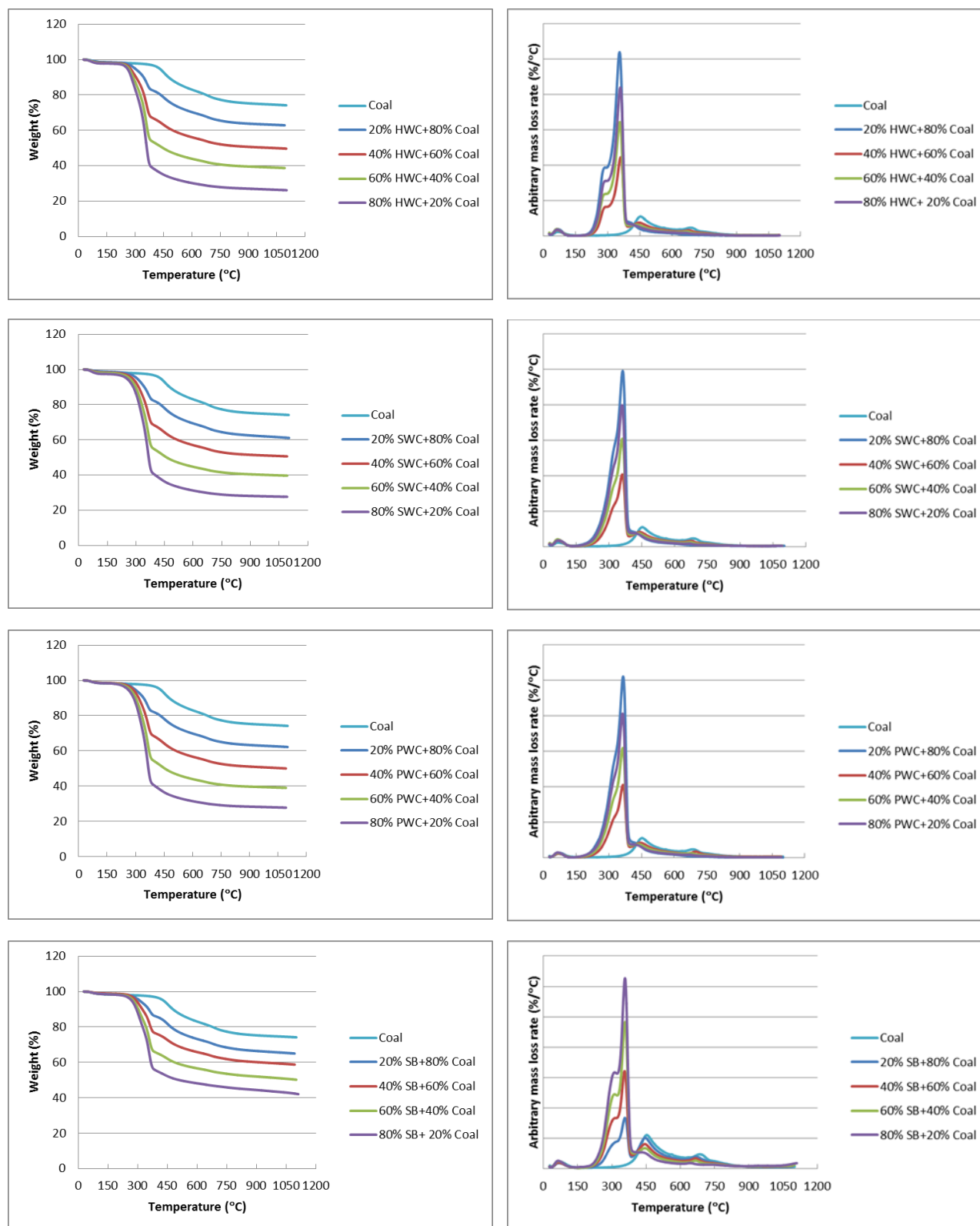


Figure 5.5: TG/DTG curves of coal and blended samples

The TG curve of the coal showed a 25% mass loss. This high residual mass could be ascribed to the high ash content and fixed carbon content of the coal [Sadhukhan *et al.*, 2008]. The coal showed two distinctive DTG peaks at approximately 451 °C and 669 °C, with mass loss rates lower for the coal in the blended samples. According to Serio *et al.* [1987] the release of primary volatiles (such as light hydrocarbons and tars) from coal predominates at approximately 500 °C. Radovic *et al.* [1983] stated that coal pyrolysis over 650 °C was due to gases released in condensation reactions, in thermal decomposition of carbonates, and breakdown of aromatic rings. The thermal behaviour of the Umlalazi coal under nitrogen is in agreement with the devolatilisation results described by Hattingh [2012], using a heating rate of 10 °C/min. The thermal behaviour of coal-biomass blended samples was shown to resemble the thermal behaviour of individual samples (coal and biomass feedstock) in the blend. These results are similar to those obtained by Moghtaderi *et al.* [2004], Sonobe *et al.* [2008] and Sadhukhan *et al.* [2008], using blended samples of coal and biomass (i.e. Radiata pine wood, corncob and waste wood, respectively). It was observed in the TG curves that, with the addition of biomass to the coal sample, the higher the amount of biomass in the blend the lower the char yield, as expected. The DTG curves showed that the overlapped peaks of the blended samples have similar temperature profiles than the individual materials. The decomposition of the biomass material started around 160 °C, and corresponded to the degradation of ligno-cellulosic materials [Sharma *et al.*, 2004; Mohan *et al.*, 2006; Yang *et al.*, 2007; Carrier *et al.*, 2011]. The coal pyrolysis started at about 300 °C and corresponded with literature [Hattingh, 2012]. This is ascribed to polycyclic aromatic hydrocarbons in the coal (with a bonding energy of around 1000 kJ/mol), which possibly causes coal to be more resistant to thermal treatment than biomass [Hattingh, 2012].

#### **5.2.1.4 Thermal behaviour of blended samples of 80% biomass to 20% coal**

The effect of the four selected biomasses on the decomposition of coal was compared with one another, and the thermograms are presented in Figures 5.6 and 5.7. The blended samples with wood origin (80% biomass (HWC, SWC and PWC) + 20% coal) reacted at earlier temperatures than the sample of 80% SB + 20% coal. The TGA profiles of woody blends are in the same temperature range with nearly 72% mass loss. The 80% SB + 20% coal sample had a mass loss of approximately 59 wt. %. This could be attributed to the high ash content of the SB-coal blend (50.8 wt. %), as observed in Section 4.1.3. The DTG curves showed overlapping peaks. The peaks are ascribed to the degradation of the macromolecular structure of the biomass, as discussed earlier [Ulloa *et al.*, 2009]. The DTG profile of coal showed a second peak at a higher temperature (669 °C), as reported in

Section 5.2.1.3. It was observed that the higher the biomass addition to coal, the lower the mass loss rate (nearly zero), which corresponded to the second peak of the coal at around 669 °C.

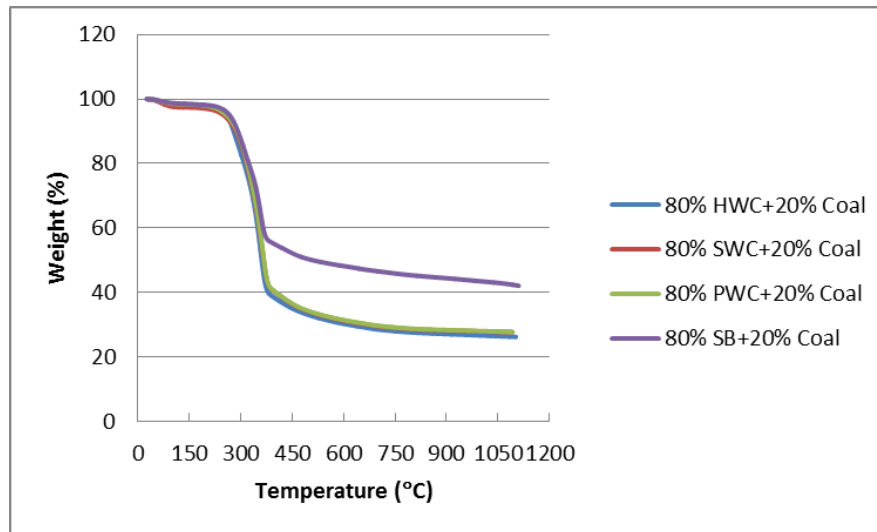


Figure 5.6: TG curves of coal and blended samples

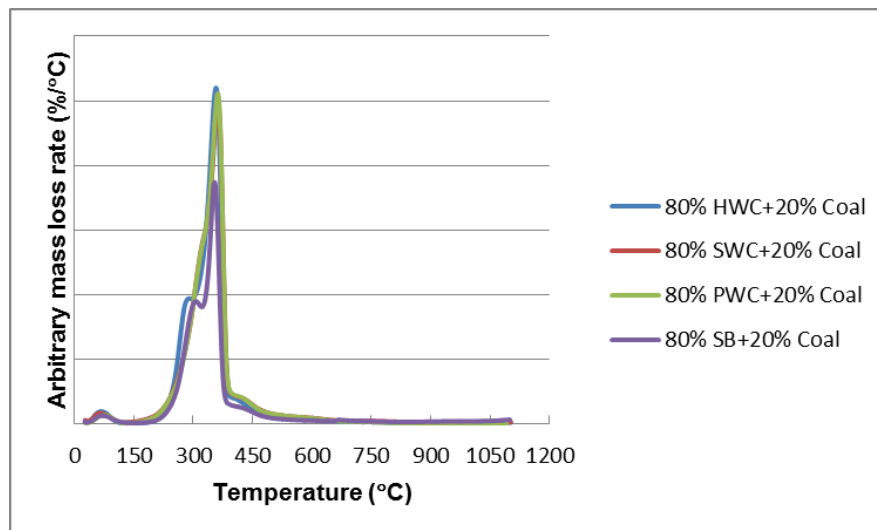


Figure 5.7: DTG curves of coal and blended samples

#### 5.2.1.5 Investigation of the synergistic effects of the blended samples of 80% biomass to 20% coal during pyrolysis

The co-pyrolysis characteristics were investigated for synergistic effects that arise from the interaction between the coal and biomass. This was done by calculating the theoretical TG curve (weighted average) [Biagini *et al.*, 2002; Sonobe *et al.*, 2008; Sadhukhan *et al.*, 2008; Niu *et al.*, 2011].

The theoretical line was used to predict the thermal behaviour of weight loss as the sum of the individual components' behaviour in the blend, as expressed by equation 5.1,

$$Y_{\text{calculated}} = x_1 Y_1 + x_2 Y_2 \quad 5.1$$

In the above equation (5.1),  $x_1$  and  $x_2$  represent the fractions of the coal and biomass in the blend, and  $Y_1$  and  $Y_2$  are the char yields of coal and biomass at the various temperatures. If the calculated weighted average line corresponds with the experimentally derived results then there were no synergistic effects. Figure 5.8 shows the comparison between experimental conversions of the blended samples of 80% biomass to 20% coal with the calculated weighted average (all the TG curves and also the DTG curves are presented in the Appendices B and C).

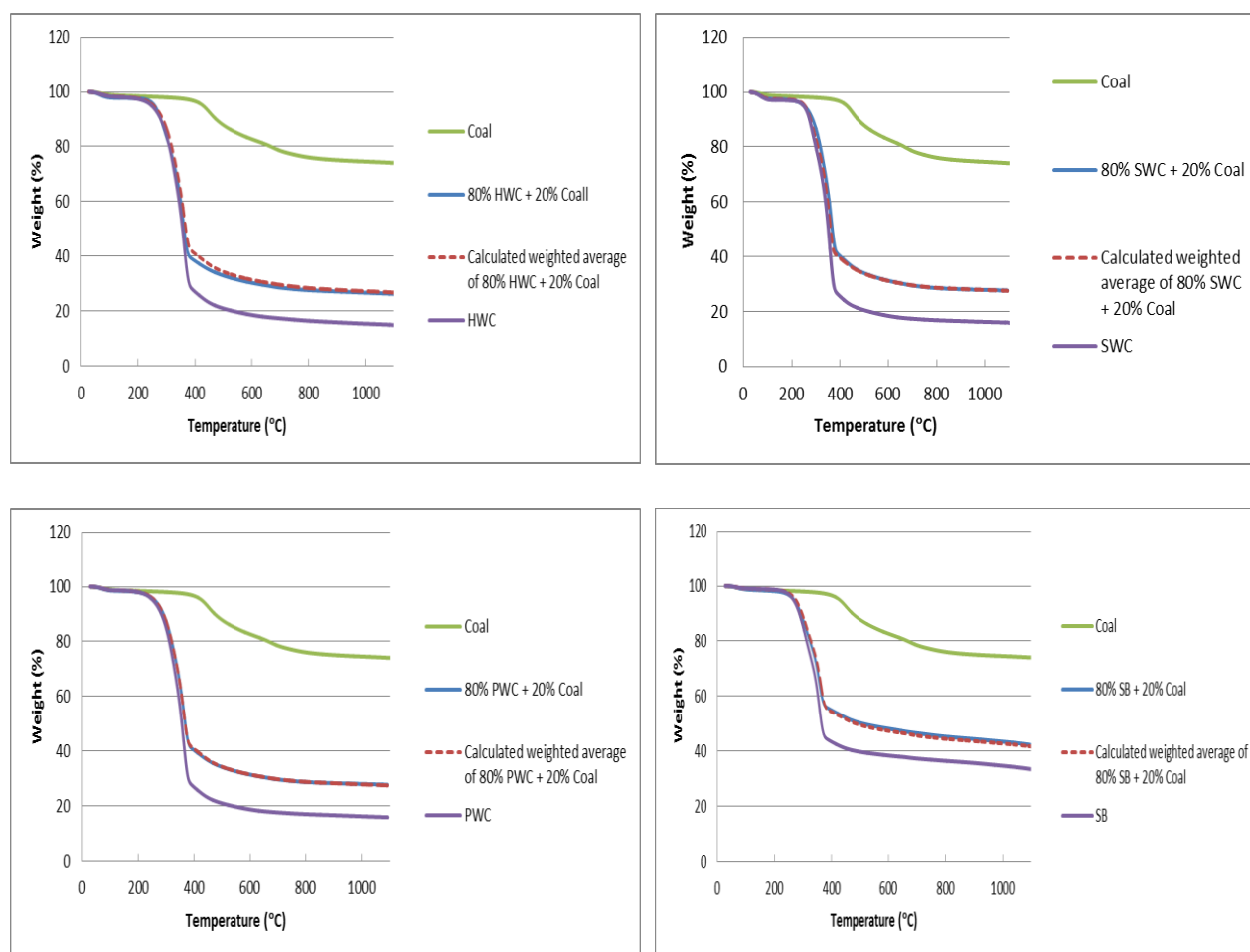


Figure 5.8: TG curves of blended samples compared with calculated weighted averages: pyrolysis of 80% biomass + 20% coal

The 20:80, 40:60, 60:40 and 80:20 wt. %:wt. % biomass addition to coal (figures of 20:80, 40:60 and 60:40 blends are shown in the Appendices B) showed similar absence of chemical interactions or synergistic effects between the coal and biomasses during the

devolatilisation process, with a maximum average deviation of 2.8%. The slight difference between the experimental and the theoretical results may be due to the quantity of biomass, which limits the effect, and also to the experimental conditions, such as the low heating rate and/or the distribution of mineral matter within the sample, which might have relatively limited the effect [Biagini *et al.*, 2002; Di Nola *et al.*, 2010; Haykiri-Acma and Yaman, 2010]. Studies conducted by Biagini *et al.* [2002] reported that coal pyrolysis occurs at higher temperatures than that of biomass during co-pyrolysis. The presence of oxygenated species released at low temperatures by the biomass seemed not to have influenced the coal pyrolysis, thus no partial combustion was observed [Senneca *et al.*, 2001]. Small sample masses were used and reactive species were flushed away by the nitrogen flow [Biagini *et al.*, 2002].

Table 5.3 lists values obtained from the deviation of calculated weighted average and experimentally determined values of blended samples at certain temperatures, using the following equation 5.2 [Haykiri-Acma and Yaman, 2010],

$$\text{Deviation (\%)} = \frac{|\text{Experimentally determined data} - \text{calculated weighted average}|}{\text{Experimentally determined data}} \times 100\% \quad 5.2$$

Table 5.3: Calculated deviations of the blended samples

| Blends   | Blending ratio (%) | Average deviation (%) | Maximum deviation (%) | T °C (maximum deviation %) |
|----------|--------------------|-----------------------|-----------------------|----------------------------|
| HWC-Coal | 20                 | 0.3                   | 1.7                   | 356-360                    |
|          | 40                 | 1.0                   | 2.0                   | 373-513                    |
|          | 60                 | 0.0                   | 3.0                   | 377-409                    |
|          | <b>80</b>          | <b>2.8</b>            | <b>10.8</b>           | <b>368-369</b>             |
| SWC-Coal | 20                 | 0.7                   | 1.8                   | 1102                       |
|          | 40                 | 0.0                   | 2.0                   | 351-369                    |
|          | 60                 | 1.0                   | 8.0                   | 362                        |
|          | <b>80</b>          | <b>0.8</b>            | <b>11.3</b>           | <b>363</b>                 |
| PWC-Coal | 20                 | 0.3                   | 1.6                   | 367-369                    |
|          | 40                 | 1.0                   | 2.0                   | 1061-1092                  |
|          | 60                 | 1.0                   | 1.0                   | 381-489, 514-1027          |
|          | <b>80</b>          | <b>0.3</b>            | <b>1.2</b>            | <b>392-407</b>             |
| SB-Coal  | 20                 | 0.6                   | 1.4                   | 1089-1091                  |
|          | 40                 | 1.0                   | 3.0                   | 349-368                    |
|          | 60                 | 1.0                   | 1.0                   | 328-1100                   |
|          | <b>80</b>          | <b>1.0</b>            | <b>4.0</b>            | <b>353-365</b>             |

### 5.3 Product composition

The release of the main gaseous products (i.e.  $H_2$ ,  $CH_4$ ,  $H_2O$  and  $CO_2$ ) from the pyrolysis process is discussed in this section. The breakdown of the coal, biomass feedstock and their blends produces a large fraction of volatiles, which could lead to secondary reactions (i.e. gas-solid) [Widyawati *et al.*, 2011]. The mechanism of the chemical reactions during the co-pyrolysis of coal and plant biomass, cellulose and lignin will form part of a further study also involving other chemical techniques.

#### 5.3.1 Gas analysis

The use of the MKS Cirrus quadrupole mass spectrometer (MS) was described in Section 3.7.9. The MS technique was used to record the temperatures where some volatiles evolved during the pyrolysis process of the different samples. The low heating rate of 10 °C/min for the thermal analysis was chosen in order to promote the evolution of low-molecular weight compounds [Jakab and Várhegyi, 1991]. The gaseous products formed are presented according to their mass-to-charge ratio ( $m/z$ ) and probable molecular ions [Helsen *et al.*, 1999]. The evolution of gaseous products could provide information with regard to the reactions occurring during the degradation process [Arenillas *et al.*, 1999]. The emissions of the volatile products are recorded in real time during thermal treatment at the TGA outlet. In order to avoid cold spots and prevent condensation of vapours, the capillary line was heated to 200 °C [Arenillas *et al.*, 1999; Sonobe *et al.*, 2008; <http://www.henniker-scientific.com>]. Table 5.4 presents the probable molecules with their assigned fragment ions according to the  $m/z$  ratio. Due to interference in the interpretation of the MS results, carbon monoxide (CO) was not included since it coincides with nitrogen ( $N_2$  was used as a carrier gas) with a mass of 28 amu (atomic mass units). It should be noted that, in this study, qualitative analysis based on the comparison of the shape and characteristic temperatures of the peak, was conducted.

Table 5.4: Selected ion masses for probable molecule(s) [Silverstein *et al.*, 2005]

| Ion mass ( $m/z$ ) | Molecule or fraction                                                                                                            |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------|
| 2                  | <b><math>H_2^+</math> (Hydrogen)</b>                                                                                            |
| 15                 | <b><math>CH_3^+</math> (Methylum)</b>                                                                                           |
| 16                 | $O^+$ , $H_2N^+$ and/or <b><math>CH_4^+</math> (Methane)</b>                                                                    |
| 18                 | <b><math>H_2O</math> (Water)</b>                                                                                                |
| 44                 | $N_2O^+$ , <b><math>CO_2^+</math> (Carbon dioxide)</b> , $CH_2NO^+$ , $CH_4N_2^+$ , $C_2H_4O^+$ , $C_2H_6N^+$ and/or $C_3H_8^+$ |

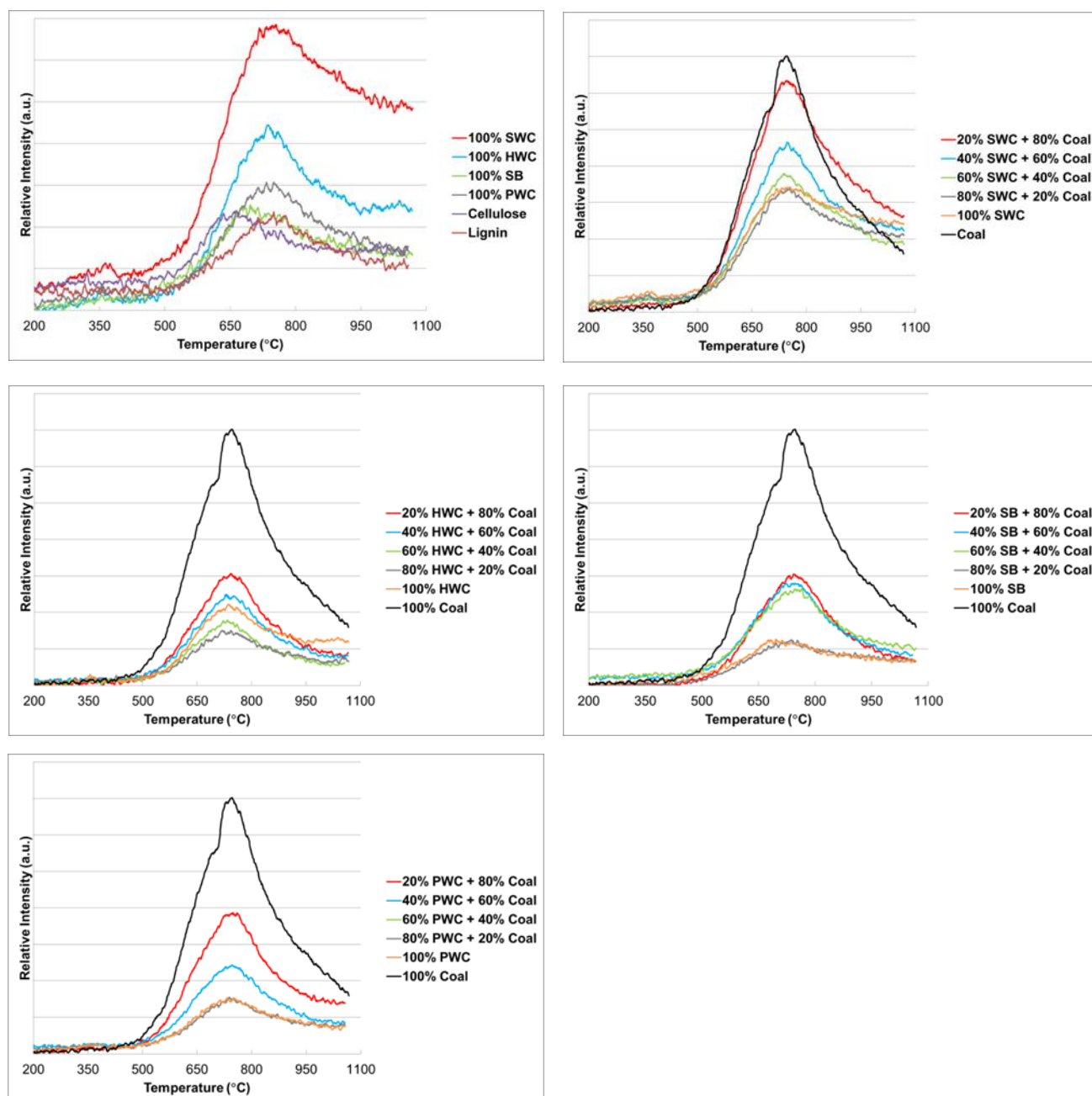
### 5.3.1.1 Evolution profile of H<sub>2</sub>

Figure 5.9 shows the gas profiles of H<sub>2</sub> evolution at a heating rate of 10 °C/min under an inert environment for ligno-cellulosic materials, biomass feedstock, coal and their blends. It can be observed from the results that the evolution rate of H<sub>2</sub> increased greatly with an increase in temperature [Arenillas *et al.*, 1999; Yang *et al.*, 2007; Hattingh, 2012]. Literature suggests that at high temperatures (last stage of thermal degradation), H<sub>2</sub> peaks are generated from the condensation of aromatic structures or the decomposition of heterocyclic compounds [Van Heek and Hodek, 1994]. The evolution of H<sub>2</sub> can be ascribed to the cracking and deformation of C=C (aromatic structure) and C-H (aromatic structure) bonds [Yang *et al.*, 2007]. In addition, the evolution of H<sub>2</sub> was also due to extensive depolymerisation of the phenyl groups, mostly in the lignin of the biomass, and secondary reactions of heavy molecular weight hydrocarbons at higher temperatures (i.e. unstable methane that cracks to form additional H<sub>2</sub>) [Xu *et al.*, 2009; Hattingh, 2012]. From the results it was evident that the cellulose started evolving H<sub>2</sub> at a low temperature of 480 °C and achieved a maximum rate ( $T_{\max}$ ) at a temperature of 652 °C. The temperature at maximum rate of H<sub>2</sub> evolution was nearly 680 °C for the SB sample. The H<sub>2</sub> evolution for lignin, biomass feedstock (HWC, SWC and PWC), coal and blends all reached a maximum value at around 740 °C. The H<sub>2</sub> gas profile of the blends stayed similar in shape with an increase of the blending ratio.

The oxygen content within the material has been known to influence the release of H<sub>2</sub> [Arenillas *et al.*, 1999]. Arenillas *et al.* [1999] stated that, the higher the oxygen content in the sample, the lower the H<sub>2</sub> evolution as a result of H<sub>2</sub>O formation. This observation could be corroborated by the ultimate analysis values in Section 4.1.3 (where the oxygen content for SB char was 51 wt. %, which corresponds with low H<sub>2</sub> emission, and also possibly due to more condensed structures present) [Arenillas *et al.*, 1999]. Table 5.5 shows the values of temperatures at maximum rate ( $T_{\max}$ ) of the evolution of H<sub>2</sub>.

Table 5.5: Temperatures at maximum rate ( $T_{\max}$ ) of the evolution of  $H_2$  (highest point of MS curve) for the ligno-cellulosic materials, biomass feedstock, coal and blends ( $^{\circ}C$ )

| Samples   | Blending ratio (%) | $T_{\max}$ |
|-----------|--------------------|------------|
| Cellulose | 100                | 652        |
| Lignin    | 100                | 742        |
| Coal      | 100                | 741        |
| HWC       | 100                | 739        |
| HWC-Coal  | 20                 | 739        |
|           | 40                 | 736        |
|           | 60                 | 730        |
|           | 80                 | 726        |
| SWC       | 100                | 739        |
| SWC-Coal  | 20                 | 739        |
|           | 40                 | 739        |
|           | 60                 | 739        |
|           | 80                 | 738        |
| PWC       | 100                | 741        |
| PWC-Coal  | 20                 | 740        |
|           | 40                 | 740        |
|           | 60                 | 736        |
|           | 80                 | 735        |
| SB        | 100                | 680        |
| SB-Coal   | 20                 | 740        |
|           | 40                 | 736        |
|           | 60                 | 731        |
|           | 80                 | 728        |

Figure 5.9: Evolution curves of  $H_2$  during pyrolysis of materials

### 5.3.1.2 Evolution profile of $\text{CH}_3^+/\text{CH}_4$

The atomic mass unit (amu) of 15 (thus fragment  $\text{CH}_3^+$ ) was chosen to represent methane ( $\text{CH}_4$ ) in this study, in order to prevent interference from other molecules which share the same molecular weight of 16 amu (i.e. oxygen) [Worasuwannarak *et al.*, 2007; Huang *et al.*, 2011; Sanchez-Silva *et al.*, 2012]. Literature suggests that methane is known to easily discharge hydrogen atoms in the electric field of the mass spectrometer [Huang *et al.*, 2011]. Figure 5.10 presents the evolution of  $\text{CH}_3^+$  with an increase in temperature. From Figure 5.10 it can be observed that the formation of  $\text{CH}_3^+$  started at temperatures above 210 °C for biomass feedstock and blends, and the evolution of  $\text{CH}_3^+$  for the coal was detected at temperatures above 400 °C. This difference is due to weaker chemical bonds in the biomass than in the coal, and thus the coal has a higher thermal stability compared with biomass (as described in Section 5.2.1.3) [Arenillas *et al.*, 1999; Hykiri-Acma and Yaman, 2010]. A similar evolution of  $\text{CH}_3^+$  was observed by other authors for the thermal degradation of coal [Arenillas *et al.*, 1999; Hattingh, 2012].

The evolution of  $\text{CH}_3^+$  during pyrolysis of the coal is proposed to have derived mainly from hydro-aromatic and/or aryl methyl groups [Charpenay *et al.*, 1996]. Di Nola *et al.* [2010] stated that rapid recombination reactions among smaller radicals and their reaction with  $\text{H}_2$  could lead to the formation of methane. In addition, the methane that is evolved at approximately 400 °C could be the result of the decomposition and/or hydrogenation of the methyl side chains from parent coal or evolved tars [Cui *et al.*, 2006]. Literature also suggests that the methane that is evolved at higher temperatures than 400 °C could be due to cross-linking reactions of coal macromolecules and/or cracking of saturated hydrocarbons [Cui *et al.*, 2006]. Khan [1989] proposed that, at temperatures higher than 725 °C, methane can become unstable and crack to form  $\text{H}_2$ . The evolution of methane from the biomass feedstock and blended samples during pyrolysis showed a similar pattern to that of the DTG curves (decomposition of ligno-cellulosic materials that started from around 200-400 °C), as described in Section 5.2. The  $\text{CH}_3^+$  evolution for the biomasses observed at temperatures higher than 470 °C could be ascribed to secondary pyrolysis as the driving force [Yang *et al.*, 2007]. The release of  $\text{CH}_3^+$  is ascribed to the cracking of methoxy (i.e.  $\text{O-CH}_3$ ) functional groups from the biomass at lower temperatures (<600 °C) [Yang *et al.*, 2007]. From the results, the profiles of  $\text{CH}_3^+$  evolution of the blends have similar characteristics compared with parent materials. The  $\text{CH}_3^+$  evolution profiles of the blends stayed similar in shape with an increase of the blending ratio. Table 5.6 shows the values of temperatures at maximum rate ( $T_{\text{max}}$ ) of the evolution of  $\text{CH}_3^+$ .

Table 5.6: Temperatures at maximum rate ( $T_{\max}$ ) of the evolution of  $\text{CH}_3^+$  (highest point of MS curve) for the ligno-cellulosic materials, biomass feedstock, coal and blends ( $^{\circ}\text{C}$ )

| Samples   | Blending ratio (%) | $T_{\max}$ |
|-----------|--------------------|------------|
| Cellulose | 100                | 323        |
| Lignin    | 100                | 409        |
| HWC       | 100                | 360        |
| Coal      | 100                | 516        |
| HWC-Coal  | 20                 | 534        |
|           | 40                 | 517        |
|           | 60                 | 357        |
|           | 80                 | 358        |
| SWC       | 100                | 366        |
| SWC-Coal  | 20                 | 536        |
|           | 40                 | 526        |
|           | 60                 | 369        |
|           | 80                 | 367        |
| PWC       | 100                | 372        |
| PWC-Coal  | 20                 | 525        |
|           | 40                 | 368        |
|           | 60                 | 367        |
|           | 80                 | 365        |
| SB        | 100                | 358        |
| SB-Coal   | 20                 | 532        |
|           | 40                 | 516        |
|           | 60                 | 362        |
|           | 80                 | 352        |

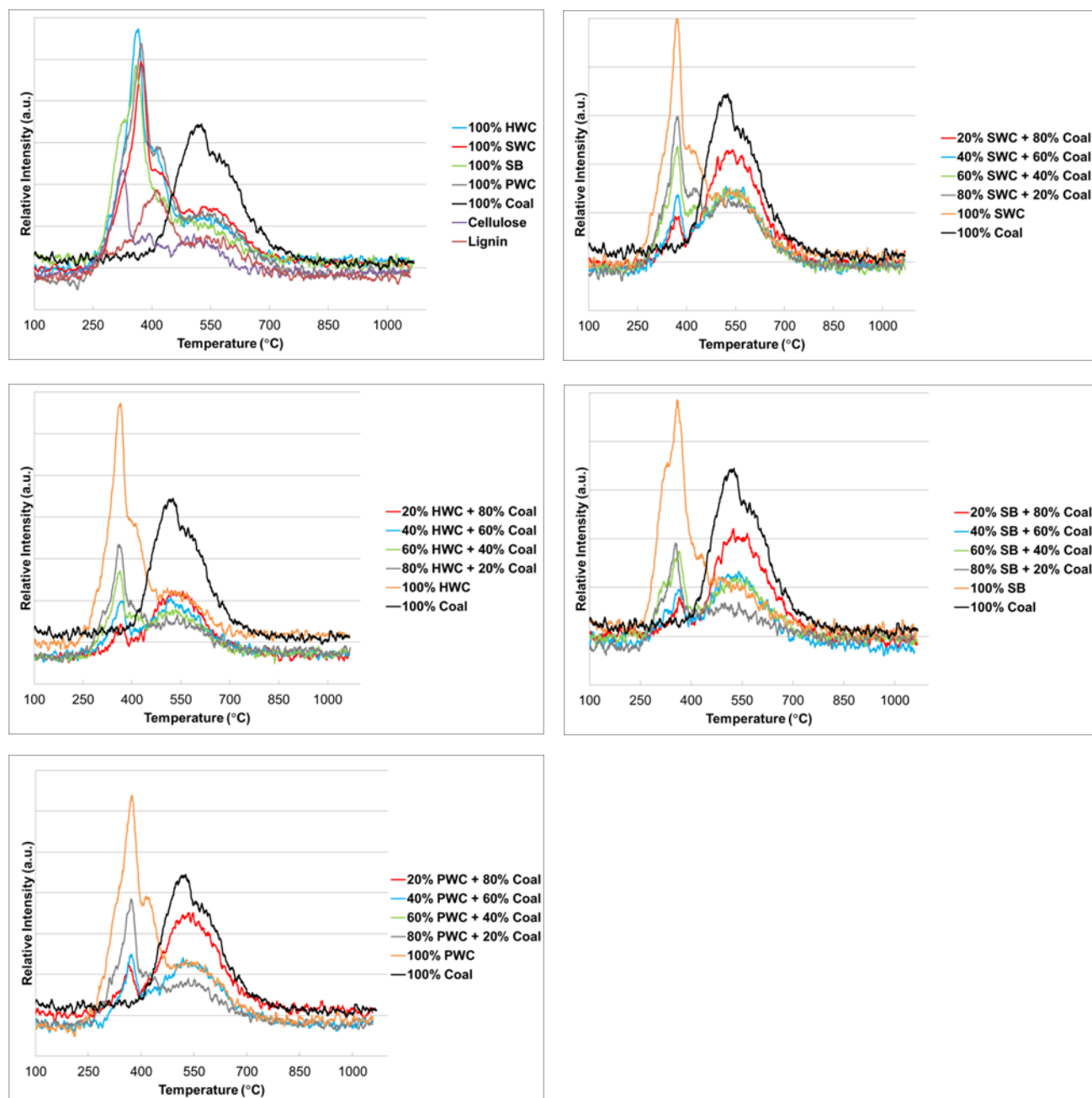


Figure 5.10: Evolution curves of  $\text{CH}_3^+$  during pyrolysis of materials

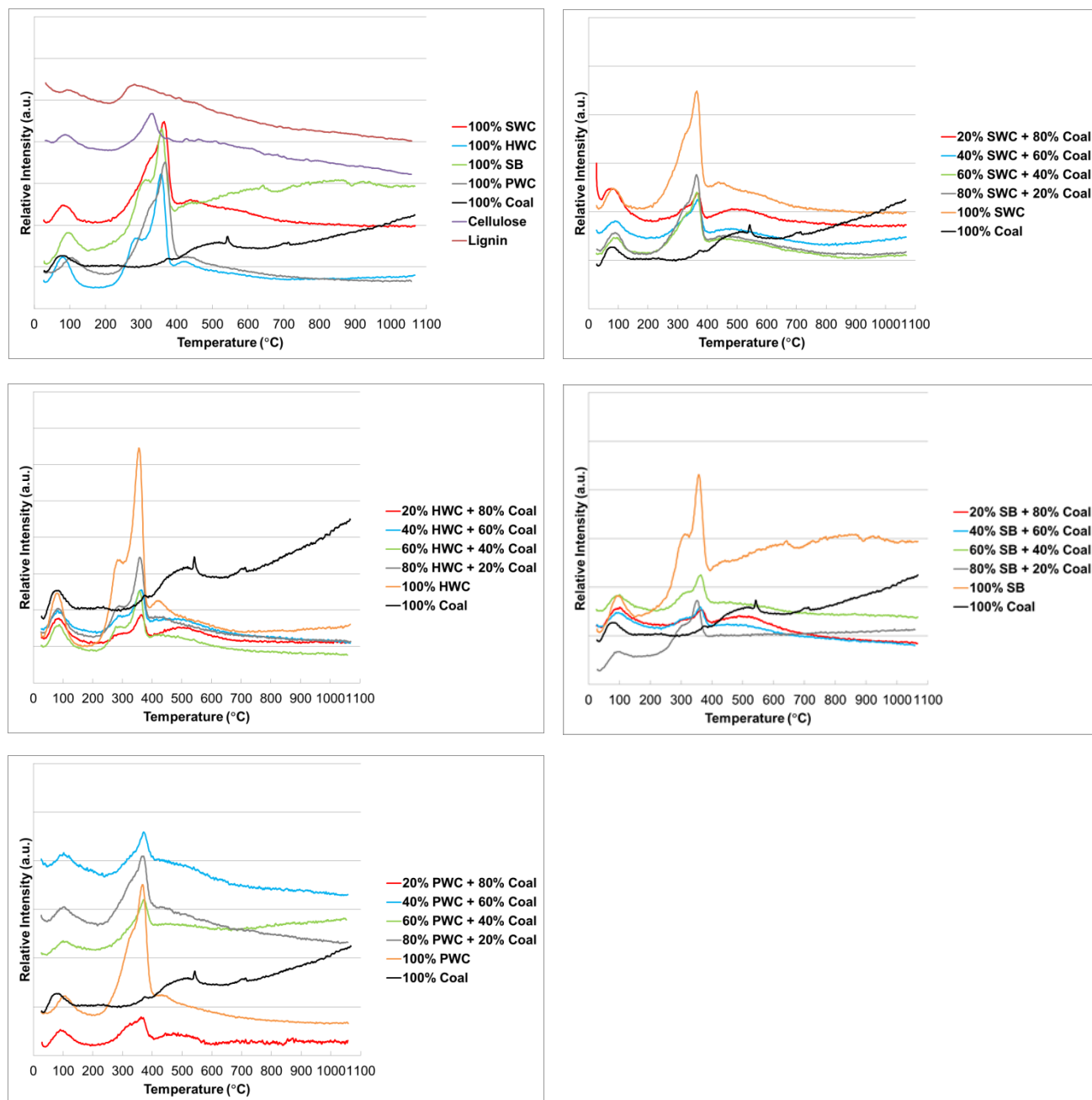
### 5.3.1.3 Evolution profile of H<sub>2</sub>O

Figure 5.11 shows the evolution of H<sub>2</sub>O with increase of temperature during the pyrolysis process. Apart from the moisture loss below 150 °C, the H<sub>2</sub>O formation during pyrolysis is known to form part of the products generated for ligno-cellulosic materials, coal, biomass feedstock and blended samples [Worasuwannarak *et al.*, 2007]. This water formation could be related to chemical reactions occurring due to increased temperature among the components of the samples [Arenillas *et al.*, 1999; Worasuwannarak *et al.*, 2007]. The first peak, observed around 100 °C, reflected the evolution of moisture in the samples (which coincided with the DTG curves in Section 5.2). The further H<sub>2</sub>O evolution in lignin was detected at a lower and broader temperature range (200-700 °C) than cellulose. Cellulose evolved H<sub>2</sub>O in a narrower temperature range (200-400 °C). The H<sub>2</sub>O evolution of cellulose and lignin reached maximum rates of evolution at 320 and 280 °C, respectively. This gaseous product profiles corroborated the thermal decomposition displayed in the DTG curves (see Section 5.2.1.1). The four selected biomass feedstock started evolving H<sub>2</sub>O around 200 °C in two distinctive steps, evident from the overlapping peaks (as also observed in Section 5.2.1.2). The evolution of H<sub>2</sub>O in this temperature range could be related to the thermal decomposition of the biomass components (i.e. hemicellulose and cellulose) [Worasuwannarak *et al.*, 2007; Huang *et al.*, 2011]. These results are in agreement with previous studies relating to the H<sub>2</sub>O evolution profiles produced during thermal degradation of hemicellulose and cellulose [Bassilakis *et al.*, 2001; Worasuwannarak *et al.*, 2007; Huang *et al.*, 2011].

The evolution of H<sub>2</sub>O was detected to start at temperatures of 320 °C, with a maximum rate at 520 °C for the coal. This is due to condensation reactions occurring and can be corroborated by the high oxygen content in the coal sample [Arenillas *et al.*, 1999; Jakab *et al.*, 1991]. The H<sub>2</sub>O evolution of the blended samples started at similar temperatures than that of the biomass samples. The production of H<sub>2</sub>O for all the blends was between 250 and 500 °C, which is within the thermal decomposition range of ligno-cellulosic materials in the biomass [Huang *et al.*, 2011]. The H<sub>2</sub>O gas profile of the blends between 200 and 400 °C stayed similar in shape with an increase in blending ratio. However, the evolution at temperatures higher than 400 °C (blends with low biomass loadings), took the shape of the evolution curves of the coal. Table 5.7 shows the temperatures at maximum rate ( $T_{\max}$ ) of the evolution of H<sub>2</sub>O.

Table 5.7: Temperatures at first maximum rate ( $T_{\max}$ ) of the evolution of  $H_2O$  (highest point of MS curve) from condensation reactions for the ligno-cellulosic materials, biomass feedstock, coal and blends ( $^{\circ}C$ )

| Samples   | Blending ratio (%) | $T_{\max}$ |
|-----------|--------------------|------------|
| Cellulose | 100                | 320        |
| Lignin    | 100                | 280        |
| HWC       | 100                | 355        |
| Coal      | 100                | 520        |
| HWC-Coal  | 20                 | 362        |
|           | 40                 | 360        |
|           | 60                 | 356        |
|           | 80                 | 354        |
| SWC       | 100                | 362        |
| SWC-Coal  | 20                 | 365        |
|           | 40                 | 364        |
|           | 60                 | 359        |
|           | 80                 | 357        |
| PWC       | 100                | 365        |
| PWC-Coal  | 20                 | 364        |
|           | 40                 | 370        |
|           | 60                 | 368        |
|           | 80                 | 366        |
| SB        | 100                | 357        |
| SB-Coal   | 20                 | 363        |
|           | 40                 | 358        |
|           | 60                 | 358        |
|           | 80                 | 349        |

Figure 5.11: Evolution curves of  $H_2O$  during pyrolysis of materials

#### 5.3.1.4 Evolution profile of CO<sub>2</sub>

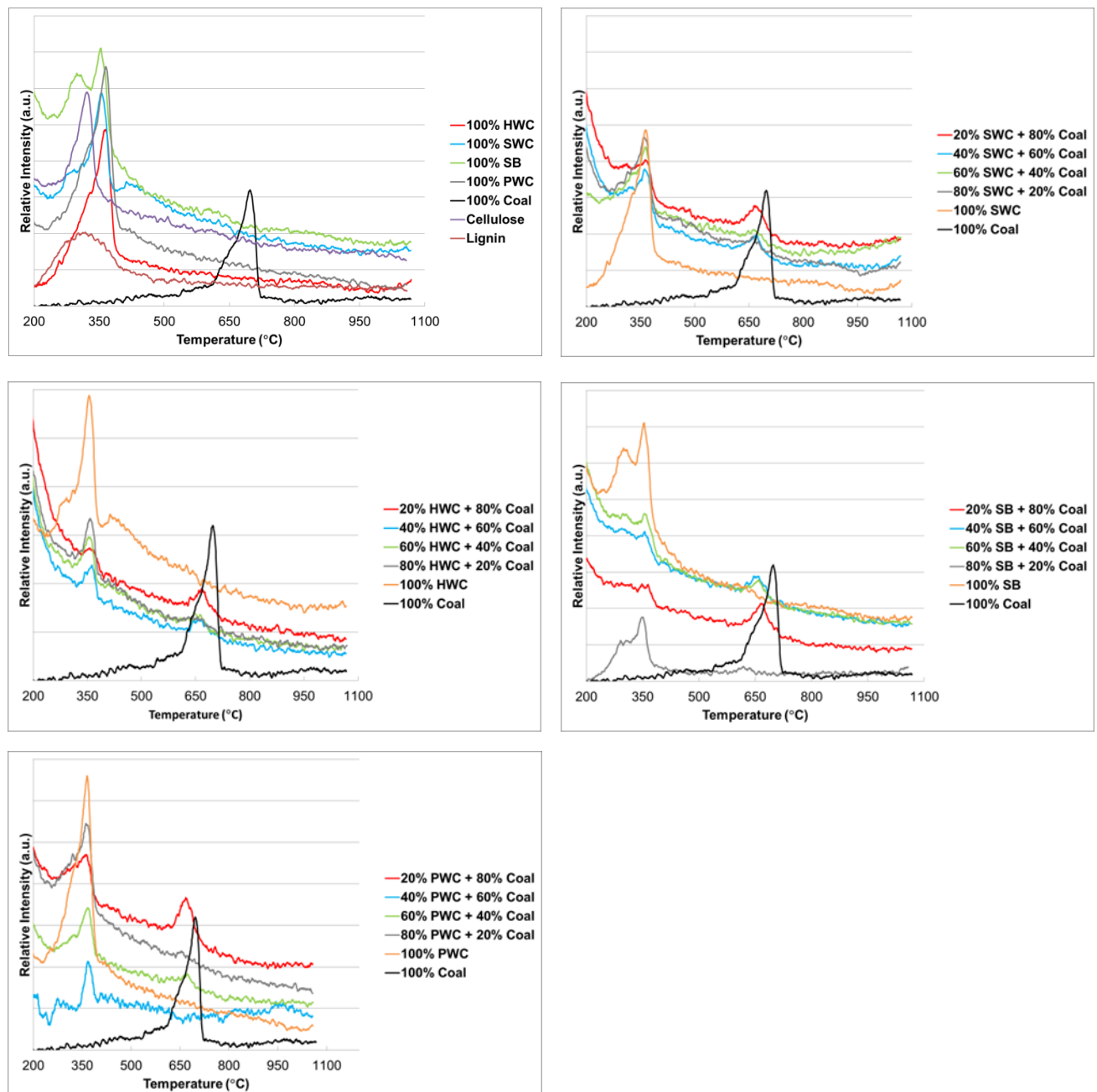
Figure 5.12 shows the evolution of CO<sub>2</sub> with an increase of temperature during the thermal degradation of all the samples. The CO<sub>2</sub> formation during pyrolysis is known to form part of the products generated for ligno-cellulosic materials, coal, biomass feedstock and blended samples [Arenillas *et al.*, 1999; Worasuwanarak *et al.*, 2007; Hattingh, 2012]. The evolution of CO<sub>2</sub> during thermal degradation of a bituminous coal is proposed to be due to the decomposition of aliphatic, aromatic carboxyl and carboxylate groups at lower temperatures [Arenillas *et al.*, 1999; Zhu *et al.*, 2000; Cui *et al.*, 2006; Xiong *et al.*, 2010]. At higher temperatures, the CO<sub>2</sub> evolution during thermal treatment is known to be ascribed to the decomposition of the more stable ether structures, oxygen bearing heterocyclic compounds and the decomposition of carbonates [Berkowitz, 1985; Arenillas *et al.*, 1999]. In addition, the existence of intramolecular carboxylic acid anhydrides in the bituminous coal has also been proposed to contribute to the formation of CO<sub>2</sub> during the pyrolysis process [Van Heek and Hodek, 1994]. The CO<sub>2</sub> evolution spectra exhibited a single peak that started from approximately 400 °C and reached maximum rates of evolution at around 695 °C for the coal. The CO<sub>2</sub> profile of the coal is in agreement with the temperature range (300-700 °C) observed during the pyrolysis of the two coal samples (low rank coal and a subbituminous coal) [Chen *et al.*, 2010].

The profiles of CO<sub>2</sub> evolution for the biomass feedstock are proposed to be mainly derived from the cracking and reforming of functional groups of carboxyl (C=O) and COOH [Yang *et al.*, 2007]. The spectra exhibited a CO<sub>2</sub> peak that started at lower temperatures of 250 °C for the biomass feedstock and blends, with the exception of the blends prepared from HWC. For the blended samples prepared from SWC added to coal, the production of CO<sub>2</sub> started at approximately 320 °C, reaching a maximum rate of evolution around 350 °C. All of the blended samples (except for blended samples of HWC and PWC prepared at 80% biomass to 20% coal) exhibited a distinctive peak at temperatures around 660 °C. This small peak corroborated the peak detected in this temperature range of the coal. However, this peak was below the coal's maximum rate of evolution of CO<sub>2</sub>. The slight shift to lower temperatures (<700 °C) of the CO<sub>2</sub> evolution in the blends may imply the influence of secondary reactions (i.e. self-gasification due to the presence of the biomass or residual char generated in earlier processes) and/or catalytic effects of inorganic compounds at these temperatures which speed up/enhance the rate of the reactions where CO<sub>2</sub> is given off (faster formation and release) [Park *et al.*, 2010; Huang *et al.*, 2011]. The peaks of the CO<sub>2</sub> profile were narrower than that of other gaseous products formed during pyrolysis of all the

samples (i.e.  $\text{CH}_3^+$ ). Table 5.8 shows the Temperatures at maximum rates ( $T_{\text{max}}$ ) of the evolution of  $\text{CO}_2$ .

Table 5.8: Temperatures at maximum rates ( $T_{\text{max}}$ ) of the evolution of  $\text{CO}_2$  (highest point(s) of MS curve) for the ligno-cellulosic materials, biomass feedstock, coal and blends ( $^{\circ}\text{C}$ )

| Samples   | Blending ratio (%) | $T_{\text{max}} (^{\circ}\text{C})$ |
|-----------|--------------------|-------------------------------------|
| Cellulose | 100                | 357                                 |
| Lignin    | 100                | 310                                 |
| HWC       | 100                | 360                                 |
| Coal      | 100                | 695                                 |
| HWC-Coal  | 20                 | 349,660                             |
|           | 40                 | 350,659                             |
|           | 60                 | 346                                 |
|           | 80                 | 346                                 |
| SWC       | 100                | 370                                 |
| SWC-Coal  | 20                 | 354,664                             |
|           | 40                 | 354,664                             |
|           | 60                 | 352, 664                            |
|           | 80                 | 351,664                             |
| PWC       | 100                | 369                                 |
| PWC-Coal  | 20                 | 347,652                             |
|           | 40                 | 354                                 |
|           | 60                 | 353                                 |
|           | 80                 | 349                                 |
| SB        | 100                | 352                                 |
| SB-Coal   | 20                 | 353,663                             |
|           | 40                 | 353,648                             |
|           | 60                 | 353,655                             |
|           | 80                 | 352                                 |

Figure 5.12: Evolution curves of CO<sub>2</sub> during pyrolysis of materials

### **5.3.2 Comparisons of the MS results between selected blended samples**

The comparisons were done between the results of the gaseous products obtained using selected biomass feedstock to coal ratios for the samples during the pyrolysis process. This was done in order to compare the extent of the influence of the specific biomass on the temperatures at which the gases previously described are emitted.

#### **5.3.2.1 The Influence of the biomasses on the temperature range of the evolution of gaseous products formed during co-pyrolysis**

##### **5.3.2.1.1 Profiles of H<sub>2</sub> evolution**

The influences of the four biomass feedstock on the H<sub>2</sub> evolution are presented in Figure 5.13 for the 20:80 (wt. %: wt. %) biomass/coal blends. The H<sub>2</sub> evolution was detected in the last stages of the devolatilisation process. Arenillas *et al.* [1999] reported that the oxygen content in the sample has a critical influence in the H<sub>2</sub> evolution observed at higher temperatures. Only a very small lowering in the temperature at maximum H<sub>2</sub> evolution of the blends was observed when compared to the coal H<sub>2</sub> profile. This indicates a very small increase in the coal's reactivity due to the presence of the biomass samples. The effect was the largest (-2 °C) for the HWC and SWC samples. The effect, however, is too small to conclusively state that the coal's reactivity was increased.

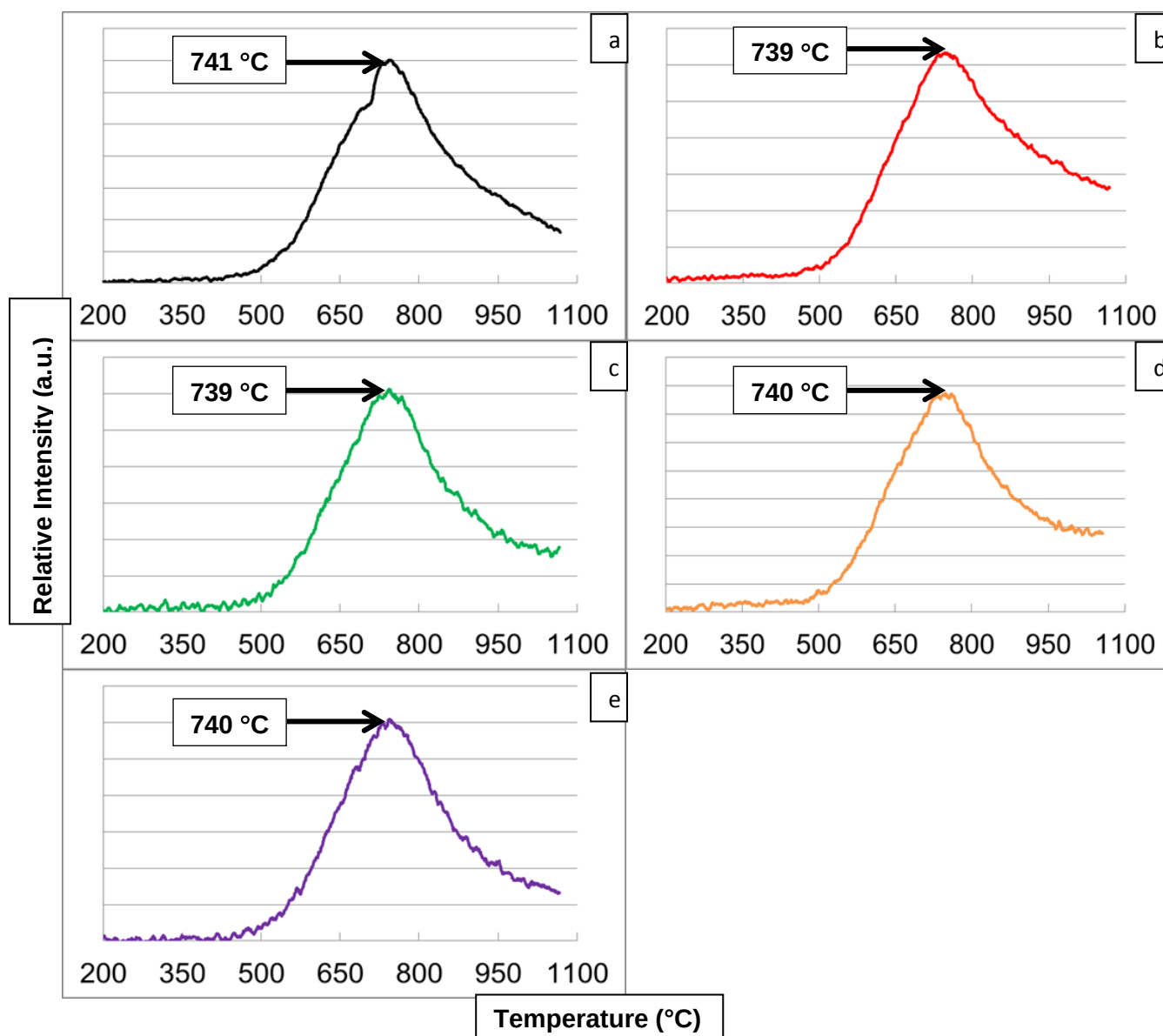


Figure 5.13: MS analysis of  $H_2$  ( $m/z = 2$ ) for coal (a), 20% SWC + 80% coal (b), 20% HWC + 80% coal (c), 20% PWC + 80% coal (d) and 20% SB + 80% coal (e)

### 5.3.2.1.2 Profiles of $CO_2$ evolution

Figure 5.14 shows the  $CO_2$  evolution of the coal and the 20% biomass to 80% coal blends, to compare the effect caused by the biomass feedstock on the  $CO_2$  evolution of the coal. The blends exhibited two peaks, a peak which correlates with the decomposition of lignocellulosic materials in the biomass feedstock, and a second peak which corroborates the maximum rate of evolution of  $CO_2$  for the coal. The temperature at the highest point of the second peak (due to the degradation of the coal) was compared with the DTG curves (as described in Section 5.2.1.3), in order to evaluate the influence of the biomass on the coal's degradation. From the results, the lowering in the temperature at maximum  $CO_2$  evolution of the blends was observed when compared with the DTG peak of the coal. The largest

decrease in this temperature was observed for the PWC sample (-43 °C), which correlates with the fact that this biomass sample also contains the highest amount of inorganic matter (as observed in Section 4.1.2). The decreased maximum temperature at the maximum rate of CO<sub>2</sub> evolution can be ascribed to a catalytic effect of inorganic compounds in the biomass material which influenced the rate at which CO<sub>2</sub> is evolved [Park *et al.*, 2010; Huang *et al.*, 2011].

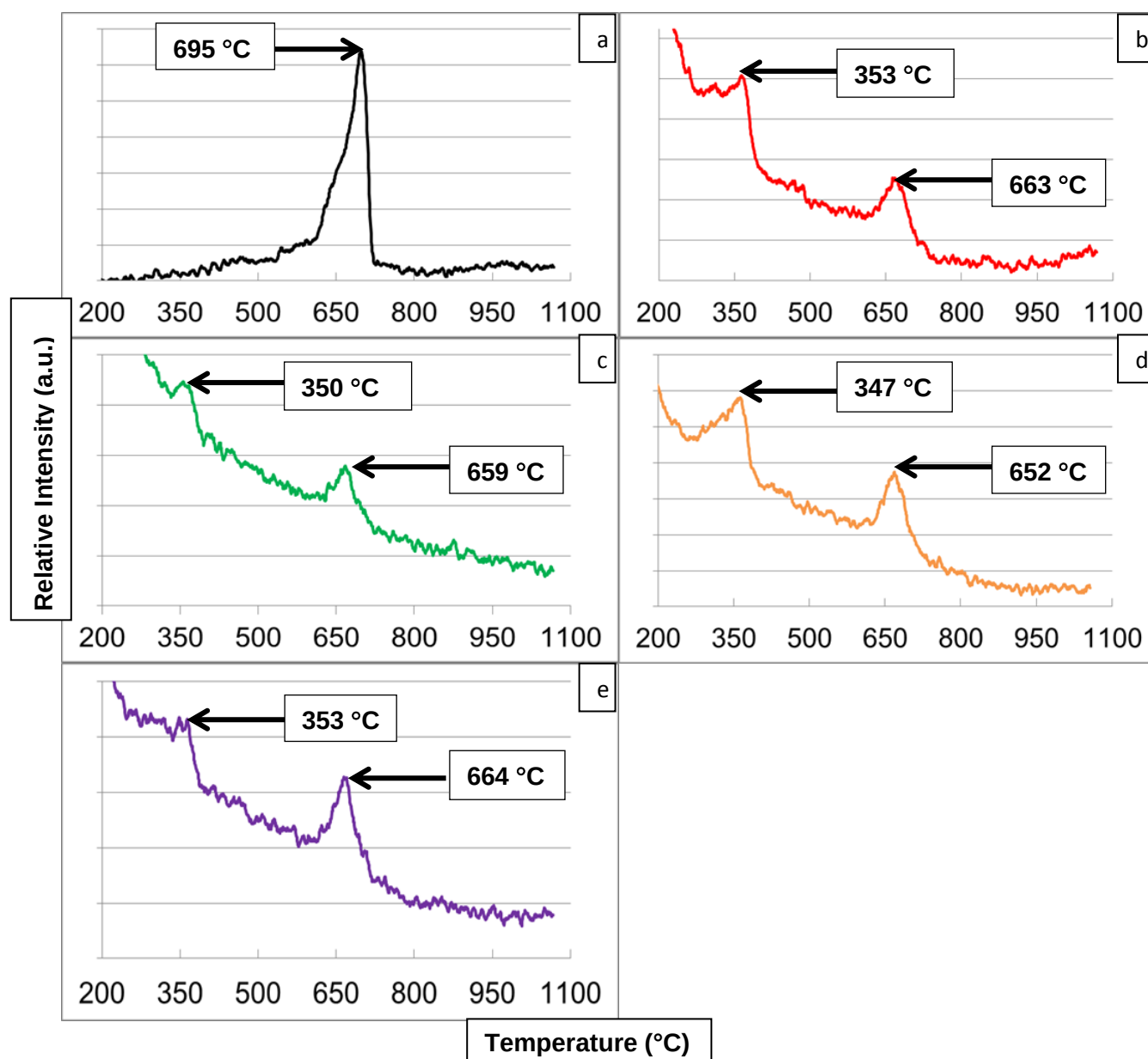


Figure 5.14: MS analysis of CO<sub>2</sub> (m/z = 44) for coal (a), 20% SWC + 80% coal (b), 20% HWC + 80% coal (c), 20% PWC + 80% coal (d) and 20% SB + 80% coal (e)

### 5.3.2.2 The relation between temperature ranges of gaseous products formation and the DTG curves

The DTG curves of the samples were used to reveal where the thermal degradation occurs. The onset temperatures, termination temperatures and also the temperature at maximum rate of pyrolysis were determined. The CO<sub>2</sub> gaseous evolution profiles were compared with the DTG results as the most pronounced shift in described characteristic temperatures was observed for the CO<sub>2</sub> evolution.

#### 5.3.2.2.1 Evolution of CO<sub>2</sub> profile

Figures 5.15-5.18 present the DTG-MS results of the blends for the CO<sub>2</sub> profile experiments. The early peaks from the DTG curves at which temperatures at maximum value corroborated with the decomposition of ligno-cellulosic materials (i.e. hemicellulose and cellulose) in samples, as described in Section 5.2.1.1. It can be seen that there was a correlation between the temperatures at maximum peaks (around 350 °C) for the DTG and the MS results of the chars.

From the MS results, the temperatures at maximum rate of evolution (>650 °C) were compared with the DTG data, in order to evaluate the influence of the biomass on the coal's degradation. From the results, the lowering in the temperature at maximum CO<sub>2</sub> evolution of the blends was observed when compared with the DTG peak of the coal. The largest decrease in the temperature, from the MS results, was observed for the 20% PWC + 80% Coal sample (-43 °C). From the DTG results, the observed temperature at maximum value was 679 °C for the 20% PWC + 80% Coal and 20% HWC + 80% Coal samples, whereas for 20% SB + 80% Coal and 20% SWC + 80% Coal blended samples, the temperatures were 674 °C and 676 °C, respectively. The deviations observed in the TG-MS results could possibly correlate with the fact that the biomass samples contain varying amounts of inorganic matter (as observed in Section 4.1.2).

Overall, the temperature range of the DTG curves could be used to relate to the maximum rate of evolution of the CO<sub>2</sub> profile, which could confirm the pyrolysis characteristics of the blends. As seen in Section 5.2.1.3, the thermograms of the blends exhibited an intermediate pyrolytic behaviour between those of parent materials [Bonelli *et al.*, 2007]. The MS measurements confirm trends observed from the DTG results. From the co-pyrolysis of the inertinite-rich coal and biomass feedstock, it can be suggested that the enhancement of the thermal decomposition of the coal at higher temperatures could be due to the minerals in the biomass and also to secondary pyrolysis reactions at higher temperatures [Biagini *et al.*, 2002; Sonobe *et al.*, 2008].

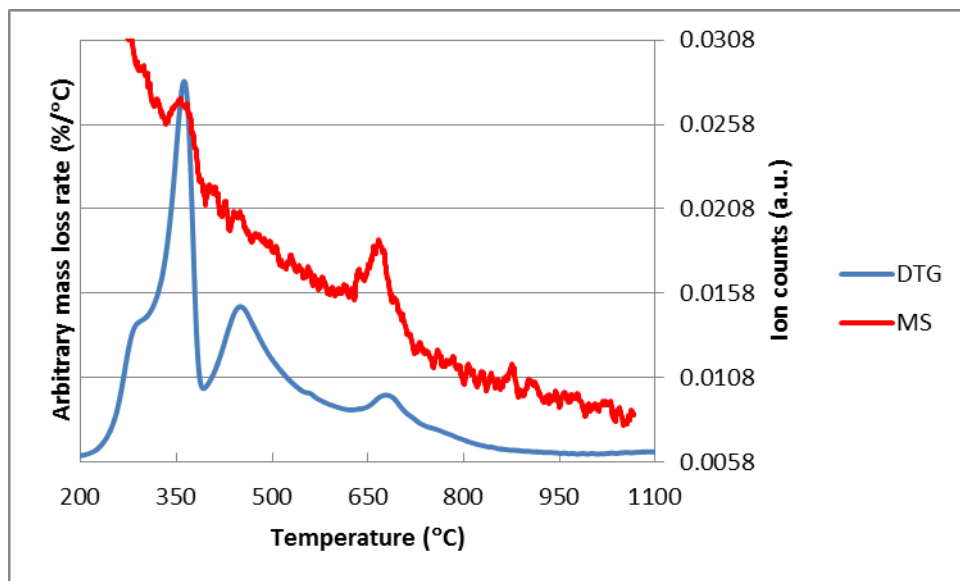


Figure 5.15: DTG-MS analysis of 20% HWC + 80% Coal during pyrolysis

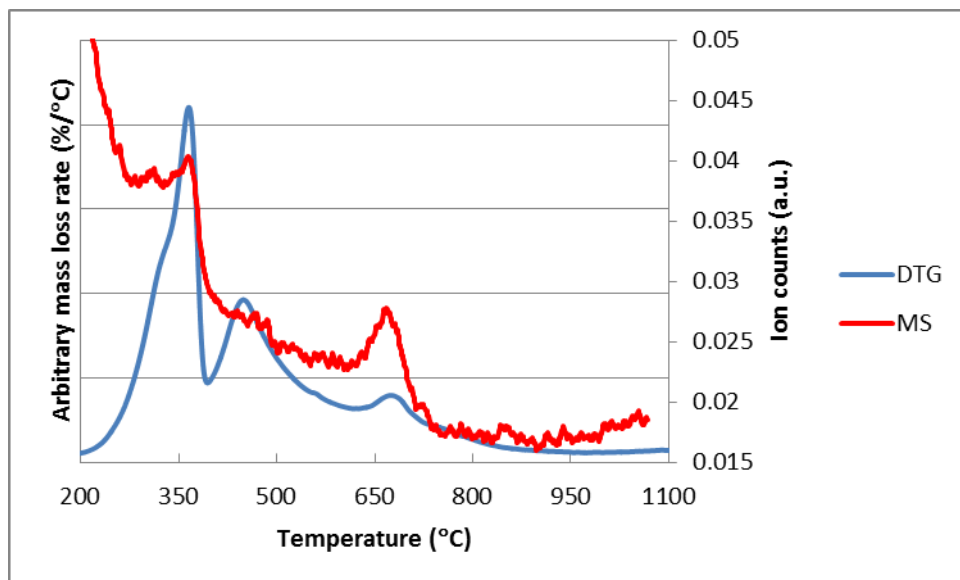


Figure 5.16: DTG-MS analysis of 20% SWC + 80% Coal during pyrolysis

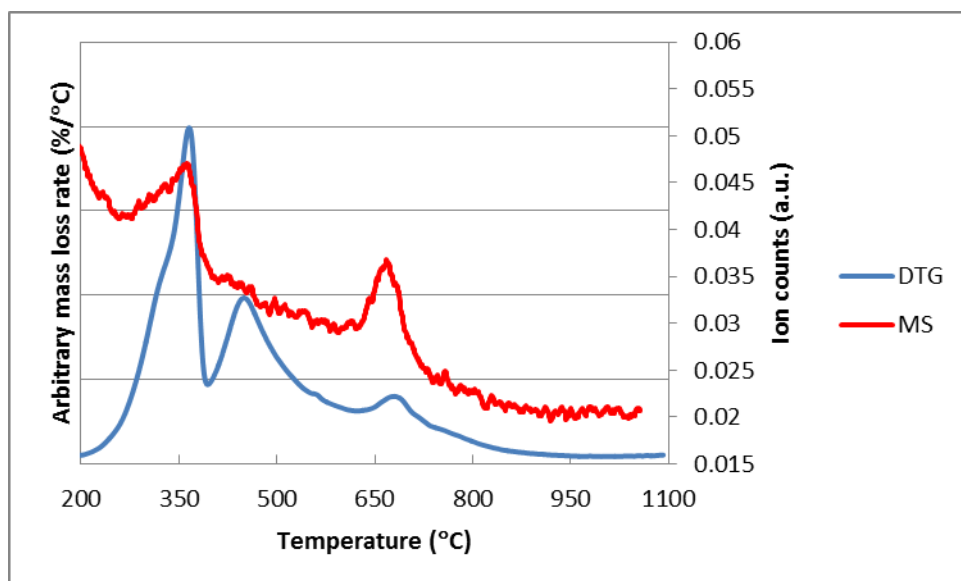


Figure 5.17: DTG-MS analysis of 20% PWC + 80% Coal during pyrolysis

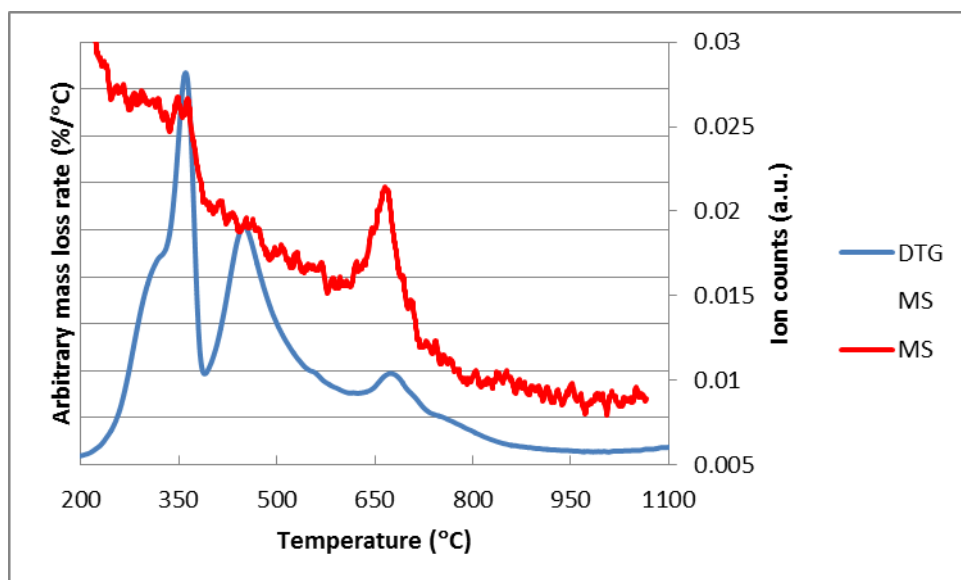


Figure 5.18: DTG-MS analysis of 20% SB + 80% Coal during pyrolysis

## Chapter 6

### Conclusions and Recommendations

The thermal decomposition behaviour during pyrolysis of four selected biomass feedstock, coal and their blends has been the main focus of discussion in this dissertation. This chapter highlights the important main conclusions relevant to the hypothesis and some trends observed, and also gives recommendations for future work concerning coal pyrolysis using biomass as additives. The hypothesis, as stated in Section 1.2 is: 'It is hypothesised that the addition of biomass will have an influence on the reactivity of the resulting coal char during pyrolysis. The alkaline compounds in the biomass may exhibit catalytic properties on the coal char. Differences in the composition of the biomasses (chemical structure of cellulose, hemicellulose, and lignin) will influence the resulting low molecular mass gas products formed during the pyrolysis process.

#### 6.1 Conclusions

##### 6.1.1 Characterisation of coal, biomass and their blends

6.1.1.1 According to analyses carried out to determine ligno-cellulosic biomass composition (see Paragraph 3.7.7), HWC, SWC, PWC and SB indicated ligno-cellulosic components, which consist of 27.8-39.9 wt. % cellulose, 17.4-21.1 wt. % hemicellulose and 8.0-32.4 wt. % lignin (see Paragraph 4.1.2). The SB contained the largest ash content (31.7 wt. %) compared to the other biomasses.

##### Conclusion 1

- ❖ The amount of ligno-cellulosic components found was in the range of the reported values for biomasses from literature (see Paragraph 4.1.2).
- ❖ The high ash content observed for SB indicates a substantial amount of inorganic matter, which could be due to the inclusion of soil in the initial sample.

6.1.1.2 The proximate and ultimate analyses indicated that the sample of 80% SB +20% Coal char has the highest ash content (50.8 wt. %), a high H/C ratio (0.06 wt. %), low volatiles (0.7 wt. %) and a low gross calorific value (16.0 MJ/kg) (see Paragraph 4.1.3) with respect to other blends.

**Conclusion 2**

- ❖ All of the chars of the biomass feedstock and blends had a low sulfur content ( $<0.4$  wt. %) and a low nitrogen content ( $<0.7$  wt. %), which makes biomass an option in terms of environmental impact for evaluation as a fuel with low emissions of  $\text{SO}_x$  and  $\text{NO}_x$ . The plant biomass can thus be co-utilised with coal and not add in high emissions of these gases.

6.1.1.3 The char from the blends containing HWC, SWC and PWC had lower ash contents (9.0-10.7 wt. % a.d.b) than coal char (18.3 wt. % a.d.b). The CV value of the coal char (26.5 MJ/kg) was comparable to that of the char produced from the HWC, SWC and PWC blends (28.5-29.1 MJ/kg) with exception to the char from the SB blend (16.0 MJ/kg). The fuel ratio (volatiles/fixed carbon) indicated that the energy obtained from devolatilisation was similar for both the coal char (0.02) and 20% coal - 80% biomass char blends (0.01-0.02).

**Conclusion 3**

- ❖ The data and results obtained using the HWC, SWC and PWC blends indicate it is beneficial it is to use during thermal processing (pyrolysis in this case). The SB blends had high ash contents possibly caused by inclusion of soil.

6.1.1.4 The XRF results confirmed a relatively larger presence of inorganic species ( $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) in the biomass chars and blended chars comparable to the coal char. The coal, biomass feedstock and 80:20 (wt. %: wt. %) blended chars contained appreciable amounts of known catalytic active species (i.e  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$ ) in the range of 0.9-7.6 wt. % a.d.b. The  $\text{CO}_2$  BET surface area measurements indicated that the chars had larger surface areas than raw samples due to the thermal degradation processes, with the SWC char having the largest surface area (332.4  $\text{m}^2/\text{g}$ ), followed by 80% HWC + 20% Coal (271.5  $\text{m}^2/\text{g}$ ) (see Paragraph 4.1.6). This high surface area of samples could be correlated with open structures seen during SEM analyses.

**Conclusion 4**

- ❖ The increase of the surface areas indicates the influence of temperature on the micropores of the samples under nitrogen atmosphere.
- ❖ The results show that the chemical and physical characteristics of the char blends are in between those of the individual parent materials.

### 6.1.2 Thermogravimetric results of coal-biomass chars

6.1.2.1 The experiments conducted by TGA showed that the biomass feedstock and coal degraded at temperatures as reported in literature (see Paragraphs 5.2.1.2 and 5.2.1.3). The decomposition behaviour of the biomass feedstock depended on the concentrations and composition of the ligno-cellulosic components.

#### Conclusion 5

- ❖ The highly fibrous woody biomass feedstock with low thermal resistance reacts at lower temperatures compared to the herbaceous biomass.
- ❖ As reported in literature (see Section 5.2.1.2), this study also found biomass feedstock to be more reactive than coal, in terms of degrading at lower temperatures (<450 °C) than coal.
- ❖ The DTG curves of plant biomass and coal-biomass blends showed two distinctive peaks which corroborates with literature (see Section 5.2.1.3). The first peak could be due to the decomposition of hemicellulose and the second peak could correspond to the decomposition of cellulose

6.1.2.2 Synergistic effects were investigated for all of the blended samples. The devolatilisation of blends implied no interactions, and small weight discrepancies at around 360 °C were considered not to be significant enough to have influenced the behaviour of the resultant chars (with average deviation less than 2.8%) during co-pyrolysis (see Paragraph 5.2.1.5).

#### Conclusion 6

- ❖ A general lack of significant interactions in the solid phase of the blended samples under inert environment was observed and literature reports similar observations (Biagini *et al.*, 2002; Sadhukhan *et al.*, 2008). The lack of synergistic effects may be caused by the low heating rate applied, which made it possible for different devolatilisation stages of both components in the mixtures to be easily separated. In addition, a high flow rate of the nitrogen in the TGA may have limited the influence of reactive species on the rate of pyrolysis of biomass feedstock, coal and their blends.

### 6.1.3 Mass spectrometry results

6.1.3.1 The TG-MS coupling was successfully used to identify the evolved gaseous products,  $H_2$ ,  $CH_3^+$ ,  $H_2O$  and  $CO_2$ , during pyrolysis. The relevant gaseous species profiles of the blends stayed similar in shape with an increase in the blending ratio. The maximum rate of evolution of  $H_2$  for all the blended samples was similar with, small differences at higher temperatures. It is reported by Arenillas *et al.* [1999] that the oxygen content within the material has been known to influence the release of  $H_2$ .

#### Conclusion 7

- ❖ The  $H_2$  evolution detected in the last stages of the pyrolysis process may indicate possible self-gasification or charring reactions occurring.

6.1.3.2 The evolution rate of  $H_2$  increased with an increase in temperature as can be observed from the MS results (see Paragraph 5.3.1.1). Only a very small lowering in the temperature at maximum  $H_2$  evolution of the blends was observed when compared to the coal  $H_2$  profile.

#### Conclusion 8

- ❖ The small decrease in the temperature range or temperature of maximum  $H_2$  evolution could be because the specific step in which  $H_2$  is evolved has possibly been enhanced (catalysed) by the addition of biomass.

6.1.3.3 The  $CO_2$  peaks of ligno-cellulosic components found in the biomass feedstock and blends correlated well with the onset and termination of the DTG results. At higher temperatures, all of the blends exhibited  $CO_2$  peaks at lower temperatures than the  $CO_2$  peak of the coal.

#### Conclusion 9

- ❖ Secondary reactions can have an influence on the formation and release of  $CO_2$  of the blended samples.

6.1.3.4 The second  $CO_2$  peaks (due to the degradation of the coal) were compared to evaluate the influence of the biomass on the coal's degradation with respect to  $CO_2$  evolution. The blended sample of 20% PWC + 80% coal seemed to have the largest decrease in the temperature (-43 °C), followed by 20% HWC + 80% coal (-36 °C), 20% SWC + 20% coal (-31 °C) and 20% SB + 80% coal (-32 °C), as described in Section 5.3.2.2.1.

- ❖ PWC has a larger effect than HWC because of the higher concentration of volatiles evolved during the pyrolysis process.
- ❖ PWC and HWC could be the best or appropriate biomass feedstock to consider for preparing a char that may be co-utilised with coal for further thermal processing (i.e. gasification process).

## 6.2 Contribution to knowledge of coal science and technology

- ❖ Chemical and physical results obtained for the coal, biomass feedstock and their blends provide a method of assessing feedstock suitability for pyrolysis, and further used for other processes (i.e. gasification and combustion).
- ❖ The characterisation results obtained provide a description of mineral- and physical structures of investigated coal-biomass samples during the pyrolysis process, adding to the available literature on applications where inertinite rich South African coal is used.
- ❖ It is reported in literature that at high temperatures properties of fuels (reported for some different ranks of coal) tend to be similar, which was observed in this study (limited literature is available on co-usage with biomass feedstock).
- ❖ The resulting char generated during pyrolysis may be useful as soil amendment for agriculture purposes, and in gasification reactors where more hydrogen is needed.
- ❖ The TG-MS technique provides a way of monitoring volatiles released during the pyrolysis process. The MS results obtained provide a description of the evolution temperature ranges of  $\text{H}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2^+$  during devolatilisation.

## 6.3 Recommendations

The following recommendations are proposed, based on the main findings, in order to develop, understand and take full advantage of biomass as possible fuel to be co-utilised with South African coal in an inert environment:

- ❖ Set up experiments including a leaching process to be applied on both biomass feedstock (HWC, SWC, PWC and SB) and coal, in order to obtain detailed XRD characteristics with less noise (for calculation of aromaticity values, determination of amorphous carbon and etc.).
- ❖ Doing ash fusion temperature experiments to determine which low-melting point species formed during the interaction of coal-biomass particles and also to provide further information regarding the suitability of coal-biomass for thermal processes.

- ❖ For better understanding of porous structures of the chars, the gas pycnometer could be used in conjunction with CO<sub>2</sub> gas adsorption analysis to accurately measure the densities of the chars.
- ❖ Set up experiments to analyse the gasses and tar produced during pyrolysis using gas chromatography (GC-MS), as well as Fourier transform infrared spectroscopy (FTIR). These techniques are more advantageous than the sole use of MS, offering quantitative analyses. The use of MS alone was restricting in terms of resolving compounds with the same mass-to-charge ratios (interference of other species) and also offered only qualitative analyses.
- ❖ For future in-depth study of the coal-biomass feedstock, methods such as semi-quantitative ss-NMR (solid-state nuclear magnetic resonance) could be applied in conjunction with the XRD measurements.
- ❖ For future studies, molecular modelling may be used to provide an insight into the behaviour of the degradation of coal, biomass and their blends.
- ❖ The devolatilisation of the cellulose, lignin, biomass, coal and blended samples may be investigated in further studies, in order to understand the mechanisms involved in governing chemical reactions during conversion in N<sub>2</sub> atmosphere.

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|                   |
|-------------------|
| <b>Appendix A</b> |
|-------------------|

**A.1 Description of standard methods used for characterisation**

SANS 5925: Specifies a method for the determination of the moisture content of coal samples intended for general analysis (air-oven method).

ISO 562: Hard coal and coke, method for the determination of volatile matter.

ISO 1171: Solid mineral fuels, method for the determination of ash content.

ISO 1928: Method for the determination of gross calorific value by bomb calorimeter and calculation of net calorific value.

ASTM D4239: Method which covers the determination of sulphur in samples of coal or coke by high-temperature tube furnace combustion.

ASTM D5373: Standard test methods for determination of carbon, hydrogen and nitrogen in analysis samples of coal and carbon in analysis samples of coal and coke

ASTM D4326: Standard test method for major and minor elements in coal and coke ash by x-ray fluorescence.

"Tests marked with an ASM number are included in the SANAS Schedule of Accreditation for this laboratory and those marked "Outsourced" are outsourced to an approved laboratory." by **ARC-Irene Analytical Services**

ASM 013: Method for the determination of total solids or dry matter.

ASM 048: Method for the determination of total ash or organic matter.

ASM 053: Method for the determination of gross energy value.

## TGA Results

### A.2 Reproducibility of TG results

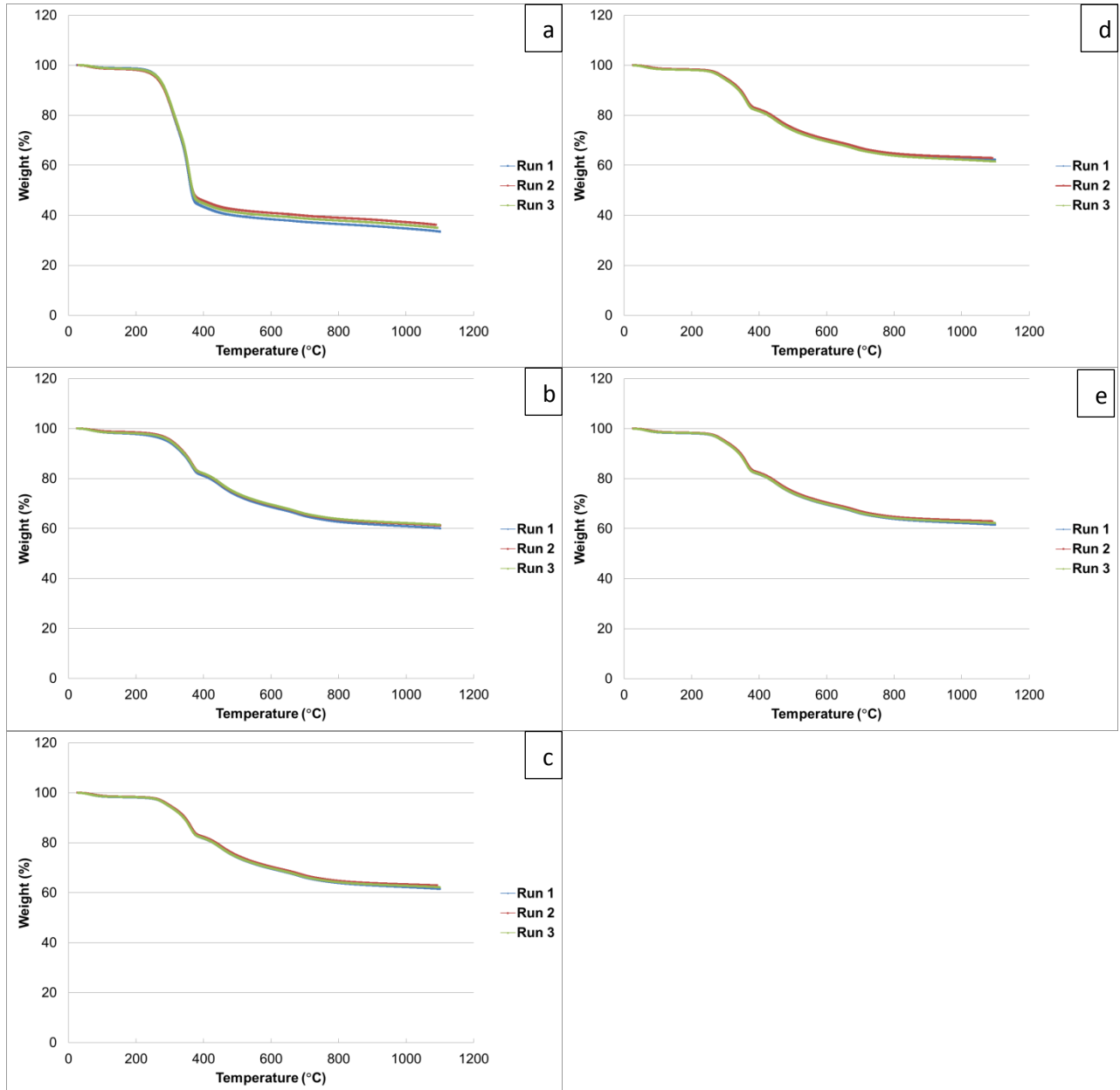


Figure A.1: Repeated TG curves of (a) SB, (b) 20% SWC + 80% Coal, (c) 20% HWC + 80% Coal, (d) 20% PWC + 80% Coal and (e) 20% SB + 80% Coal

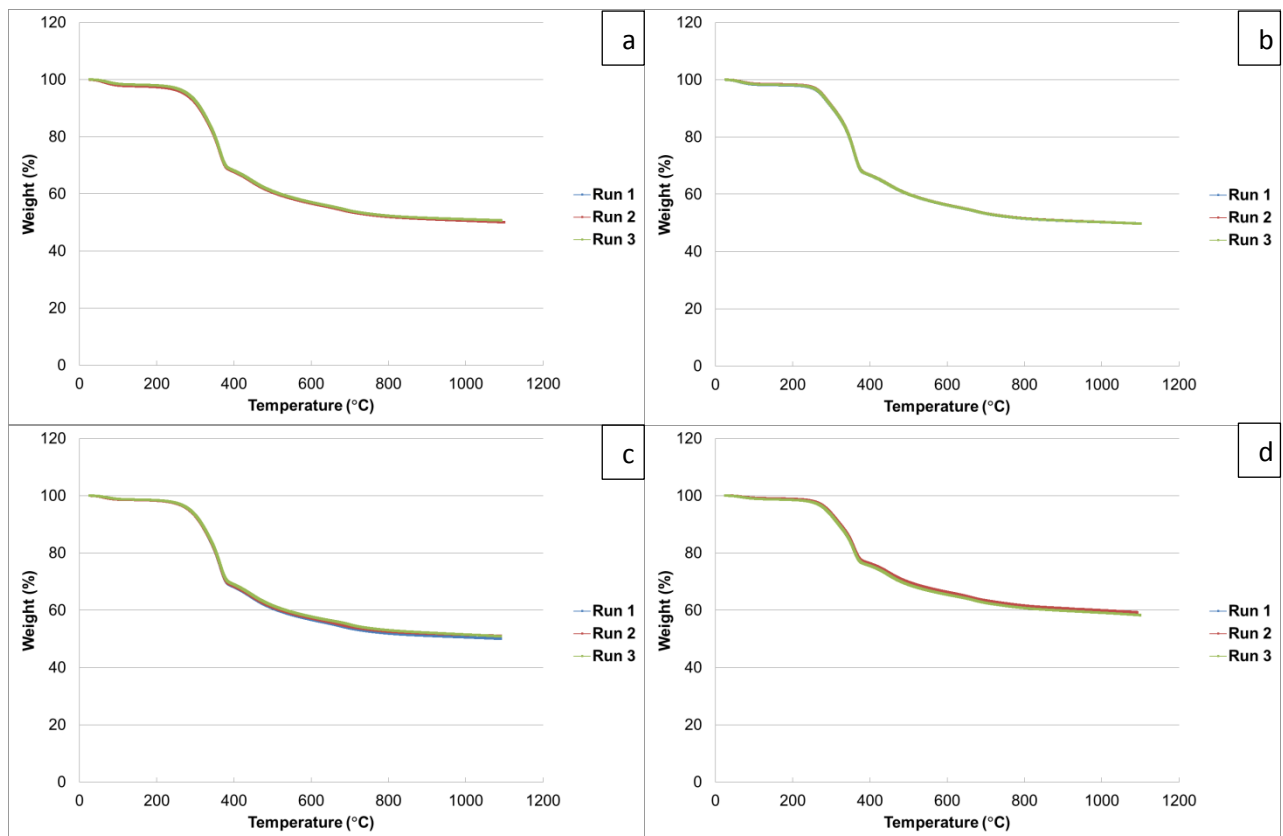


Figure A.2: Repeated TG curves of (a) 40% SWC + 60% Coal, (b) 40% HWC + 60% Coal, (c) 40% PWC + 60% Coal and (d) 40% SB + 60% Coal

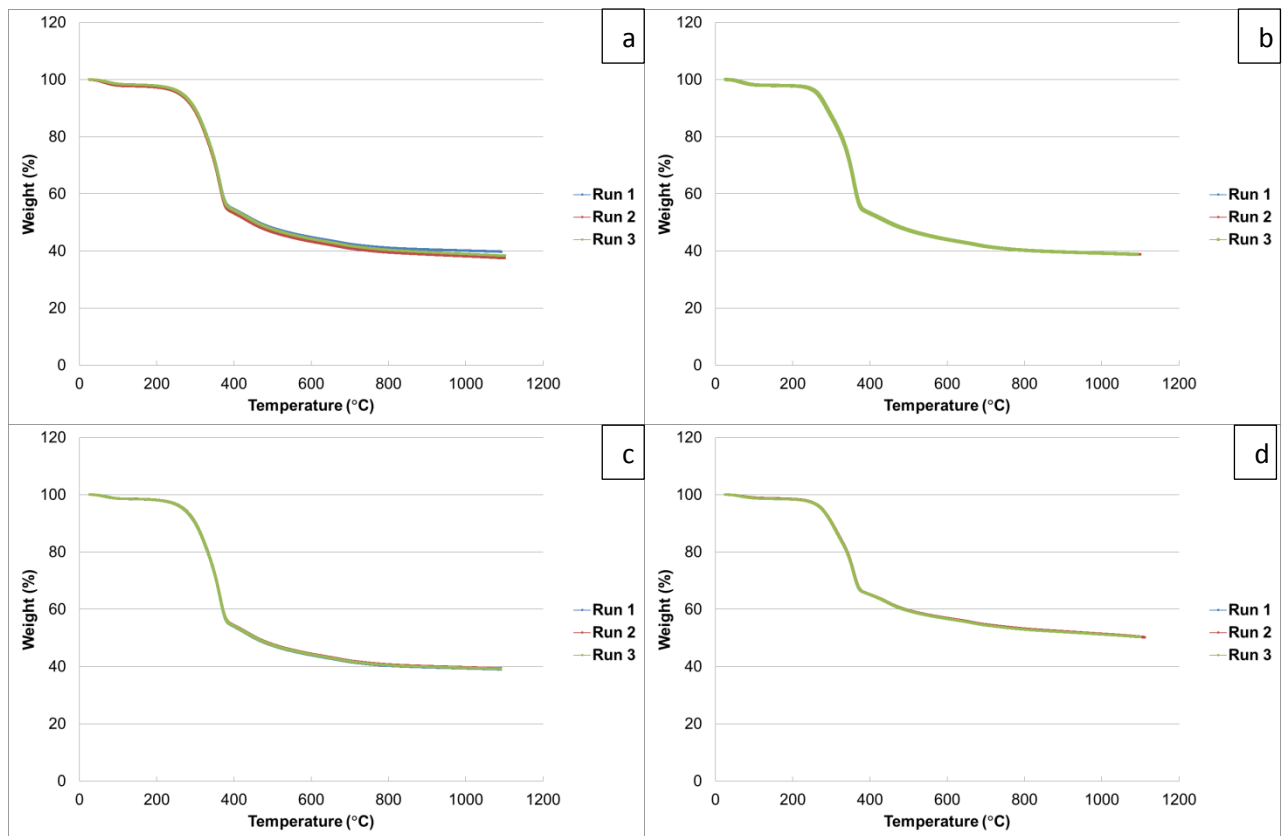


Figure A.3: Repeated TG curves of (a) 60% SWC + 40% Coal, (b) 60% HWC + 40% Coal, (c) 60% PWC + 40% Coal and (d) 60% SB + 40% Coal

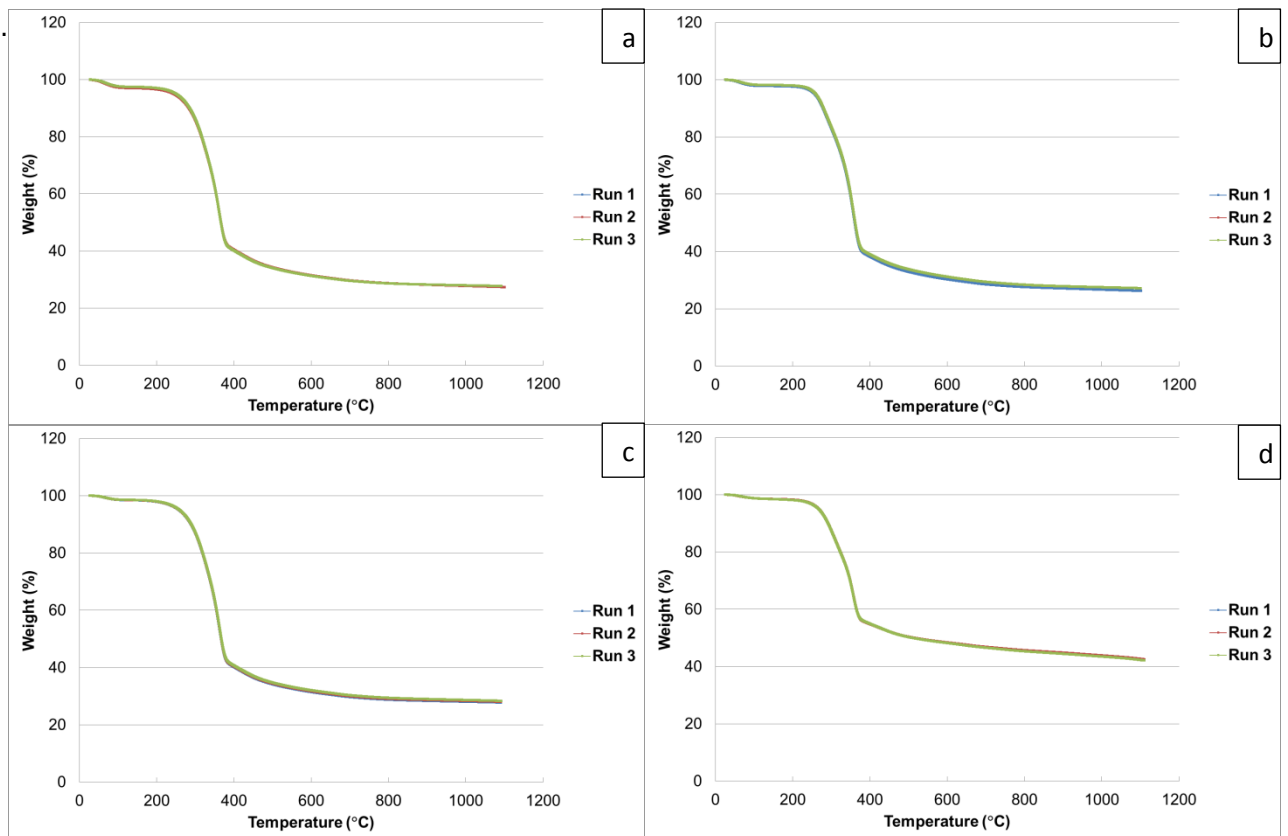


Figure A.4: Repeated TG curves of (a) 80% SWC + 20% Coal, (b) 80% HWC + 20% Coal, (c) 80% PWC + 20% Coal and (d) 80% SB + 20% Coal

## Appendix B

### TGA results of blended samples compared with calculated weighted averages

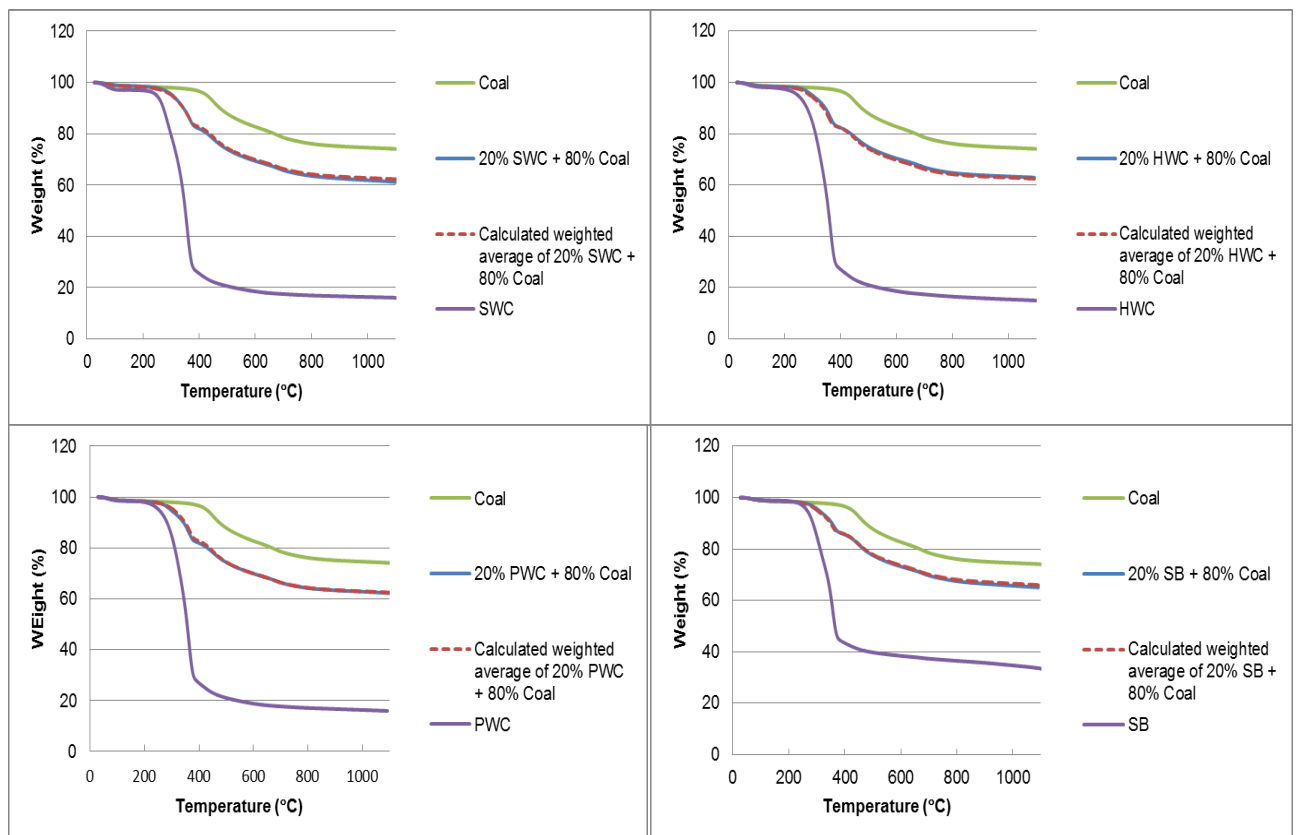


Figure B.1: TG curves of blended samples compared with calculated weighted averages: pyrolysis of 20% biomass + 80% coal

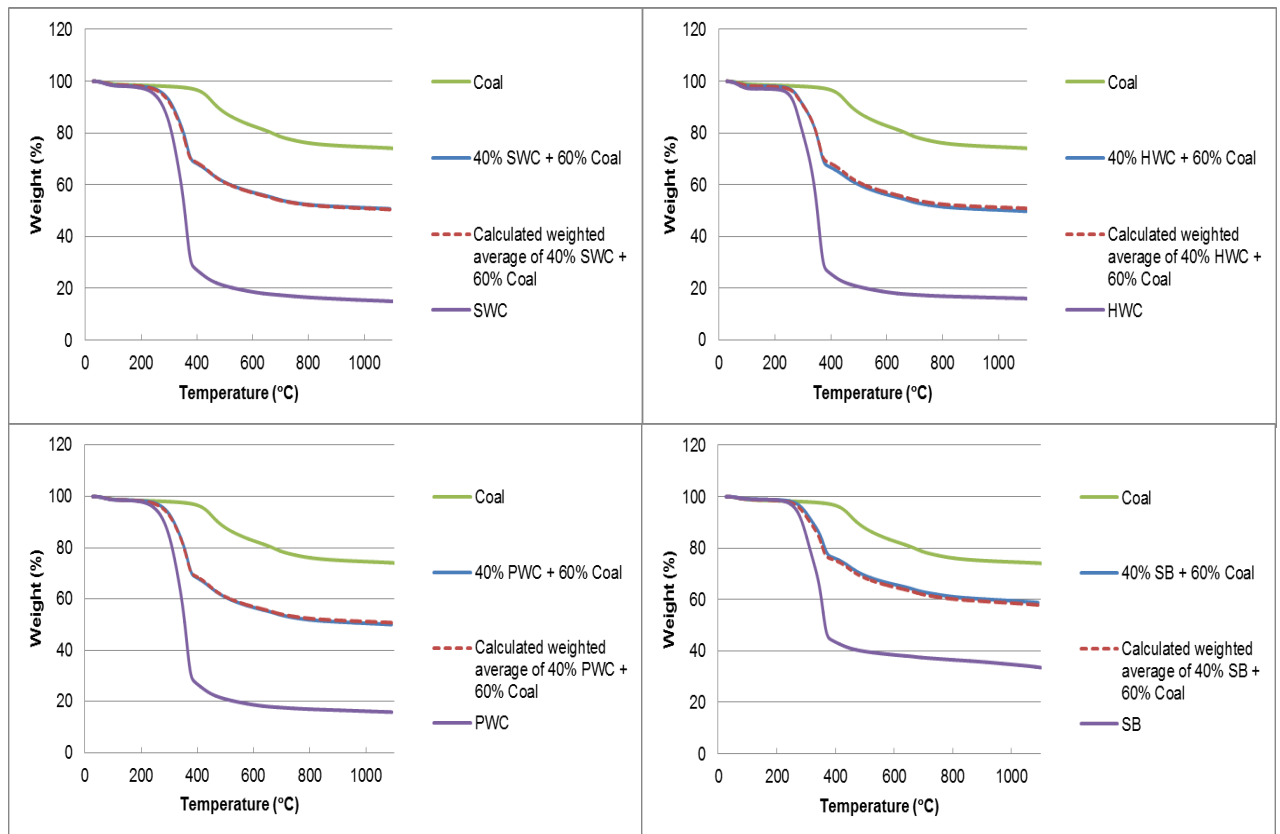


Figure B.2: TG curves of blended samples compared with calculated weighted averages: pyrolysis of 40% biomass + 60% coal

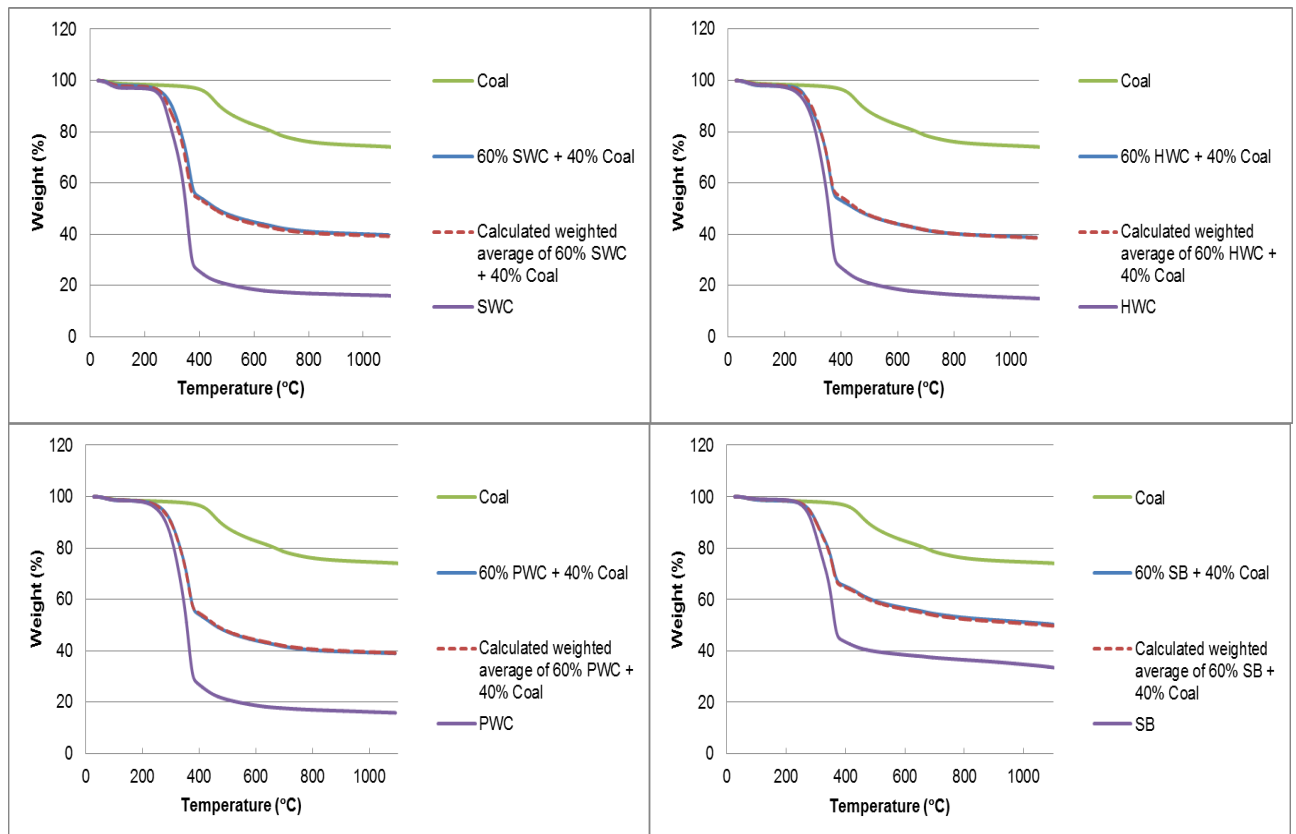


Figure B.3: TG curves of blended samples compared with calculated weighted averages: pyrolysis of 60% biomass + 40% coal

## Appendix C

### DTG results of blended samples compared with calculated weighted averages

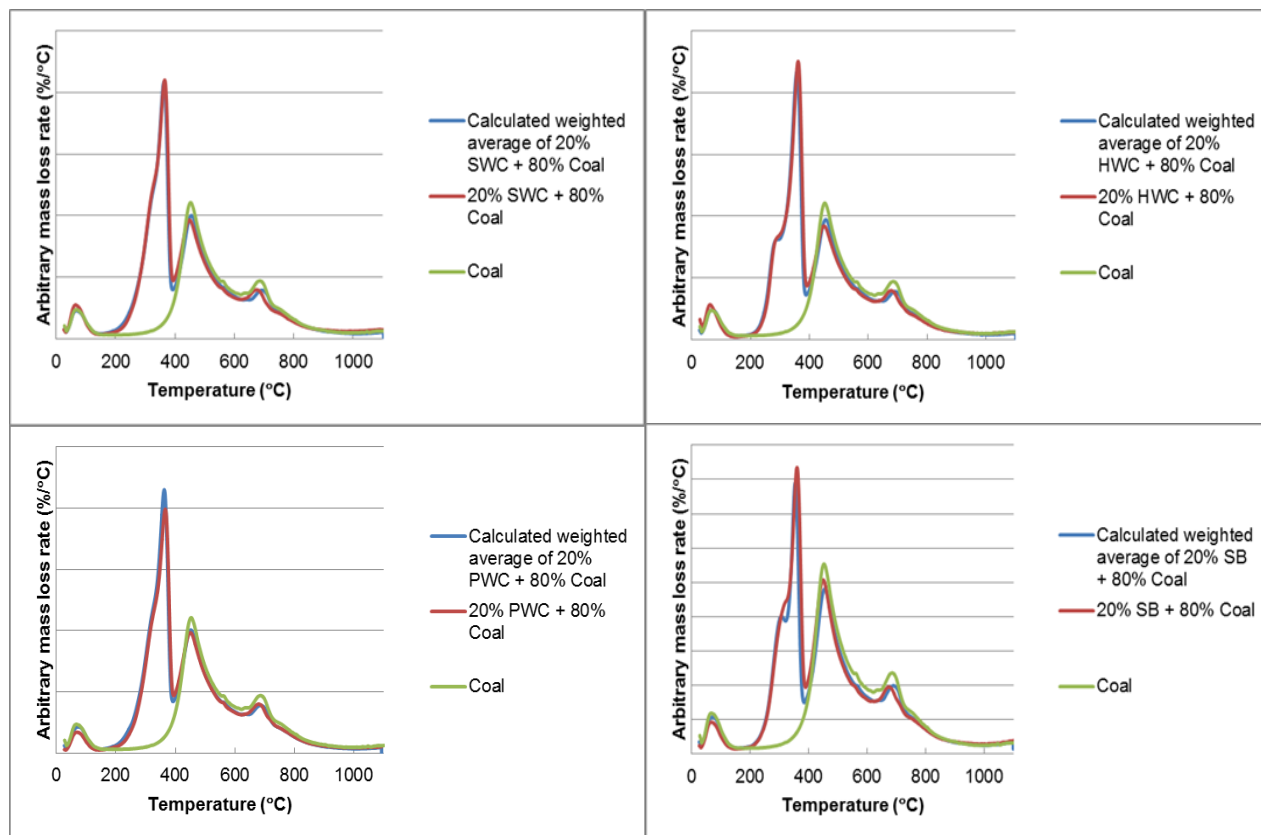


Figure C.1: TG curves of blended samples compared with calculated weighted averages

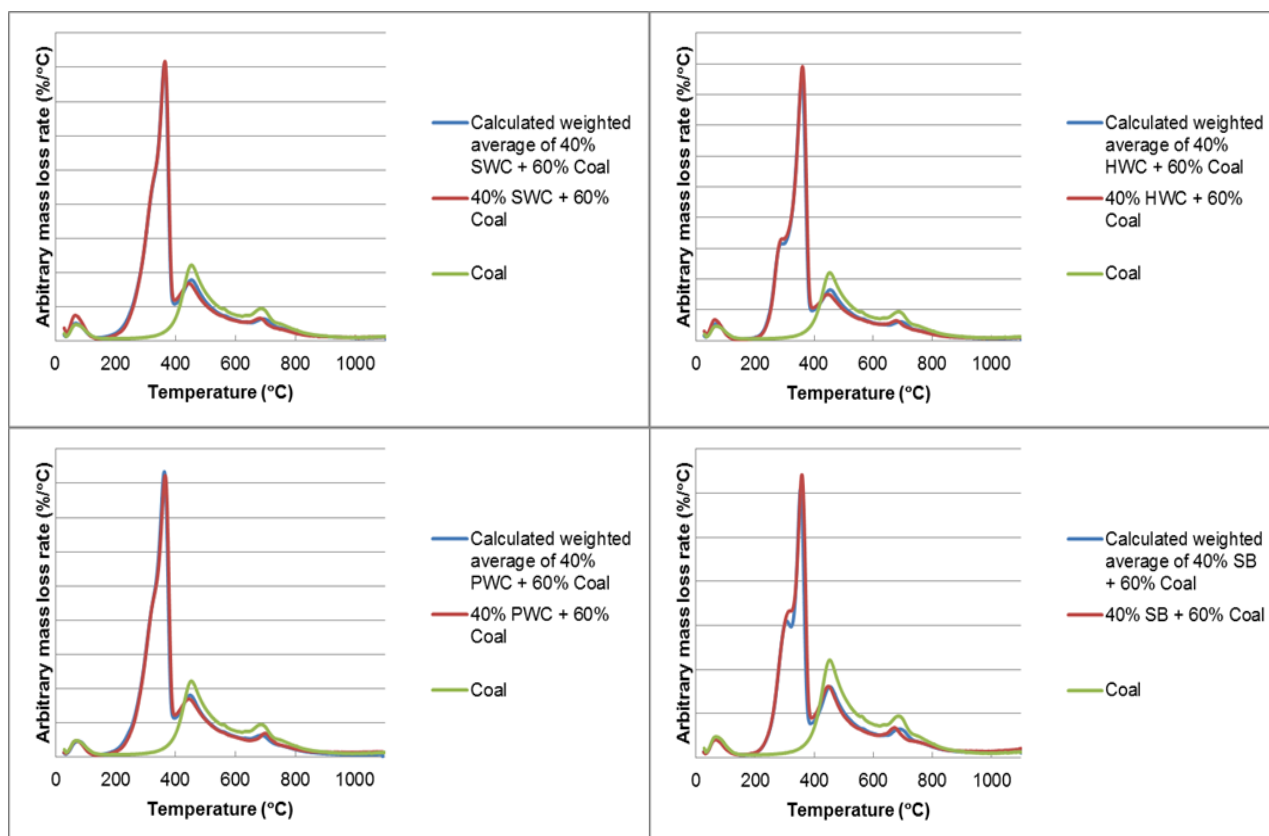


Figure C.2: TG curves of blended samples compared with calculated weighted averages

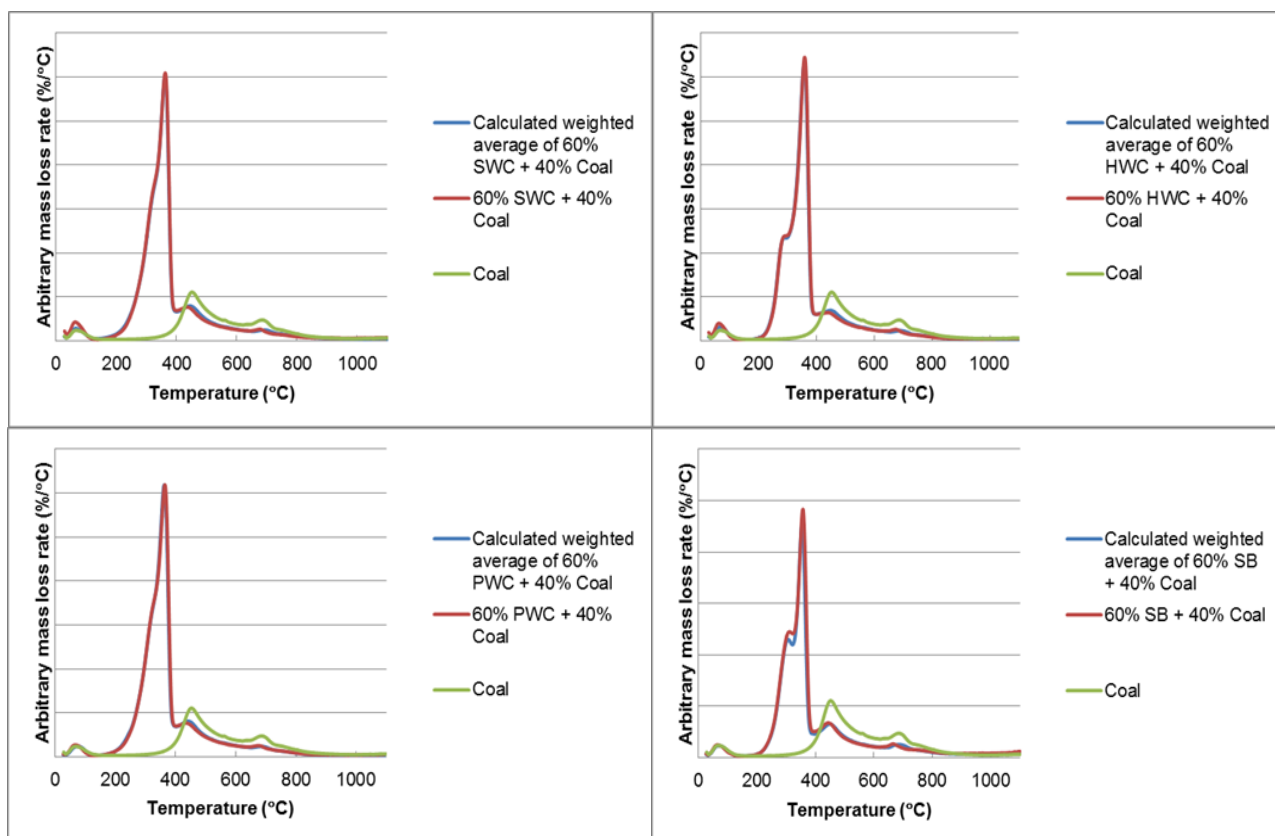


Figure C.3: TG curves of blended samples compared with calculated weighted averages

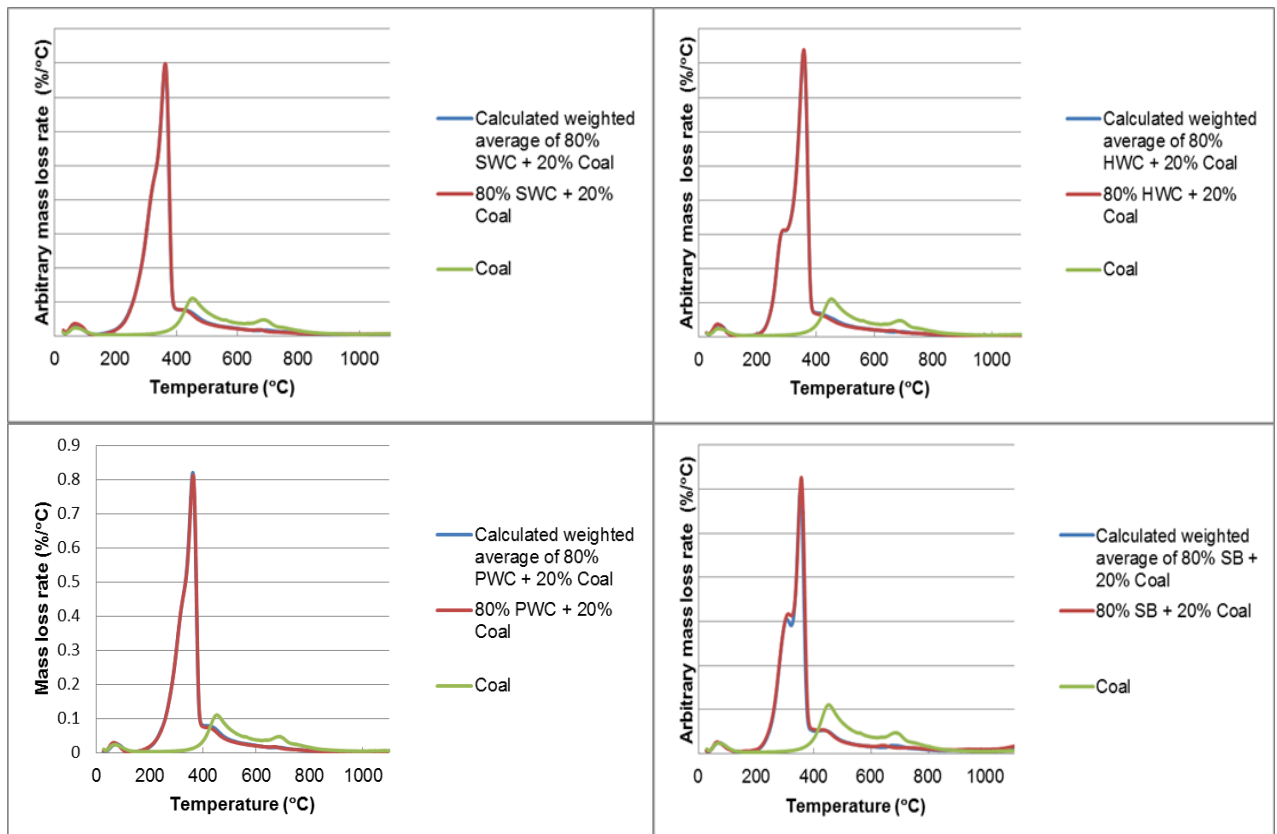


Figure C.4: TG curves of blended samples compared with calculated weighted averages