

Cranfield University

René Laryea-Goldsmith

Concurrent combustion of biomass
and municipal solid waste

School of Applied Sciences

This thesis is submitted for the award *philosophiæ doctor* (PhD)

2010

Supervisor: Dr N J Simms

30 September 2010

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Abstract

This PhD research project is primarily an investigation of the gaseous pollutant emissions arising from concurrent combustion of biomass and municipal solid waste materials, using a fluidised bed combustor. Of the wide range of biomass energy resources available, dried distillers' grains with solubles and wheat straw were chosen as two example agricultural by-products of the human food supply chain. To consider an integrated waste management programme, a residual waste resource from a materials recycling facility was identified as a waste materials source that could be utilised *after* materials recycling was performed (which is a higher priority activity with respect to energy recovery).

An experimental test method plan was developed to investigate the aforementioned renewable energy fuels, using a pilot-scale fluidised bed combustor to enable thermal conversion. Gaseous emissions data obtained during this project indicated that compared to combustion of biomass alone (e.g. 100 % wheat), fuel mixtures containing an optimum quantity of non-recyclable waste materials were found to reduce emissions of some pollutants, notably hydrogen chloride. A mechanism for these observations is the occurrence of competitive reactions between intermediate compounds with the effect of reducing the extent of formation of certain pollutants. A novel method was devised to measure the presence of trace organic compounds (i.e. PCDD/F congeners) and volatile metals within flue gas emissions during combustion tests; results suggested that neither PCDD/F congeners or trace metals were emitted in significant quantities. Such observations would have implications upon appropriate designs of air pollution control devices and evaluation of the corrosion risk to power systems.

This PhD project is a contribution to the SUPERGEN Bioenergy UK research consortium and is expected to assist development of theoretical models of similar combustion scenarios in the future.

Acknowledgements

I am grateful to the UK Engineering and Physical Sciences Research Council for financing this research project and the advice, assistance of my supervisor Dr Nigel Simms.

I thank Daniel and Sarah for the inspiration; Sylvia; last but not least, Samuel and Margaret for the roots.

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Nomenclature

AR	as received
CCHP	combined cooling, heating and (electrical) power
CHP	combined heat and power (cogeneration)
Da	Dalton, unified atomic mass unit defined as $\frac{1}{12}$ mass of a ^{12}C atom, $\approx 1.661 \times 10^{-27}$ kg
DAF	dry ash free
DDGS	dried distillers' grains, with solubles
EDX	energy dispersive X-ray
EfW	energy from waste
FT-IR	<i>Fourier</i> -transformation infrared radiation
GCV	gross calorific value
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
MBT	mechanical biological treatment
MRF	materials recycling facility
MRFR	materials recycling facility residue
MSW	municipal solid waste

NCV	net calorific value
ODT	oven dry tonne
PCDD	poly-chlorinated dibenzo-p-dioxin
PCDF	poly-chlorinated dibenzofuran
RDF	refuse derived fuel
SEM	scanning electron microscope
SRC	short rotation coppice
SRF	solid recovered fuel
TIC	total ion chromatogram
TPA	tonnes per annum

Chapter 1

Introduction

1.1 Outline

Fossil fuels constitute approximately 80 % of primary global energy supply (IEA, 2004). The origin of these fuels (coal, natural gas, oil) is the sedimentary deposition of animal matter and vegetation within favourable geological rock formations, such that anaerobic decomposition to organic compounds occurs under geological processes of increasing temperature and pressure (O'Neill, 1985). These geochemical changes were long-term during ancient millenia and by definition renders fossil fuel use to be un-sustainable relative to the rate of current consumption by humans. It must follow therefore that alternative energy sources are required to maintain, and indeed improve for many, human standards of living. In contrast, renewable energy sources are “environmentally friendly”, considering the following definition of sustainable development (of which renewable energy forms a part):

“...meeting the needs of the present without compromising the ability of future generations to meet their own needs...” (United Nations, 1987)

Forms of renewable energy are both numerous and diverse, ranging from wind and tidal to solar and geothermal sources amongst others. Biomass is a renewable energy source, however the definition of what constitutes biomass does vary internationally, as is accepted by European legislation regarding renewable energy sources of electricity (European Parliament, 2001). For example

the UK government includes: “the degradable fraction of industrial and municipal waste;” as part of the definition of biomass (Great Britain, 2003), whereas within European reporting convention (European Commission, 2007), such waste is recorded as a separate sub-set of MSW, usually estimated at 50 % of (un-sorted) municipal solid waste. In contrast to the British interpretation, German renewable energy law does not classify MSW as a renewable energy source (British Standards, 2003). For the purposes of this report the definition of biomass as described in the UK is used:

“...means the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste...” (Great Britain, 2003)

Biodegradation is the process of chemical destruction of organic matter by microorganisms for subsequent re-use by other lifeforms. This process may occur in either aerobic or anaerobic conditions, to produce carbon dioxide, water and numerous organic compounds. The characteristics of biomass offer several advantages in the context of this research project. Biomass is easily combustible, providing a stable environment for solid waste to burn. Unlike energy from sources such as photo-voltaic solar cells, biomass can act as an “energy carrier” and store energy for subsequent thermal conversion concomitant with changes in energy demand. Similarly, wind energy is primarily exploited for electricity whereas biomass is able to provide both heat directly from its combustion and as an option, simultaneous electricity. Typical examples of biomass available in Great Britain are:

- Cereal crop (e.g. wheat) straw;
- Miscanthus reed canary grass and switchgrass;
- Short rotation coppice (willow, poplar, ash, alder, hazel, silver birch, sycamore, sweet chestnut and lime).

With the exception of straw, reed canary grass and switchgrass, these aforementioned crops qualify for state subsidies on production. Although anthro-



Figure 1.1: SRC willow (photograph courtesy of NEF (2008))

pogenic in origin, municipal solid waste is also a renewable energy source on account of its recurrent production, especially in relation to a commonly accepted definition of renewable energy:

“...energy obtained from the continuous or repetitive currents of energy recurring in the natural environment...” (Weir, 1986) cited in (Boyle, 2004)

The “waste hierarchy” (Figure 1.2) is one aspect of the use of MSW that this project seeks to incorporate. The preferred actions of this hierarchy to adopt, in decreasing order of priority are: reduce (waste minimisation at source); re-use (secondary use of materials); recycle/recover (subsequent return of materials or equally recover energy from waste); disposal (e.g. landfill, as a last resort). In terms of energy recovery, whether and how waste (especially MSW) should be exploited is contentious. If MSW is burnt without any prior sorting/grading, such waste incineration may be said to be both inefficient and contradictory to the waste hierarchy. More energy may be recovered from waste incineration if non-combustible material (such as discarded wet food) is removed from combustible paper, for instance. However if cardboard is burnt in a waste incinerator this could be considered to be detrimental to the perceived preference for recycling.

A more effective fuel may be obtained from appropriately separated bulk waste. A solid recovered fuel (SRF) is defined as being derived from selected non-hazardous wastes (British Standards, 2003). These wastes themselves may be derived from various sources such as (municipal) residential, commerce and

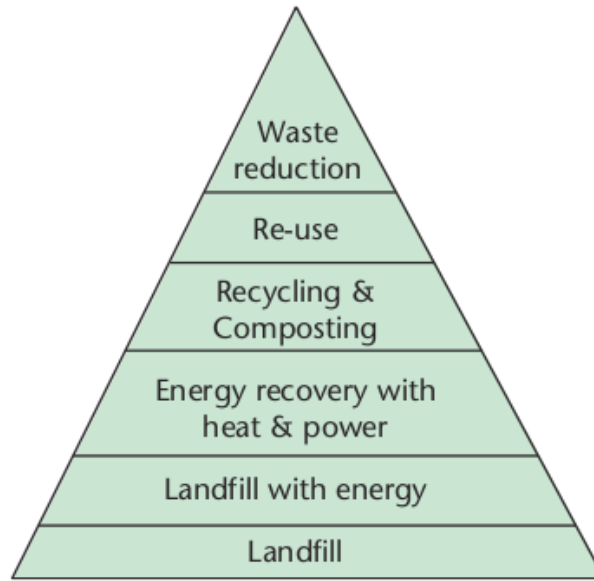


Figure 1.2: The waste hierarchy (adapted from (Great Britain, 2002))

industry. Previous terminology such as “refuse derived fuel” and “waste derived fuel” which were produced often from non-sorted MSW and were characterised as being of low, variable quality, whereas the acronym SRF is applicable only to solid fuels produced to a specific standard quality (Archer *et al.*, 2005a). Opponents to ‘energy from waste’ (EfW) schemes are of the opinion that components of SRF (e.g. paper) should instead be recycled and that the existence of MSW combustion facilities reduces recycling rates (FOE, 2007). However, recent evidence in Europe has shown clearly that countries such as France, Germany, Norway and Sweden have relatively higher levels of *both* incineration and materials recycling (Kloek & Jordan, 2005). It is proposed in this research project that an alternative SRF need not affect materials recycling, if the residual waste produced by recycling processes is used as a fuel source. Historical research into thermal conversion of biomass and MSW is dominated by the use of coal as a primary, majority component fuel where either biomass or waste materials and secondary fuels consumed simultaneously with coal (examples such as: Freeman *et al.* (2000); Gulyurtlu *et al.* (2005); Yan *et al.* (2006)). It is evident from these types of studies that biomass has been co-fired

with coal primarily to reduce fossil fuel pollutant emissions, whilst co-firing of waste with coal is employed as a method of waste disposal. Combustion of biomass with waste materials appears to be scarcely researched, especially in the absence of using a fossil fuel as a majority component of the fuel mixture. In addition, consideration of the impact on materials recycling of thermal conversion of waste materials does not appear in the literature in the context of energy conversion research.

The intention of this PhD research project is to investigate the concurrent combustion of biomass and a municipal solid waste dry residual waste fraction, obtained from a materials recycling facility and hence termed ‘materials recycling facility residue’ (MRFR). The PhD research hypothesis is that combustion of both biomass and MRFR can be optimised to maintain gaseous pollutant emissions to within acceptable levels, prior to the (mandatory) application of air pollution control devices. For the purposes of this project, MRFR represents the fraction of municipal solid waste (MSW) that has been despatched to a materials recycling facility, yet has been rejected for recycling due to economic or technical factors. It is analogous to the formal definition of dry residual waste (British Standards, 2003), as “the residue of MSW after separation from biological and hazardous wastes”. Consequently, use of MRFR may be interpreted as an attempt to consider the effect of thermal conversion of waste materials on other activities such as materials recycling and integrated waste management overall.

Assessment of concurrent combustion of biomass and MRFR will contribute towards the Supergen Bioenergy Research Consortium, the programme through which the Engineering & Physical Sciences Research Council provides finance for this PhD research project. Activities performed throughout this PhD research project are relevant to the part of the research consortium, ‘Supergen Bioenergy Phase II, Theme 4 Power and Heat’ and in particular ‘Task 4B Co-firing and co-utilisation of biomass and waste materials’. The data obtained from this PhD research project is expected to be used to validate previous work on development of theoretical models (Supergen, 2007), specifically characterisation of combustion flue gas compositions. A practical study of biomass

and MRFR combustion will be beneficial to those considering an energy source for combined cooling, heating and electricity power (CCHP, or tri-generation) provision to both commercial and residential recipients. This author suggests that the research may be of interest to power systems of a scale 5–50 MW output (for CCHP, urban environment location and fuel supply limitations) and where various fuel mixtures need to be investigated to reflect the dynamic variation in MRFR composition as well as seasonal variation in characteristics and/or geographic availability of biomass.

1.2 Aims & Objectives

The overall aim of this PhD research project was to assess the feasibility of combustion of fuel mixtures comprising biomass and MRFR. A range of combustion conditions were monitored, in terms of variations in fuel mixture (between biomass and MRFR) and consequent air:fuel ratio.

The research project objectives may be summarised as follows:

- To investigate the combustion conditions and behaviour for various mixtures of biomass and MRFR using a pilot-scale fluidised bed combustion system;
- To assess two types of biomass samples, to represent examples of agricultural cereal crop by-products as the standard biomass fuel component;
- To incorporate the concept of integrated waste management, i.e. the “waste hierarchy”, in terms of sustainable thermal conversion of waste materials by utilisation of MRFR as a source of non-recyclable residual waste fuel component;
- To measure gaseous and fly ash emissions for determination of: oxides (and pre-cursors) of various elements such as nitrogen and sulphur; organic compounds gaseous pollutants (e.g. PCDD and PCDF congeners); a selection of metals;
- To understand the mechanisms for optimum combustion conditions;

- To contribute to a specific task of the Supergen Bioenergy Research Consortium by way of interpretation of new empirical data for concurrent combustion of biomass and waste materials, for future validation of theoretical combustion behaviour models.

An additional biomass fuel — dried distillers' grains with solubles — was utilised throughout the project, to represent an example agricultural waste product that can be used as a biomass fuel resource. It was conveniently stored in the form of pellets, which was easy to handle manually, had relatively low moisture content and was physically dense. These characteristics made the fuel well suited for concurrent combustion with the more variable qualities of MRFR.

A local materials recycling facility was used as the source of the MRFR. By definition, the chemical composition and physical characteristics of this fuel source was variable. From the bulk waste collected, a series of representative samples for combustion in the pilot laboratory was obtained. With use of both material balance calculations and flue gas chemical composition data, it was envisaged that the quality of the MRFR may be deduced and compared to the quality standard for combustion of SRF in a fluidised bed combustion system. This quality standard declares acceptable quantities for calorific value, chloride, mercury, cadmium, thallium (British Standards, 2006a). Analysis of flue gas content was a method of fuel quality assessment proposed as an alternative to expensive and laborious chemical analyses of each MRFR sample prior to combustion.

1.3 Scope

The research project was limited by numerous practical constraints.

- Fossil fuels were excluded as a primary energy source.
- A range of the major types of biomass were investigated concomitant with the geographic constraints within the UK.

- Biomass and waste fuels were considered “renewable” only in the context of the rate of fuel supply being sustainable relative to energy demand.
- Determination of gaseous pollutants. Some pollutants were determined qualitatively, for example, dioxin group chemicals were monitored for their presence, but isomeric and molecular characterisation of those dioxins and furans congeners was not determined.
- An economic analysis of the use of biomass and waste for energy was outside the scope of this study.
- Life cycle analysis of carbon dioxide emissions was excluded from this study.

1.3.1 Fuels

There is a vast range of possible fuels, from both biomass and waste sectors, to choose from and it was not the intention of this research project to evaluate the merits of each permutation of fuel mixture. The initial choice of fuels was restricted to existing stocks of the following fuels available within the university department.

DDGS (bio-ethanol waste)

Ethanol may be produced from cereal crops via fermentation. From this process, the biological waste (obtained from the dried solid residues of production of ethanol by fermentation) is formed into biomass pellets and thus this fuel constitutes an example agricultural waste biomass resource.

Cereal crops’ straw

The waste matter, such as stems, remaining after harvesting of cereal crops (e.g. barley, oats and wheat) may be utilised and converted into straw pellets, the form of which is utilised in this research project.

Willow

Short rotation coppice (SRC) is the arboricultural practice of cutting trees' stumps (to a height of a few centimetres from ground level) during dormancy in the winter season, resulting in the stimulated growth of multiple new stems in the subsequent summer growth season. Many fast growing species may be subjected to coppicing but currently, poplar and willow are the most common SRC crops in UK (Rolls, 2008).

MRFR

The inevitable residue from the recycling of municipal solid waste materials is available from a local materials recycling facility (MRF). It was comprised predominantly of combustible material such as non-recyclable plastics and fibres (e.g. cardboard, laminated paper, etc.).

1.3.2 Thermal conversion processes

There are three common methods of exploiting the energy from biomass and waste, to do work such as generating electricity and producing heat simultaneously.

Pyrolysis

Organic matter (biomass) is heated to a temperature (500–1000 °C) sufficient for chemical and physical decomposition to occur (Klass, 1998). Heating must occur in an environment free of oxygen, to produce a combustible gas comprising hydrocarbons (methane and others at increasing temperatures of pyrolysis operation), hydrogen and carbon oxides. A liquid is also formed by the process, a complex mixture of oils and other chemicals resembling crude (mineral) oil. Charcoal is also produced as a solid by-product of the process.

Pyrolysis of biomass offers a sustainable source of hydrogen, potentially up to 70 % by volume (Palz & Chartier, 1980). Moreover the liquid fraction offers a potentially lucrative alternative to many chemicals currently obtained from crude oil. Barriers to increased usage are: high capital costs; an unclear

market demand for the liquid fraction; production of a low value gas depending on the pyrolytic oxidation process used.

Gasification

Gasification is a complicated procedure involving partial oxidation of a (biomass) fuel and the formation of the syngas (*synthesis gas*) — with the principal gaseous species being carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen — via multiple chemical reactions.

The syngas can be directly used in a gas turbine and as an option additional indirect use with a steam turbine to generate heat and steam for increased system efficiency. One major hindrance is the formation of tar (a highly viscous, corrosive liquid) which can block the syngas flow path if tar is allowed to condense in the wrong part of the flow path. Another hindrance is the presence of sulphur, chlorine and alkali species within the tar that can cause significant damage if deposits are allowed to be formed onto metallic components of the gasifier system. These risks can be minimised by the use of syngas cleaning equipment, although operational costs will be increased, whilst system efficiency is reduced.

Combustion

The oldest technique known, may be defined as the production of heat by complete oxidation of a fuel. A complete reaction with an organic fuel produces carbon dioxide and water. Combustion is a well understood phenomenon and is the thermal process utilised for this research project. Common combustion techniques are fluidised bed, grate-fired and pulverised fuel, where fluidised bed combustion was used for the purposes of this research project. The combustion of biomass and waste produces gases that are both interactive with the Earth biosphere and detrimental to human health. Anthropogenic emissions of pollutants are expected to have an impact upon the Earth's atmosphere. Biomass combustion is often claimed to be 'carbon neutral' since carbon dioxide is used for biomass growth prior to combustion (Twidell & Weir, 2006), although fos-

sil fuel derived emissions are associated with production and transportation of biomass materials.

Chapter 2

Literature review

To establish the relevance of this project to the wider research community, an initial literature review was conducted, as were additional reviews made throughout the duration of this project.

2.1 Fuel supply

Generally, there are two major types of energy sources that are available and of relevance to this project: biomass, of which numerous vegetation species have potential within Great Britain; municipal solid waste, where only non-recyclable components are considered.

Both fuels are characterised by a complex supply chain from production to energy conversion. Biomass vegetation must be harvested, dried and then packaged into a physical form suited to the energy conversion system. Similarly, MRFR has to be separated from other undesirable components of MSW, such as glass or metal which should subsequently be processed for recycling. Furthermore, MRFR must also be made more uniform in physical dimensions in order to facilitate effective combustion and manual handling of the material.

2.1.1 Biomass resource in UK

One consideration to make regarding the potential of biomass as an energy resource is whether to focus upon dedicated resources, i.e. energy crops where

vegetation is grown primarily for energy exploitation, or as a by-product of another higher priority activity (for example straw cultivation after wheat harvesting). As a result of government initiatives, selected “energy crops” qualify for subsidies in order to help develop the market for biomass energy resources. These energy crops that are approved to receive subsidies are: short rotation coppice (Alder, Ash, Hazel, Lime, Poplar, Silver Birch, Sweet Chestnut, Sycamore, Willow); and Miscanthus (Natural England, 2008). To date, a total of 15 000 ha of both SRC and miscanthus crops have been planted within UK (DEFRA, 2007a). On the basis of annual yield 10 oven dry tonnes per hectare (ODT ha^{-1}), such acreage represents an available biomass reserve of 155 000 tonnes. Cereal straw in UK is obtainable as a by-product from barley and wheat production. Whilst the majority of the material is recycled for other agricultural uses (animal feed, soil fertilisation), a surplus exists within the eastern region of England where the majority of cereal crops are grown in the country; potentially 3 million tonnes, where 200 000 t per annum (TPA) is currently exploited for energy recovery (DEFRA, 2007a). On a national scale, a total of approximately 18 million tonnes of straw have been produced in the UK, of which 7.5 million tonnes were burnt in fields (Martindale, 1985), a traditional agricultural activity which was declared illegal by the Environmental Protection Act 1990 and effective from 1993 (Great Britain, 1993). Of interest to note, this level of usage of straw for fuel is less than a forecast made that by 2000, output of 230 000 tpa and a maximum fuel demand of 4.3 million tonnes of straw for this geographical region would occur (Clegg *et al.*, 1985). The disparity could be attributed to increases in efficiency of fuel consumption and perhaps even changes in the characteristics of the cereal crop such as the reduction by 30 % in straw content as a proportion of the cereal plant edible portion due to improvements in crop yield (Pellizzi, 1985).

An additional biomass energy resource by-product of ethanol manufacture is dried distillers’ grains with solubles (see § 1.3.1). Common sources of DDGS are maize (prevalent in USA) or wheat (Europe), although within Europe other crops such as sugar beet are also chosen to generate ethanol. The yield of DDGS from 1 kg of maize is approximately 0.3 kg, based upon production of

approximately 0.4 litres of anhydrous ethanol (Tiffany *et al.*, 2008) and an agricultural yield of maize, 1.6 tonnes ha⁻¹. In comparison, 1 kg of wheat produces approximately 0.4 litres of ethanol and 0.4 kg of DDGS, based upon previous studies (Kim & Dale (2004) and Power *et al.* (2008)). Despite this resource, this review of published literature did not reveal any specific research into combustion of DDGS, but instead research involved the current use for DDGS as an animal feed supply and its nutritional value. Waste wood is also available on a UK national scale but energy recovery must be performed in accordance with waste incineration regulations, since the chemicals used for wood treatment are potentially hazardous. Typical wood treatment chemicals include: *a*) chromated copper arsenate, a fungicide and insecticide containing poisonous arsenic; *b*) creosote, a carcinogenic preservative; borates (preservatives); *c*) copper citrate and other organic compounds; *d*) wood stain; *e*) paint; *f*) varnish; *g*) fire retardants (Forest Research, 2008). The potential quantity of waste wood has been estimated at 5.5 million tonnes (DEFRA, 2007a).

The British government had commissioned a report (Clayton *et al.*, 2005) to propose initiatives for the development of biomass as an energy source. The report makes a significant statement that there is an absence of government policy regarding the use of biomass, especially concerning provision of space and process heat. In the report are a series of recommendations for government to consider, some of which are shown below:

- Energy recovery (after re-use and recycling) should be encouraged, especially in the form of combined heat and power in order to “optimise carbon savings”;
- Wood waste should be exploited as an energy resource;
- The Energy Crops Scheme should be continued, to subsidise the commercial development of biomass supply infrastructure;
- Biomass heating provision should be attributed a ‘carbon saving’ economic value as exists with regards to the Renewable Obligation for electricity generated by renewable energy sources.

Following publication of this report, a formal response to the various recommendations was published (Johnson & Beckett, 2006). Subsequent actions by government show that some recommendations were worthy of implementation, such as extension of the Energy Crops Scheme. Unlike the Biomass Task Force report, the government response makes an acknowledgement of the public hostility to the concept of energy from waste.

2.1.2 Municipal solid waste as a fuel resource

Historically, the majority of municipal solid waste (MSW) has been disposed of within the UK via landfill, the practice of depositing waste into (i.e. underground) or onto land (European Parliament, 1999). Fewer than ten years ago, approximately 80 % of MSW produced in England was disposed of via landfill (DEFRA, 2002b). In contrast Denmark, Netherlands and Switzerland are examples of countries with rates of landfill utilisation less than 10 % (Kloek & Jordan, 2005). The primary strategy of the British government is to divert waste from landfill, by increasing rates of waste minimisation activities and materials recycling. With specific reference to energy recovery, of the various technologies available a preference for anaerobic digestion is declared (DEFRA, 2007b). Moreover, combined heat and power (CHP) is also stated as an aim in terms of maximising energy recovery; an incentive to achieve this is the increase in enhanced capital allowances for investments that use SRF for CHP. Assuming targets are met for composting and recycling of household waste, government forecasts for energy recovery are expected to comprise 25 % of MSW disposal by 2020; current rates are 10 % (DEFRA, 2007b). There is an explicit expectation from the strategy document that unavoidable, residual waste from recycling processes must be exploited for energy recovery as part of an overall energy policy.

Two sources of fuels from MSW are potentially available: SRF from MBT processing; residues from MRFs. Of the former, current UK output is 765 000 tonnes (Arias-Garcia & Gleeson, 2009). The potential residue from MRFs is estimated at 250 000 tonnes, on the basis of median residue of 11 % produced

by MRFs (WRAP, 2007). In addition to these sources, the residual waste from the collection of “black-bag” domestic is also available potentially, in localities where kerbside collection of recyclable materials is performed. Within England, approximately 25 million tonnes of household waste is collected and about 40 % is recycled; approximately 15 million tonnes of residual waste is available potentially for energy exploitation in one form (e.g. combustion) or another (e.g. anaerobic digestion).

2.2 Fuel production

Depending upon the type of biomass of interest, specialist agricultural equipment are necessary to cultivate the biomass resource, in a series of processes such as the following applicable to wood crops (Serup, 2002):

- felling of trees;
- chipping of logs, branches;
- haulage of chips;
- storage and transportation of chips;
- (optional) production of wood pellets;

Whereas one study (Serup, 2002) makes reference to the risk of bacterial infection only to tree stumps after tree felling, another report (DEFRA, 2002a) instead focusses upon the decomposition of freshly made wood chips during the first 24 hours of storage as a primary concern for biological activity, when temperatures may reach 60 °C. It also claimed that calorific value is lost during this period, but these risks may be avoided via effective natural air drying. Both aforementioned reports declare that moisture content will decline after drying from 50 % initially to 30 %. Three commonly used methods of producing wood chips are disc, drum and screw based machinery. The ultimate objective of producing wood chips (and pellets) is to make fuel feed more reliable to the combustion chamber of the energy conversion system. The disc chip design

consists of a metal disc fitted with usually 2–4 blades, against which the wood log is positioned. The wood is cut against an anvil, which can be varied in distance from the metal cutting disc, for example 12–35 mm. A drum design features blades mounted on a cylinder, the blades being positioned parallel to the axis of the cylinder. Wood in the form of whole trees, logs and logging residues is fed to the rotating cylinder blades and cut against an anvil. Whilst the drum chipper is capable to cut a wider range tree forms and to tolerate pollutants such as sand, it has been reported that the disc chipper design is advantageous in terms of producing a more uniform wood-chip output at lower energy consumption (Serup, 2002). A screw-cone chipper consists of a spiral blade, positioned horizontally, that has a combined action of pulling the wood from the feed hopper and into the blade for subsequent cutting.

Wood pellets are a form of wood particle made dense by mechanical compression, to a standard pellet dimension such 6 mm diameter, 30 mm length. Various physical forms suitable for commercial trading of biomass pellets are described within technical specifications, e.g. a wood pellet of dimensions 8 mm diameter and 30 mm length would be classified ‘D8’ (Standards, 2005). The main advantage of wood pellets is the uniform dimensions which are of high importance to the residential market for wood pellet boilers. A traditional method of making pellets comprises the following: (Geißelhofer & Hahn, 2000)

drying— established methods such as rotary drum, (in)direct steam or hot air are used to remove water from the biomass.

Pelletisation is possible only when moisture content is reduced to less than 18 %;

milling— biomass raw material is reduced to a uniform size for entry to the pelletisation machine, usually via a hammer mill;

pelletisation— either a circular rotating die or static die and a roller are used, with adjustable blades to cut pellets to desired length;

cooling— mechanical compression creates heat, where pellets are produced at a temperature of 90–95 °C. Cooling promotes

stabilisation of the pellet structure, due to the lignin content in the biomass. Cooling is also necessary for subsequent packaging into lightweight (e.g. 15 kg) bags.

Whilst the advantages of wood pellets are accepted by consumers who are prepared to pay a premium price for the benefits, to energy producers the single most significant disadvantage is the cost. Any costs associated with supplying the fuel have a detrimental effect on financial viability, consequently wood chips remain a more acceptable compromise between fuel cost and fuel feed efficiency to the power plant. Pelletisation of biomass is of additional benefit such as reducing transportation and storage costs, as well as facilitating combustion of such fuels in conventional boiler equipment, but the value of these benefits has to be compared to the capital cost of the pelletisation process itself. In the case of straw, transportation farther than 35 km is said to reduce the economic attraction of using straw as a biomass fuel and furthermore, it has been claimed that the capital cost of pelletisation equipment is too high relative to oil prices and straw transportation costs (Lappin, 1986). In consideration of the volatility of oil prices in recent years, further economic analysis would be required to assess if this historic observation remains valid today. Another advantage of pelletisation of biomass is to improve the reliability of fuel supply to the combustion chamber. With biomass forms such as large chips (e.g. greater than 50 mm size), there is a risk of disruption to the supply of fuel due to blockages occurring in a screw-feed type system, with the resultant interruption to power generation. This type of scenario may be a good justification to use pelletisation as a fuel preparation stage.

Production of SRF may be achieved from various sources: commercial wastes including construction, demolition; industrial processes; municipal (solid) waste. This project is focussed only on MSW, which consists of *a*) residential waste (nearly 90 % of total MSW) *b*) environmental wastes (e.g. street litter, public parks' wastes) *c*) commercial properties such as retail, council offices where local authority collection exists (Serup, 2002). Regardless of the method, the quality of the resultant SRF must be achieved to the standard specification; § Appendix C describes the specification in more detail. The following

list summarises the stages of the SRF production process, some of which are optional, in order to produce a standard SRF:

waste reception— separation of waste into various components for materials recycling, decomposition and subsequent energy conversion;

comminution— use of shredding equipment to create material of homogenous size, beneficial especially to fluidised bed combustion;

drying— removal of water to improve further the calorific content of the fuel and as an option to produce fuel pellets.

Due to the heterogeneous composition of MSW, separation may be a complicated procedure. In order to create SRF many separation tasks are required: comminution; magnetic separation; eddy-current non-ferrous metal separation (e.g. aluminium containers) size screening; optic separation (i.e. use of near-infra red sensors to identify plastics).

Separation of both biomass and MSW was not found to have been collated in a way comparable to this PhD project. Regarding biomass, consideration of higher priority use (e.g. food production) is simple to integrate into this project; a biomass form such as straw could be utilised to represent a biomass resource available after all existing demands (animal feedstock, or building materials) have been met. However this simplicity is not the case with MSW. A potential source of SRF production is from mechanical biological treatment. There are numerous forms of MBT that may be designed to maximise specific outputs such as compost for soil conditioning or bio-gas for electricity generation. Of interest to this review is the form of MBT that is designed to produce SRF. Historically MBT was developed in Germany as a method of waste preparation before disposal to landfill, to meet the EU Directive on landfill by making the waste biologically stable and therefore minimising methane (green-house gas) emissions (Archer *et al.*, 2005a). The waste input to a MBT facility may be either non-separated “black-bag” waste or separated waste such as “residual MSW” after separation of recyclable fractions has been completed. The choice

of waste input to the MBT system has important consequences when considering the impact of SRF upon recycling initiatives. Opponents of EfW claim that using MBT as a source of SRF would prevent the preferred recycling of materials; clearly this would occur with MBT where the waste input is non-separated MSW. In a study of the commercial operation of MBT (Archer *et al.*, 2005b), where SRF is the priority output, four systems made use of separated MSW as the input, compared to three MBT systems that utilised non-separated waste. Where separated, residual MSW is the input to the MBT system, this input consists of card(board), glass, metals, plastics rejected by recycling operations (e.g. due to contamination by food remnants). This input is similar to the rejected material from an MRF; both systems will reduce the total volumes of materials available for energy conversion, but the composition suggests that waste of useful calorific value will remain for exploitation.

2.3 Fuel characteristics

The characteristics of many fuels (biochemical, chemical composition; calorific value) have been extensively studied and published in the form of a reference database (van Doorn, 1999). This database (*'Phyllis'*) collates a vast range of fundamental analyses performed by individual research groups, for example analysis of wheat (Table 2.1). Table 2.2 summarises the chemical composition (proximate, ultimate and elemental analyses) of a selection of common biomass fuels.

Table 2.1: An extract from an example analysis of wheat properties stored in the Phyllis database (van Doorn, 1999)



ECN

PHYLLIS

the composition of biomass and waste

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[how to use Phyllis](#)
[definitions used in Phyllis](#)
[preferences](#)

[composition of a single material](#)
[average composition of a group of materials](#)
[selection via NTA 8003](#)
[search for materials](#)

General information

Sample information

Group

straw (stalk./cob/ear)

Subgroup

wheat

Material

waste wheat straw (China)

ID-number

2321

Reference:

ECN laboratories.

Remarks:

Straw (WSW) from China

Material composition

Proximate analysis (wt. %)				Ultimate analysis (wt. %)				Elemental analysis (mg/kg sample (dry))												
	dry	daf	ar		dry	daf	ar													
Ash	18.9		17	C	38.6	47.5	34.7 Msr	Al	5041 Msr	Fe	2455.5 Msr	Pb	5.2 Msr	As	1.3 Msr	Hg	- ND	Sb	0.7 Lim	
Water		10.1		H	5.07	6.2	4.6 Msr	B	27.2 Msr	K	22450 Msr	Se	0.2 Lim	Ba	86.4 Msr	Mg	3400 Msr	Si	30000 Msr	
Volatiles	-	-	-	O	36.3	44.7	32.6 Msr	Ca	8172 Msr	Mn	100 Msr	Sn	0.8 Lim	Cd	0.1 Msr	Mo	1.5 Msr	Sr	75 Msr	
				N	1.07	1.32	0.96 Msr							Co	2.3 Msr	Na	2800 Msr	Te	- ND	
				S	0.29	0.36	0.26 Msr							Cr	81.2 Msr	Ni	423 Msr	Ti	179 Msr	
				Cl	1.47	1.811	1.322 Msr							Cu	5.7 Msr	P	1015 Msr	V	5.9 Msr	
Calorific value (kJ/kg)																				
	dry	daf	ar																	
HHV	16188	19948	14559	F	-	-	- ND													
LHV	15082	18585	13319	Br	-	-	- ND													
HHV _{mine}	15162	18684	13637	Total:	101.6	102	101.4													

Table 2.2: Analysis of common biomass fuels, based upon data stored by Energy research Centre Netherlands, van Doorn (1999). Values expressed on an ‘as received’ (ar) by weight (wt) basis.

Biomass material	Chemical composition (% wt ar)						Volatile content % wt ar	Ash % wt ar	Water % wt ar	Calorific value (gross, MJ kg ⁻¹ ar)
	C	H	O	N	S	Cl				GCV
Beech (chipped)	43.8	5.4	40	0.13	0.02	0.0004	74.5	0.9	10.2	17
Birch (1–3 mm)	46.4	5.8	42.1	0.09	0.01	-	-	0.4	5.3	18
Coal (UK Hem Heath)	77.9	4.6	7.5	1.77	0.88	0.688	34	5	1.7	32
Miscanthus (fresh)	44.9	5.4	40.3	0.51	0.08	0.447	71.5	4.6	4.4	18
MSW (Netherlands)	40	6	22	0.4	0.2	0.534	-	7	23	20
Pine	49.8	5.9	40	0.12	0.03	0.019	81.3	0.1	4	19
Paper clarifier sludge	27.1	2.4	12.3	0.4	0.39		-	-	-	23
Poplar (hybrid)	46.7	5.6	37.6	0.56	0.02	0.009	79	2.5	6.9	18
RDF with plastics	60.8	13.4	13.9	0.32	-	-	83.4	8.7	2.9	29
Reed canary grass	41.5	5.3	35.9	1.29	0.13	0.059	67.9	8.2	7.7	17
Switch grass	41.5	5	37	0.65	0.07	0.03	71.1	3.1	12.6	16
Willow (incl. bark)	48.5	6	41.6	0.39	0.03	0.004	78	1.2	2.4	19

Due to the varied nature of the research groups, the analyses of the fuels within the database are not consistent. As an example, within Phyllis the analysis of pine declares carbon content on an “as received” basis whereas in contrast, analysis of birch states only carbon content in terms of “dry” and “dry ash free” (daf). Consequently the comparison of the data needs to make use of a conversion factor. (see § Appendix B).

The Phyllis database was started in 1997, initially as an internal database project of the Energy research Centre of the Netherlands (ECN), before being made available to the public via the internet in 1998. Initially the data sources were from analyses performed by the ECN and Technical University Vienna. Currently there are greater than 2340 data records of the compositions of a range of biomass and waste materials. A feature of the database is the ability to choose a selection of different fuel sources which then computes average composition values for display in an internet web browser. ‘BIOBIB’ is the database that was developed by Technical University Vienna, Wein, Austria. It pre-dates Phyllis; development had begun in 1992 (Reisinger *et al.*, 1996). The initial stage of the database was a compilation of the analyses of 64 biomass fuels using a range of standard analytical methods. Biomass fuel types are predominantly wood, straw, energy crops and biomass industry waste (treated wood, paper & pulp). The database now comprises more than 647 different fuel samples. The ‘*Biomass Feedstock Composition and Properties Database*’ stores characteristics data for various biomass resources and is managed by the USA Department of Energy, Energy Efficiency and Renewable Energy Biomass Program (NREL, 2001). The database includes biomass fuels not extensively available elsewhere; for example miscanthus is native to Asia and has been extensively researched within Europe, but equivalent research data is not included and instead analysis has been made of a native perennial grass, switchgrass. Reference methods used to measure each analyte are cited. Similarly, the ‘*Biofuel Database*’ of Australia is focussed upon data for native biomass species but data for widespread crops such as wheat is included. This database also indicated the analytical method used to determine each sample result, published in a separate reference document (Stein & Tobiasen, 2007).

A comparison of data values for a selected fuel reveals differences in the reporting of information. For example a miscanthus fuel is reported in Phyllis database to have a gross calorific value of approximately 19 MJ kg^{-1} , based upon analysis performed by Technical University Vienna. Inspection of the BIOBIB database shows that there are ten types of miscanthus samples that exist in the database, classified in terms of geographical sources or seasonal frequency. The value in Phyllis appears to be based upon an average value from 11 measurements of calorific value of a single source. As another example, ash behaviour is described in BIOBIB in terms of various stages: *a)* sintering (agglomeration of ash particles); *b)* softening (surface change); *c)* hemispheric point (temperature at which bulk ash forms hemispheric shape, height being 50 % half base length); and *d)* flow point (bulk ash height declines by two thirds). This information would be useful in relation to fluidised bed combustion, where agglomeration of biomass due to relatively low ash melting temperatures is a common problem. In contrast, Phyllis makes no reference to these observations. Table 2.3 is an example of the data published in these aforementioned databases; with the exception of the USA database, all data is expressed on an ‘as received’ condition of these fuel samples. The conditions of fuels tested for the USA database are not known. There are a number of observations about the presentation of this data that must be considered:

- With reference to the USA database, the condition of the wheat sample subjected to analysis is not known, i.e. whether samples were analysed on an “as received”, “dry” or similar conditions;
- Both Australian and USA databases measure “fixed carbon”, however it has been proposed that this measure (defined as the combustible residue from removal of ash, volatile, water by anaerobic decomposition) is not applicable to biomass because fixed carbon was originally developed for use in coal chemistry to measure elemental carbon, which does not exist in biomass (Klass, 1998);
- Ash measurements are omitted from the USA database;

- The USA database does not publish data in SI units of measurement.

Table 2.3: Comparison of data from different biomass databases for analysis of wheat samples.

	Location of biomass database		
	Australia	USA	Netherlands
Proximate analysis			
Ash (% weight)	1.2	10.22	7
Fixed carbon (% weight)	7.4	21.54	-
Volatile matter (% weight)	34.6	69.38	-
Water (% weight)	56.8	-	10.2
Gross calorific content (MJ kg ⁻¹)	7.98	3.58	17.382
Ultimate analysis			
Carbon (% weight)	20.3	43.88	40.8
Hydrogen (% weight)	2.52	5.26	5.5
Oxygen (% weight)	19.0	38.75	35.9
Nitrogen (% weight)	0.15	0.63	0.47
Sulphur (% weight)	0.03	0.16	0.12
Chlorine (mg kg ⁻¹)	3320	-	-

Within a study concerning combustion of biomass (Demirbas, 2003), analytical data was presented to show that in general, coal comprises 80 % carbon (as dry fuel, commonly referred to as “dry ash free”) whilst many biomass fuels including beech, wheat straw, maize cob and sunflower shell contains 50 % carbon and more than ten times as much oxygen, 40 % (Table 2.4 and Table 2.5). Alternative energy conversion techniques were compared. Pyrolysis was declared to be the most efficient form of energy conversion, attributed to the high ratio of fuel output to biomass feed. The ratios of fuel-to-feed were not indicated for direct comparison. The combustion chemistry discussed within

this paper focussed upon gravimetric analysis, i.e. weight loss and concomitant temperature variation during burning. However the “old rule” for combustion — time, temperature, turbulence — was not considered, especially in terms of the effect of residence time (of biomass in the combustion zone) upon combustion efficacy (Basu, 2006). The effects of these characteristics is more explicitly described elsewhere. For example, carbon content is said to correlate positively towards gross calorific value of the fuel of interest. Moreover, hydrogen content also contributes towards (net) calorific value and water formation. In contrast, oxygen content has the effect of attenuating calorific value as evident in the higher calorific content of coal and lower oxygen composition compared to a biomass fuel with opposing respective values. The importance of good air and fuel mixing, together with combustion zone residence time (> 1.5 seconds) are acknowledged.

Table 2.4: Ultimate analyses of various fuels (Demirbas, 2003)

sample	C	H	N	S	Cl	O (diff.)
Coal type 1	81.5	4.0	1.2	3.0	—	3.3
Red oak wood	50.0	6.0	0.3	—	—	42.4
Wheat straw	41.8	5.5	0.7	—	1.5	35.5
Olive husk	49.9	6.2	1.6	0.05	0.2	42.0
Beech wood	49.5	6.2	0.4	—	—	41.2
Spruce wood	51.9	6.1	0.3	—	—	40.9
Corncob	49.0	5.4	0.5	0.2	—	44.5
Tea waste	48.0	5.5	0.5	0.06	0.1	44.0
Walnut shell	53.5	6.6	1.5	0.1	0.1	45.4
Almond shell	47.8	6.0	1.1	0.06	0.1	41.5
Sunflower shell	47.4	5.8	1.4	0.05	0.1	41.3

2.4 Fuel quality

Instead of designing equipment able to tolerate the wide variation in characteristics of both biomass fuels and waste resources, manufacturers of boiler equipment impose specifications on the types of fuels suitable for use. In

Table 2.5: Ash composition of various fuels (Demirbas, 2003)

Fuel sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl
Coal type 1	42.0	20.0	1.2	17.0	5.5	2.1	1.4	5.8	5.0	–	–
Coal type 2	59.7	19.8	2.1	8.3	2.1	1.8	0.8	2.1	2.0	0.2	–
Coal type 3	51.5	22.6	2.0	14.9	3.3	0.9	1.0	2.0	3.5	0.2	–
Red oak wood	49.0	9.5	–	8.5	17.5	1.1	0.5	9.5	2.6	1.8	0.8
Wheat straw	48.0	3.5	–	0.5	3.7	1.8	14.5	20.0	1.9	3.5	3.6
Walnut shell	23.1	2.4	0.1	1.5	16.6	13.4	1.0	32.8	2.2	6.2	0.1
Almond shell	23.5	2.7	0.1	2.8	10.5	5.2	1.6	48.5	0.8	4.5	0.2
Sunflower shell	29.3	2.9	0.1	2.1	15.8	6.1	1.5	35.6	1.3	4.8	0.2
Olive husk	32.7	8.4	0.3	6.3	14.5	4.2	26.2	4.3	0.6	2.5	0.2
Hazelnut shell	33.7	3.1	0.1	3.8	15.4	7.9	1.3	30.4	1.1	3.2	0.1

addition, to develop an active, efficient market in the trade of standardised renewable energy fuels, certified standards for the quality of fuels sold is necessary to encourage consumers of renewable energy to buy these fuels and the concomitant thermal conversion equipment (Standards, 2005). Standards are often developed internationally and formally adopted by institutions such as the International Organisation for Standardisation (ISO) and within the European Union, technical standards relevant to this research project have been developed by the European Committee for Standardisation (CEN).

2.4.1 Biomass quality standard

The production of biomass fuels involves a complex supply network and a requirement to tolerate the diverse characteristics of the numerous forms of biomass matter. A quality assurance standard to evaluate the supply chain for biofuels is described within a technical specification document (CEN, 2006a), which has not been formally accepted as a standard but currently published as draft status. Two main objectives are defined for the purpose of the standard: to enable the end-user to identify a suitable biofuel; to enable the producer/supplier to demonstrate that the biofuel is of an acceptable, homogeneous quality. The supply chain is described as: *a)* biomass raw material; *b)* identification and collection of biomass raw material; *c)* preparation/production of solid biofuels; *d)* distribution; *e)* reception of biofuel by consumer; *f)* thermal conversion by consumer. The biomass resource is iden-

tified by confirmation of both the origin of biomass and the biomass production process. Distribution of the biomass requires confirmation of the recommended handling and storage of the biomass products, after which the consumer should receive documentation to confirm the final declaration of the fuel specification that has been supplied. It should be noted that the biomass raw material (a) is outside the scope of the quality assurance document (it is impossible to standardise natural vegetation!), as is the thermal conversion of solid biofuels (f). Also important to note is that these technical standards for biomass relevant to this project are restricted *only* to solid biofuels.

A specific range of materials are defined as a solid biofuel (Standards, 2005):

- agricultural and forestry derived products;
- vegetable waste from agricultural and forestry derived products;
- wood waste;
- fibrous vegetable waste from paper production;
- cork waste.

The definition of wood waste is an exclusion of treated (preservatives and surface coatings) wood where the chemical treatment may consist of halogenated organic compounds and/or heavy metals and the treated wood originates from construction and/or demolition waste. Moreover as a consequence of the definition of types of solid biofuels (CEN, 2004), DDGS and wheat straw pellets may be considered to be vegetable waste from agricultural products (ethanol and wheat grain respectively). Each type of solid biofuel is classified further, such that DDGS is considered a herbaceous biomass industrial process residue. Wheat straw is classified as a herbaceous biomass material, ‘herbaceous’ being defined as plant origin of non-wood type stem that dies at the end of the growth season.

2.4.2 Solid Recovered Fuels (SRF) quality standard

Refuse Derived Fuel (RDF) is a predecessor term to SRF and it is claimed (Porteous, 2003) to be defined by the UK government as:

“turning the combustible portion of waste, such as paper and plastics, into a fuel which can be stored and transported, or directly used on site to produce heat and/or power”

However it is claimed elsewhere that there is no legal definition of RDF (no Act of British Parliament defines RDF) and the acronym is interpreted differently throughout Europe (Gendebien *et al.*, 2002). Supply of RDF was often in two forms; coarse loose fuel particles or densified pellets (dRDF). The technology for RDF production was developed from the 1970s but the UK market did not develop as initially envisaged, with the subsequent closure of RDF production facilities for a number of reasons such as the following (Frith & Last, 2009):

- Early UK plants showed poor experience of reliability and air pollution control;
- Perception of greater propensity of RDF to cause increased corrosion to power plant pipework;
- High operating costs such as power consumption for the production of RDF.

Moreover, the arrival of the European Directive on incineration of waste (European Parliament, 2000) meant that many RDF combustion facilities were closed due to the costs of investment required in air pollution control devices to meet compliance with the legislative limits on pollutant emissions.

However, recent changes in waste management legislation (ultimately as a consequence of EU Directive on landfill of waste, European Parliament (1999)) has regenerated interest in RDF, primarily as part of an integrated waste management programme where a fraction of the many outputs from mechanical biological treatment processes are used for RDF manufacture. The term ‘solid recovery fuels’ has been introduced as new fuel with a higher specification

standard, presumably to provide further confidence to the development of the market for both consumers and manufacturers of SRF, formally defined:

“solid fuel prepared from non-hazardous waste to be utilised for energy recovery in incineration or co-incineration plants and meeting the classification and specification requirements laid down in CEN/TS 15359.

NOTE ‘prepared’ here means processed, homogenised and upgraded to a quality that can be traded amongst producers and users.”

(CEN, 2007)

The current draft technical standard (CEN, 2006b) proposes that the specification of SRF is based upon three parameters:

- net calorific value**— to represent an economic factor for assessing the fuel;
- chlorine content**— an indication of the technical quality;
- mercury content**— a measure of environmental impact.

The intention is that these parameters give a general basis for classification of SRF and then greater technical detail is published to provide precise properties of the fuel to the consumer, as a formal quality declaration document. Details of how the fuels evaluated in this research project are classified are shown in § Appendix C.

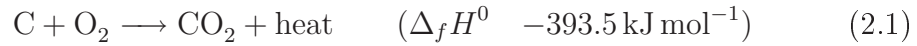
2.5 Thermal conversion technologies

The need to perform thermal conversion of biomass and MRFR resources is a natural consequence of the laws of thermodynamics, or changes in energy. These three laws are as follows: *a)* energy is conserved and neither created nor destroyed, *b)* spontaneous reactions are irreversible, (O’Neill, 1985) *c)* perfect crystals at absolute zero have zero entropy (or extent of order, Atkins (1994)).

A chemical reaction is an example of a change in energy, either emitted to the environment in the form of heat (i.e. an exothermic reaction), or absorbed to cause cooling of the environment surrounding the *endothermic* reaction.

2.5.1 Combustion

Combustion of biomass may be considered simply as oxidation of carbon and hydrogen to carbon dioxide and water respectively (Tillman *et al.*, 1981). This oxidation process also results in a change of thermal energy (most commonly an increase, to generate heat) governed by the fundamental laws of chemical thermodynamics. As a consequence of this conversion of chemical energy (oxidation) to thermal energy (heat), the heat is exploited in a power system to do work, such as converting water to steam and subsequently generating electricity using the mechanical power of a turbine.



In the case of wood combustion where wood is represented chemically by cellulose $(\text{C}_6\text{H}_5\text{O}_5)_n$, the combustion reaction becomes:



This approximation of the empirical molecular formula of wood is acceptable in terms of the composition of wood comprising 40–50 % cellulose and 20–30 % lignin (Tillman *et al.*, 1981). There are various engineering techniques that have been deployed in order to achieve combustion efficiently, some of which are subsequently outlined.

Fluidisation

A fluidised bed is a material of predominantly inert granular material (e.g. sand) that is made to behave like a turbulent, flowing liquid by injecting a gas — commonly air — through that material via a series of nozzles. There are numerous benefits and advantages of the fluidised bed technique that have been usually described in a theoretical treatise of the concept of fluidisation

(such as minimum fluidisation velocity), beyond the scope of this document. However some theoretical aspects of fluidised bed design deserve brief mention. The fluidised bed combustor is based upon the bubbling fluidised bed design, in which hot air of sufficient velocity is injected into a bed of inert particles (e.g. silica sand) to cause the particles to move dynamically in similar way to a viscous, bubbling liquid. The fluidised bed process offers a range of advantages, some of which are particularly relevant to the combustion of the fuels involved in this study. The following advantages have been well documented:

Heat and mass transfer[†]— is very effective because of the high total surface of fluidised bed particles; for example bed particles of diameter 100 μm and occupying one cubic metre will have a total surface area of 30 000 m^2 ;

High solids mixing[†]— the high degree of solids mixing ensures that heat transfer is effectively high and temperature gradients within the bulk fluidised bed are rendered negligible;

Operation[‡]— maintenance costs are low and can be attributed to the absence of moving mechanical parts;

Size[‡]— a fluidised bed reactor is vertical in design, saving space and hence minimising land costs for location considerations;

Labour[†]— skilled labour is not required to operate a fluidised bed reactor, enhancing the economic viability of such systems;

[†] (Botterill, 1975); [‡] (Sathiyamoorthy, 1999).

Minimum fluidisation velocity is a measure of the conditions necessary to create fluidisation of particles, determined predominantly by particle diameter and affected by both pressure and temperature (Botterill, 1975); pressurised conditions are not used in this research project and therefore temperature effect is of interest. The minimum fluidisation velocity increases with particle size as shown in Figure 2.1–Figure 2.3. Although temperature can be seen to have an effect on minimum fluidisation velocity, for the combustion temperatures expected for this project, this effect will be negligible. Referring to

particle diameter, agglomeration tendency is also affected such that small particles ($< 50\text{ }\mu\text{m}$) are susceptible to agglomeration due to inter-particle forces greater than those forces imparted by the fluidising gas, ultimately causing bridging and subsequent channel formation within the bed (Botterill, 1975). In addition, agglomeration is also favoured when the fluidised bed container dimensions have a high height-to-cross sectional area ratio (Knowlton, 1999). These effects are not expected to be experienced during combustion with the sand and combustor dimensions used in this project although the friable characteristic of limestone will produce a higher proportion of fine particulates.

Various fluidisation gas distributor designs have been developed to perform the following typical requirements (Botterill, 1975):

- promote uniform, stable fluidisation;
- minimise attrition of bed material;
- minimise erosion of any heat exchanger tubes immersed in the bed material;
- prevent loss of bed material below the gas distributor both during and without operation of the combustor

The pilot scale fluidised bed combustor used in this research project features a “nozzle” or “tuyere” type gas distributor grid. In this design the depth of the bed material relative to the distance between the gas orifices needs to be sufficiently high, otherwise the bed is susceptible to “spouting” of material immediately above the orifices to leave stagnant material in between; this behaviour would increase the tendency of agglomeration to occur (Botterill, 1975). The disadvantage of agglomeration tendency with the nozzle — or “bubble cap” lateral flow — design is also confirmed elsewhere, as is the recommendation not to use with solids that are liable to adhere (Karri & Knowlton, 1999). Examples of other designs of gas distribution grids are shown in Figure 2.4. The conical design produces lateral gas flow and is advantageous in terms of superior mixing performance, but demands high quality design to ensure good gas

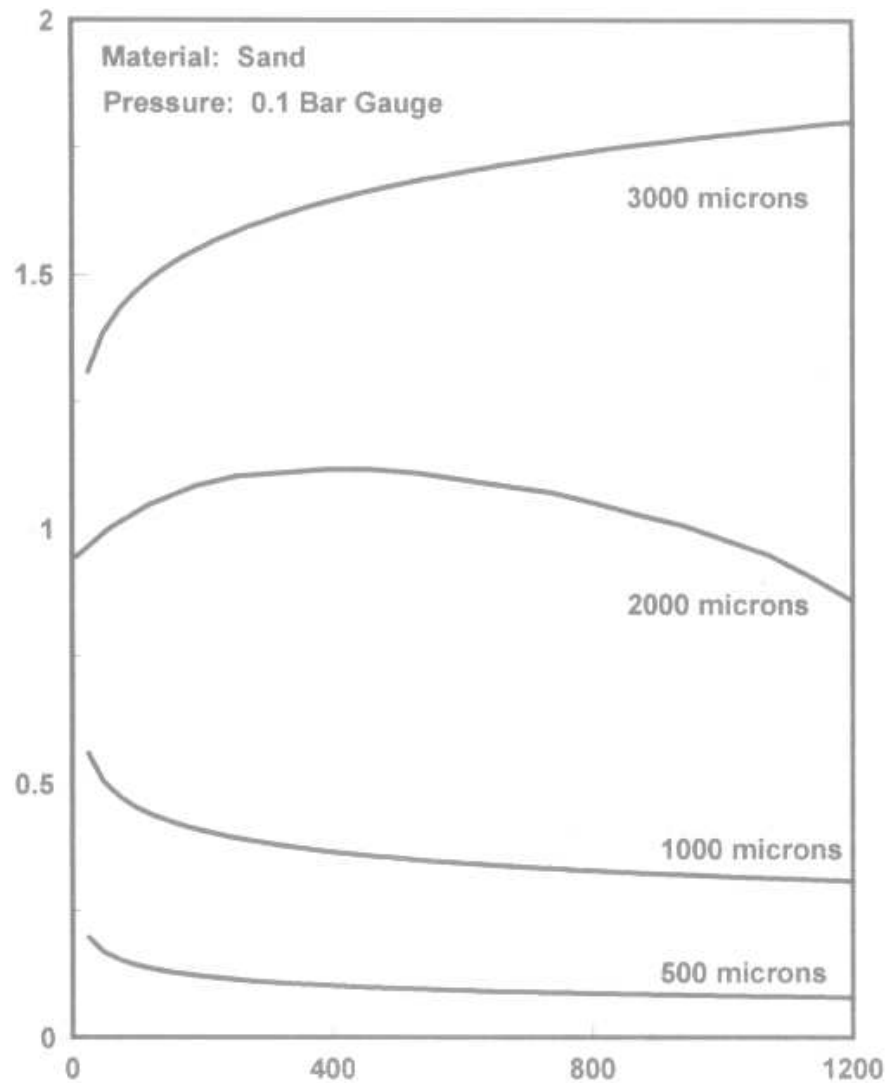


Figure 2.1: Effect of temperature on minimum fluidisation velocity, for a range of particle sizes. Unit of measurement for the ordinate axis is ms^{-1} , for the abscissa is temperature ($^{\circ}\text{C}$). Graph courtesy of Wen & Yu (1966), cited in Knowlton (1999)

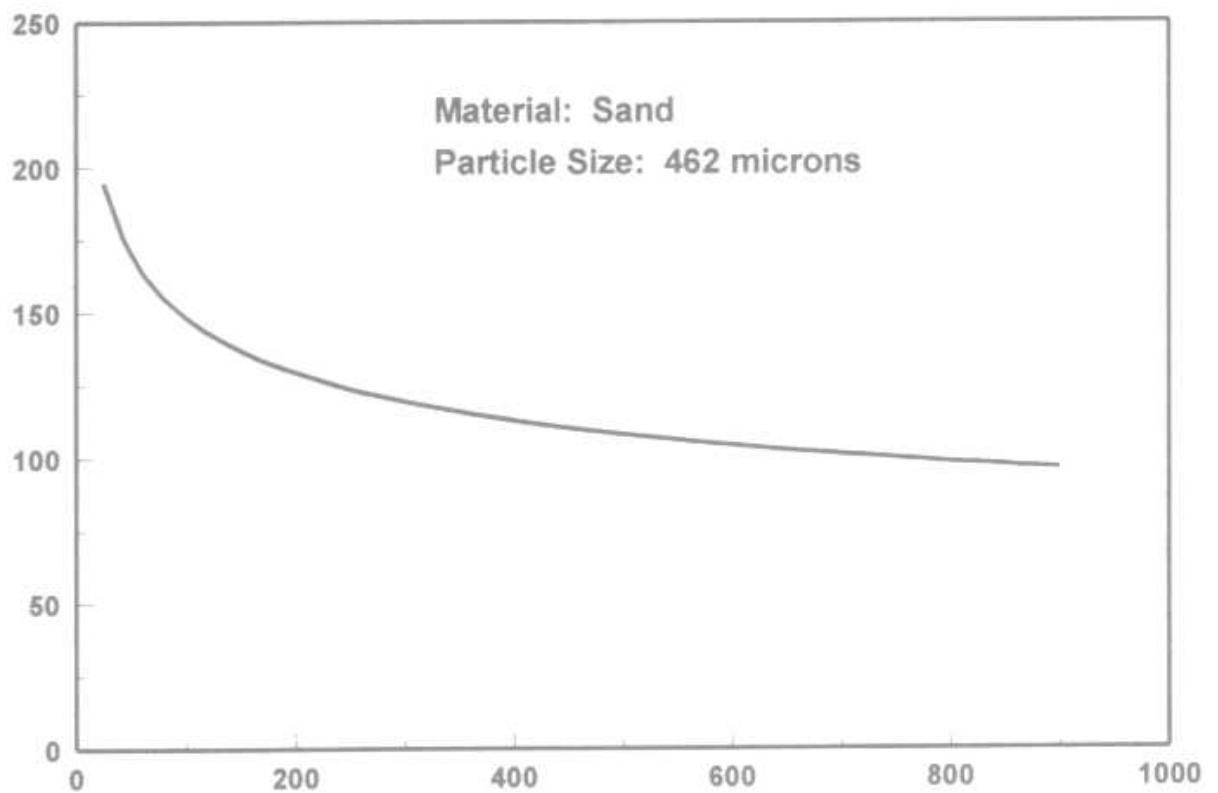


Figure 2.2: Effect of temperature on minimum fluidisation velocity. Unit of measurement for the ordinate axis is mm s^{-1} , for the abscissa is temperature ($^{\circ}\text{C}$). Graph courtesy of Botterill & Teoman (1980), cited in Knowlton (1999)

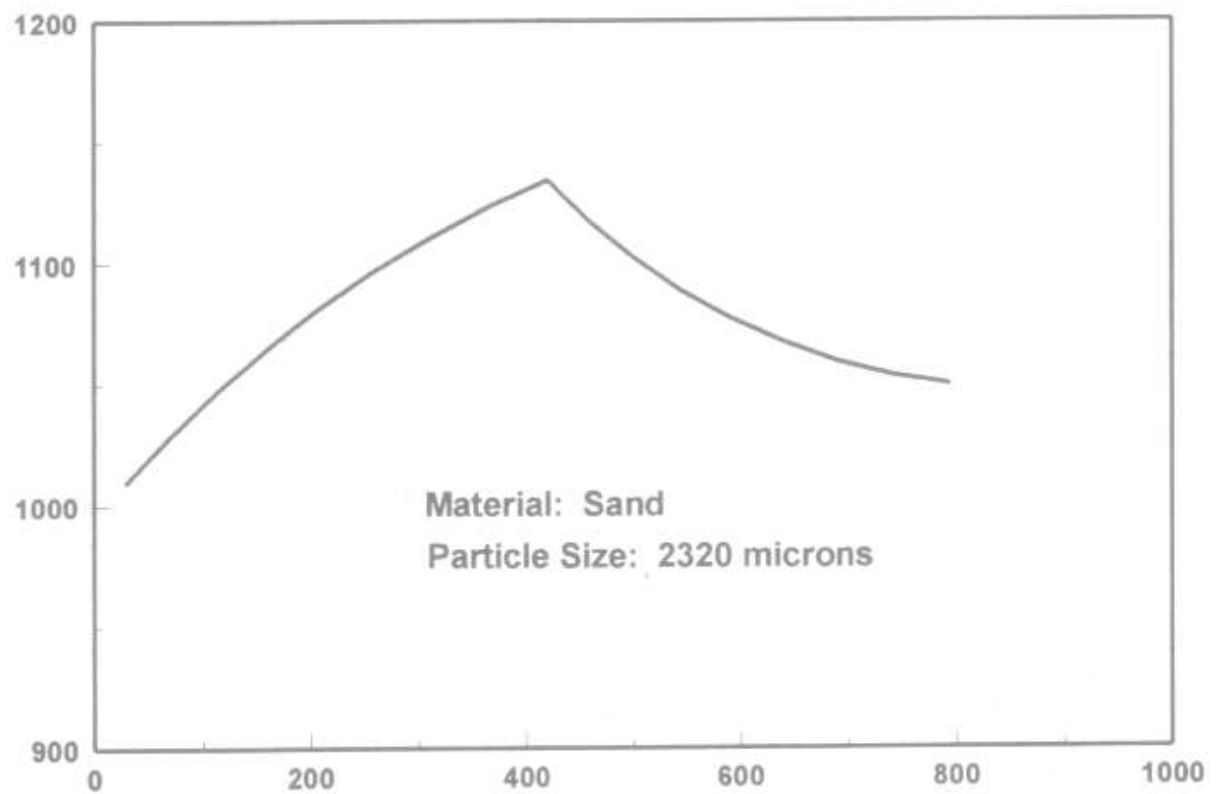


Figure 2.3: Effect of temperature on minimum fluidisation velocity. Unit of measurement for the ordinate axis is mm s^{-1} , for the abscissa is temperature ($^{\circ}\text{C}$). Graph courtesy of Botterill & Teoman (1980) cited in Knowlton (1999)

distribution and also has a high pressure drop. The perforated plate (where apertures are positioned for upward gas flow) is a simple, cheap design but suffers from loss of fluidised bed material. The sparge pipe (with downward or lateral flow) is characterised by minimal loss of bed material, but bed material below the pipes is static and so is not involved in fluidisation. The bubble cap and sparge pipe designs are also claimed to offer good “turndown” ratio, which is defined as a measure of the ability of the fluidised bed combustor to operate over a range of loads (CSL, 2005a).

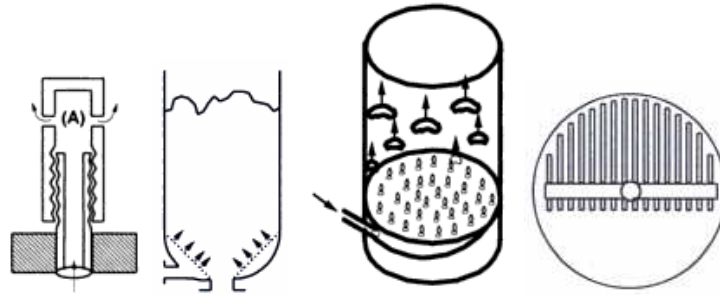


Figure 2.4: Various designs of fluidised bed gas distribution grids (from left to right: bubble cap; conical; perforated plate; sparge pipe, adapted from Karri & Knowlton (1999))

Grate fired

The use of grate firing systems for combustion of biomass fuels is well established within commercial scale operation and the various forms of grate firing have been reviewed (Yin *et al.*, 2008). These combustion systems are characterised by a surface, or grate that supports the fuel when placed into the combustion chamber and the grates may be designed to be fixed (position), or moving. Generally, moving grates are capable of achieving a more controlled combustion of the fuel compared to fixed grate, by promoting a better mixing of the fuel. A review of the latest grate-fired combustion technology has recently been published, (Yin *et al.*, 2008) which includes selected comparison with fluidised bed combustion systems. Grate-fired combustion is claimed

to be a preferable technology, although 10 000 bubbling fluidised bed boilers are said to be installed globally, having replaced almost all traditional stoker-fired systems (Basu, 2006). Current research into grate-fired boilers involves development of secondary air supply (e.g. over-fire air where this secondary air supply is directed immediately upon the area of flames in the combustion chamber), to overcome the historic disadvantage of grate-fired systems: incomplete combustion of fuel leading to high carbon monoxide and nitrogen oxide emissions. Earlier studies have demonstrated that it is essential that secondary air is supplied to the combustion zone in order to achieve complete combustion of RDF, especially with reference to the relatively high volatile content of these fuels (Burnley, 1987). Similarly, efforts to reduce sulphur dioxide emissions are analogous to those employed in fluidised bed systems; addition of sorbent material (such as limestone) onto the grate above the fuel. However it was acknowledged that reducing conditions predominate at the grate area, which discourages calcium sulphate formation.

Pulverised fuel

It has been estimated that 40 % of global electricity supply is generated using coal power stations, where pulverised coal is the dominant technology deployed since introduction during 1920s (DTI, 2001). Pulverisation of (coal) fuel is the comminution of coal into fine particles (e.g. of size $\approx 60 \mu\text{m}$ and moisture 3 % by weight, de Jong *et al.* (2007)) with pneumatic transport of the fuel (usually with air) to the combustion chamber (van Loo & Koppejan, 2008).

2.5.2 Gasification

Unlike combustion, gasification is a partial oxidation reaction that yields a synthesis gas (or *syngas*) comprising carbon oxides and hydrogen:



where cellulose is a representative biomass composition formula in equation 2.3. The calorific value of the syngas is classified into three general levels:

a) low ($4\text{--}12\text{ MJ m}^{-3}$), produced when gasification is performed using air and the nitrogen content dilutes the calorific fractions of CO and H_2 ; *b)* medium ($12\text{--}30\text{ MJ m}^{-3}$), obtained from pure oxygen as oxidant; *c)* high ($> 30\text{ MJ m}^{-3}$), where methane is produced and therefore of course has a calorific value approaching that of natural gas 40 MJ m^{-3} . Medium calorific value syn-gas may also be produced by using air and indirect heating of the gasifier with heat transfer via an inert solid medium. Indirect heating avoids dilution of the syn-gas by nitrogen since the heat transfer is separated from the gasification reaction products (Klass, 1998). The production of high calorific value syn-gas involves a series of simultaneous reactions and although full characterisation is beyond the scope of this project, typical high energy methanation reactions are shown (equations 2.4 and 2.5):



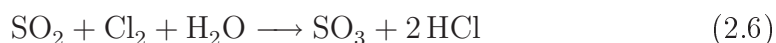
2.5.3 Pyrolysis

In the absence of oxygen, biomass can be subjected to thermal decomposition (thermolysis). Although a product with calorific value is obtained, historically pyrolysis has been used as a method to access a source of chemicals (from coal) and it could be argued that pyrolysis of biomass is more beneficial as a sustainable source of chemicals currently obtained from fossil fuels, instead of primarily a renewable fuel supply. Conditions for the pyrolysis process can be varied to favour certain products; traditional pyrolysis of wood involves relatively low temperatures (400°C) being applied for long duration of hours or even days, to produce charcoal. In contrast, fast pyrolysis at high temperatures of about 800°C for less than two seconds will result in the production of low calorific value gases and predominantly liquids (solid char residue may comprise as little as 5% of final products). Pyrolytic liquids may be considered to resemble crude oil, comprising distillates of variable viscosities and requiring further refinement to yield useful chemicals such as *inter alia*, alcohols, aldehydes, water. Of historical interest, the term ‘wood alcohol’ for methanol

is derived from the historic source of methanol via pyrolysis of hardwood.

2.6 Concurrent combustion of fuels

The majority of research into combustion of MSW with other fuels has been with coal, either as low quality non-separated or as higher quality separated waste. Such research has investigated the ability of coal to minimise toxic pollutant emissions. For example, the sulphur naturally present in coal was said to be effective in reducing PCDD/F concentration when MSW was burnt in an industrial scale incinerator and coal added to the waste (Lindbauer *et al.*, 1992). The study states that PCDD/F formation occurs via chlorine, but that the presence of sulphur dioxide (itself formed by the oxidation of sulphur in the coal during combustion; equation 2.21) causes the formation of hydrogen chloride, preventing chlorine generation (equation 2.6):



Of course, this solution to the problem of PCDD/F formation creates a new problem of acidic gases formation which is not discussed in the paper; presumably the author expects such emissions to be controlled by flue gas pollutant abatement technology. The paper acknowledges that the quantity of sulphur dioxide necessary for PCDD/F inhibition may exceed standard flue gas desulphurisation controls, so that extra desulphurisation capacity would be required. It was claimed that lignite coal (1.6 % sulphur) was added to the MSW at calculated time intervals to produce a continuous concentration of sulphur dioxide, but details of the time intervals, quantities, target SO_2 were not declared either within the paper or bibliographic references. The paper concludes that a coal:MSW ratio of 60:40 was sufficient to achieve effective reduction of PCDD/F congeners; a fuel mixture containing 30 % coal was found to be ineffective.

Combustion of waste wood with (pulverised) coal has been investigated, to assess emissions of various attributed to the chemicals used to treat wood against bacterial decay (Freeman *et al.*, 2000). Examples of these wood treatment chemicals are penta-chlorophenol and creosote (distillates from thermoly-

sis of coal or wood) and exploiting waste wood is stated as being advantageous in terms of reducing emissions of nitrogen and sulphur oxides, due to the low content of the corresponding elements in the fuel (compared to coal). Pilot-scale combustion emissions data suggested that waste wood combustion with coal did not produce organic gaseous pollutants such as PCDD/F congeners, or PAHs greater than legislative limits, when such measurements were performed *before* any standard air pollution control equipment. Many studies on combustion of fuel mixtures containing MSW have concerned PCDD/F emissions, most probably because this has been of highest priority with regards to public anxiety. As well as dioxins and furans compounds, other compounds — often termed “persistent organic pollutants” (POPs) — such as polychlorinated biphenyls and polyaromatic hydrocarbons have also been investigated.

Combustion of wood and RDF using fluidised bed technology was investigated (Raini & Martti, 1996), in terms of analysing the gaseous and fly ash emissions. The MSW was separated firstly by removal of iron metals and then biological material, forming the resultant RDF. The resultant fuel mixtures were characterised as being of particle size 50 mm, with other properties as shown in Table 2.7. (Explanation of the fuel mixtures for each sample test are shown in the Table 2.6, although the journal article does not state explicitly whether the mixtures are expressed by mass, energy content or other parameter). The fuel combinations researched by Raini & Martti (1996) were of nearest analogy to this project. The authors of this article (Raini & Martti, 1996) commented that combustion was found to be hindered by difficulty with fuel feeding into the fluidised bed combustion system, attributed to a particle size that could have been smaller. Considering the moisture content (Table 2.7), this factor may have also affected combustion efficiency. A lack of a stable combustion environment was also evident from the variation in temperature measured throughout various points in the combustion apparatus (Table 2.8; the temperature recordings shown correspond to the following positions: (a) fluidised bed temperatures (TIRS-132, 133, 134); (b) above bed (TIRS-135); (c) freeboard (TIRS-154).). Some practical advantages of concurrent combustion of biomass and wastes have been outlined (Pinto *et al.*, 2002), for example

the difficulty feeding plastic waste to the combustion chamber is susceptible to blockages occurring due to the melting of plastics in the sample feed pipework. This problem was overcome by the addition of biomass pellets.

This author could not identify any published research into combustion of biomass and MRFR, the latter declared as defined in this research project. This suggests that the “waste hierarchy” (reduce, reuse, recover energy) has not been considered within the context of a MSW source of energy that minimises impacts upon waste recycling. The popular research investigations were concurrent combustion of biomass and coal (e.g. Freeman *et al.* (2000)), or coal and (e.g. MSW Pandelova *et al.* (2007)).

Table 2.6: Fuel mixtures of experimental tests for combustion of either wood or peat with RDF (Raini & Martti, 1996)

test 1:	wood chips 100 %
test 2:	wood chips-RDF 85-15 %
test 3:	wood chips-RDF 70-30 %
test 4:	wood chips-RDF 55-45 %
test 5:	peat 100 %
test 6:	peat-RDF 85-15 %
test 7:	peat-RDF 85-15 % (to evaluate bed temperature effect)
test 8:	peat-RDF 70-30 %

Table 2.7: Properties of wood, RDF, peat fuels mixtures (Raini & Martti, 1996)

Test	Moisture %	Volatile matter %	Ash content %	Low heating value (dry) MJ/kg	Carbon content %	Hydrogen content %	Nitrogen content %	Sulphur content %	Chlorine content %
1	45.2	80.4	2.60	18.75	49.9	5.30	0.23	0.01	0.04
2	41.8	78.9	3.45	19.43	50.8	5.57	0.68	0.07	0.12
3	42.0	77.8	5.78	20.04	50.8	6.46	0.73	0.12	0.19
4	41.6	77.6	6.70	20.14	51.2	6.70	0.66	0.12	0.33
5	46.0	68.6	4.33	21.23	55.5	5.34	1.83	0.17	0.03
6	45.7	69.1	4.87	21.05	54.5	5.58	1.93	0.15	0.05
7	46.7	67.6	7.32	20.49	53.2	5.58	1.95	0.16	0.08
8	44.4	69.1	6.45	20.85	53.7	5.43	2.02	0.17	0.10

Table 2.8: Temperature variation within fluidised bed apparatus (Raini & Martti, 1996).

	TIRS-132	TIRS-133	TIRS-134	TIR-135	TIR -154
Test 1 Wood chips 100 %	781	852	805	829	719
Test 2 Wood chips 85 %, RDF 15 %	797	871	823	876	735
Test 3 Wood chips 70 %, RDF 30 %	786	859	812	868	730
Test 4 Wood chips 55 %, RDF 45 %	783	855	808	840	737
Test 5 Peat 100 %	745	816	774	846	805
Test 6 Peat 85 %, RDF 15 %	711	765	724	797	755
Test 7 Peat 85 %, RDF 15 %	710	767	721	772	715
Test 8 Peat 70 %, RDF 30 %	654	700	671	779	830

2.7 Combustion pollutants

In thermodynamic theory, complete combustion of organic fuels will result in production of carbon dioxide and water; however thermodynamics cannot account for the *kinetics* of chemical reactions and this has a critical importance for environmental chemistry. For example, carbon dioxide from combustion of fuel may be produced by an intermediary step to produce carbon monoxide. A combustion zone of insufficient capacity would not allow enough time for carbon monoxide to be oxidised further, resulting in emission of this poisonous gas. Environmental pollution may be defined as the anthropogenic addition of noxious substances that are harmful to both animal and plant life (Radojević & Bashkin, 2006). Pollutants arising from combustion of biomass and MRFR are naturally prevalent but it is the anthropogenic contribution that is of interest to environmental management. Elements present in the fuels such as nitrogen and chlorine will contribute towards gaseous pollutants such as “smog” and “dioxins” respectively. In addition cadmium and chromium are example metals that are detrimental to human health.

2.7.1 Carbon monoxide

Numerous factors are responsible for the emission of carbon monoxide due to incomplete combustion, where reaction kinetics are responsible for relationships between these factors (van Loo & Koppejan, 2008):

- inadequate mixing of oxygen-air and fuel within the combustion zone;
- insufficient residence time of fuel within the combustion zone;
- insufficient combustion temperatures;
- insufficient general supply of oxygen to the combustion system;
- insufficient free radical concentration.

Where mixing of the oxygen with fuel is not optimal for complete combustion, local regions within the combustion zone will be fuel-rich, in effect forming

a condition for gasification to occur via sub-stoichiometric oxidation. Carbon monoxide is an intermediate species before complete oxidation to carbon dioxide, the rate of which is determined significantly by temperature; high combustion temperatures favour complete oxidation.

The availability of free radicals is a complex factor with respect to oxidation of carbon monoxide, affected by the presence of other pollutants. For example, carbon monoxide emissions are potentially higher in the presence of hydrogen chloride (Wei *et al.*, 2004), an effect attributed to the catalysis of the re-combination of free radicals that reduces the availability of free radical intermediates for consequent carbon monoxide oxidation and has been observed experimentally (Figure 2.5; periods of elevated levels of carbon monoxide are attributed to potential changes to the fuel feeding rate). Studies of the effect of chlorine to cause enhanced carbon monoxide emissions within a fluidised bed combustor have also been demonstrated (Becker *et al.*, 1990). This observation is in itself affected by the combustion temperature; higher temperatures (which *per se* discourage carbon monoxide) reduces the impact of hydrogen chloride. It has been demonstrated also that the combined presence of hydrogen chloride and nitric oxide inhibits the oxidation of carbon monoxide, to greater effect than if either of these species were in existence alone (Roesler *et al.*, 1995). Similarly, sulphur dioxide has also been shown to prevent carbon monoxide oxidation by reducing the concentration of free radicals available, although this effect is attenuated by the presence of nitric oxide (Glarborg *et al.*, 1996).

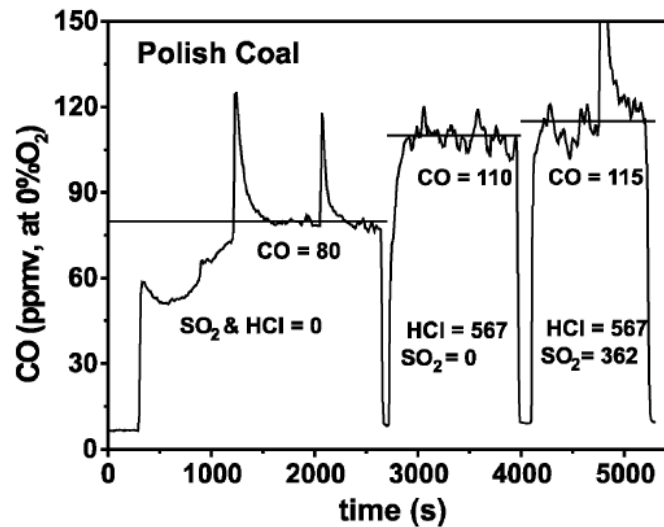


Figure 2.5: Interactions between CO, HCl and SO₂ during combustion of coal (Wei *et al.*, 2004).

2.7.2 Nitrogen oxides

Within the geochemical nitrogen cycle of Earth, production of gaseous nitrogen oxides has occurred historically by thunderstorm activity where higher temperatures cause dissociation of nitrogen and oxygen molecules (equation 2.7 and equation 2.8). High temperatures achieved during combustion of fuels also produces the same effect and the quantity of nitrogen monoxide (or nitric oxide) produced increases with combustion temperature; such formation is termed generally as *thermal*-nitric oxide. Combustion of pulverised coal is usually performed at temperatures greater than 1000 °C where *thermal*-nitric oxide is significant; for fluidised bed combustion temperatures (800–900 °C) the majority of nitric oxide emissions are attributed to fuel bound nitrogen, not atmospheric nitrogen (Oka, 2004a). The vast majority of nitrogen oxide emissions are in the form of nitric oxide; less than 10 % of fuel-bound nitrogen is converted to nitrogen dioxide (NO₂) and therefore the latter is not referred further. In addition, thermal nitric oxide may be also formed via cyano-compounds (equations 2.11, 2.12) within the combustion flame zone and this is indicated by the detection of hydrogen cyanide (HCN), produced

under fuel-rich conditions between hydrocarbon fuel and atmospheric nitrogen (Glassman & Yetter, 2008); this source of nitric oxide is known as *prompt* NO as postulated by Fenimore (1965, cited in Glassman & Yetter (2008)).



The production of nitric oxide via oxygen and nitrogen free radicals is known as the *Zeldovich* mechanism (equation 2.9, equation 2.10). A second source of nitrogen is from within the fuel itself; so-called *fuel-bound* nitrogen. In a biomass fuel such as wood, fuel-bound nitrogen exists as amines in proteins which make up the structure of the tree, whereas in contrast coal contains nitrogen in the form of more stable aromatic compounds such as pyridines, quinoles and pyrroyles. As a consequence, biomass fuels can be expected to yield fuel-bound nitrogen more readily from a more reactive source (Tillman *et al.*, 1981). Fuel bound nitrogen increases significantly emissions of nitric oxide, by up to an order of magnitude (Glassman & Yetter, 2008). The cyano-compounds are involved in subsequent reactions with oxygen and nitrogen free radicals ultimately to form *chemical*-NO, so-called because of the various low molecular weight nitrogen compounds utilised. The nitrogen oxides then engage in further reactions ultimately to produce nitric acid or ammonium nitrate, where the former is associated with ‘acidic rain’ (equation 2.13 and

equation 2.14):



Nitrous oxide (N_2O) is also formed during combustion of fuels and is of importance both directly as a “greenhouse gas” and indirectly as a source of nitric oxide. The global warming potential (Solomon *et al.*, 2007) of nitrous oxide is approximately 300 relative to carbon dioxide, whilst nitric oxide contributes towards ozone layer depletion in the upper stratosphere. Initially, dissociation of nitrous oxides is achieved by high energy ultraviolet radiation in the upper stratosphere (equation 2.15 and equation 2.16), to produce nitric oxide as well as highly reactive intermediate free radicals, of which oxygen completes this cyclical chain reaction (equation 2.17). Emission of nitrous oxide during combustion is attributed to two routes (Basu, 2006): fuel char (equation 2.18) reducing nitric oxide; oxidation of fuel-bound nitrogen (equation 2.19). Considering biomass fuels are generally characterised as containing low levels of nitrogen, nitrous oxide generation via oxidation of fuel-bound nitrogen is not expected to be a dominant source (even though the fuel-bound nitrogen in biomass is more reactive than corresponding nitrogen in fossil fuels). For relatively lower temperature combustion of biomass fuels in fluidised bed combustors, the vast majority ($> 90\%$) of NO_x emissions are likely to be due to atmospheric nitrogen supplied via air as the combustion oxidant. For relatively low combustion temperatures ($< 1173\text{ K}$) it has been suggested that hydrogen cyanide is the primary source for nitrous oxide formation (Boavida *et al.*, 1996).



Industrial-scale combustion of fossil fuels as a primary energy source is usually performed at high temperatures in order to maximise thermal efficiency. At high temperatures, NO_x emissions are maximised, whilst N_2O emissions are minimised, therefore for a fluidised bed combustor where temperatures are relatively low, NO_x emissions can be expected to be low and nitrous oxide to be comparatively high. Power generation is one of many sources of emissions from human activities, although total anthropogenic contributions have been estimated at less than 10 % of total global concentration (O'Neill, 1985). Nevertheless, concentration of nitrogen oxides may be as high as 2 ppmv in urban areas whilst global levels average 3×10^{-3} ppmv.

Reduction in the emission of NO_x can be achieved by a variety of primary methods, i.e. actions to prevent formation of the pollutants:

Preparation of fuel — direct removal of fuel-bound nitrogen in biomass fuels is not practical, however consideration of other fuels' characteristics can be effective; one example is the washing of straw to reduce chlorine content;

Lower combustion temperature — there is a positive correlation between combustion temperature and NO_x emissions;

Staged air supply — biomass fuels have significant content of volatile compounds; insufficient air is supplied at the initial stage to promote reduction of NO by NH_3 and HCN (forming N_2) whilst volatiles are burnt, afterwhich additional air is supplied to facilitate complete combustion of fuel char;

Lower excess air — NO emissions can be reduced by concomitant reduction in excess air supply;

Ammonia injection — a potentially hazardous method due to the risk of leakage to the atmosphere, but ammonia addition to the upper combustion zone (especially to circulating fluidised bed combustors) is an established method of NO_x control, either by use of a transition metal

catalyst or controlled elevated flue gas temperature to induce reduction of NO_x .

On initial view, the proposal to control NO by consideration of chlorine content in the fuel would seem illogical. However, numerous studies have indicated complex interactions between the main gaseous pollutants from combustion of both fossil (i.e. coal) and biomass fuels, such that NO emissions are either enhanced or inhibited by hydrogen chloride. This contradictory behaviour is summarised in one study which cites a number of preceding studies where some experiments showed nitric oxide emission to be increased with hydrogen chloride, or decreased (Gokulakrishnan & Lawrence, 1999). The discrepancy between increased and decreased emissions is attributed to differing combustion environments where increased NO emissions occurred via formation at the solid fuel surface during combustion of the char, whilst the decline in NO emissions is due to the exclusive gas phase reactions dependant upon concentration of hydroxyl and oxygen free radicals. Since the free radicals concentrations are reduced by the chlorine, the result is reduced NO emissions. Incidentally, carbon monoxide emissions were simultaneously increased, presumably by similar reaction mechanisms as stated previously (§ 2.7.1).

In the fluidised bed combustion environment, the use of limestone to control sulphur dioxide emissions also has an impact on nitrogen oxides (the mechanisms of sulphur control are described in successive § 2.7.3). Lime has been proposed as the primary intermediary for redox reactions with sulphur. In a study (Hansen *et al.*, 1992), controlled laboratory conditions were created to resemble an atmospheric pressure fluidised bed combustor. Reduction of nitric oxide was shown to occur only in the presence of carbon monoxide and limestone, whilst carbon dioxide is said to inhibit reduction of nitric oxide due to poisoning of the limestone active surface sites. Under reducing conditions and in the presence of sulphur dioxide, calcium sulphide is produced (sulphation of the limestone particle from fuel-sulphur) and the resulting calcium sulphide surface catalyses the reduction of nitric oxide. Furthermore, in oxidising conditions calcium oxide is formed from calcium sulphide, for subsequent conversion to calcium sulphate (equation 2.27). Reaction kinetics is a factor to consider

for understanding the dynamism of these reactions; direct sulphation of limestone (equation 2.28) is relatively slow compared to calcination of limestone (equation 2.24). For example sulphation of a lime particle (equation 2.27) has been calculated to take 1200 seconds and calcination 50 seconds (Basu, 2006), which is an interesting observation considering the desirable exothermic process of sulphation and the “energy-cost” of endothermic calcination. The effect of limestone in the fluidised bed during combustion of coal and MSW has been shown to be catalytic, enhancing the reduction of nitrous oxide and production of nitric oxide (Li *et al.*, 2004).

The effect of hydrogen cyanide was mentioned at the start of this section, as an intermediary for *prompt* nitric oxide formation. Together with ammonia, both of these compounds are also involved as indirect precursors to *fuel*-nitric oxide formation, although the mechanisms are not fully understood due to complexity of numerous nitric oxide formation reactions (greater than 80) and hydrogen cyanide reactions (greater than 90). Many studies on the combustion of coal have resulted in the conclusion that gaseous nitric oxide is formed predominantly from ammonia and hydrogen cyanide. There are two general, separate routes for nitric oxide and nitrous oxide (dinitrogen monoxide, N_2O):

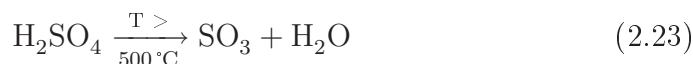
- homogeneous gas phase reactions where ammonia, amine (NCO) group compounds and hydrogen cyanide are reduced during combustion of volatile components of the solid biomass fuel (Hämäläinen & Aho, 1995);
- heterogeneous oxidation of fuel-bound nitrogen in the char solids and reduction of nitrogen at char surfaces.

As examples, it is believed that hydrogen cyanide is oxidised either to nitric oxide via amine oxidation or to nitrous oxide via reaction between amine and nitric oxide. Also, ammonia is said to be the source of nitric oxide formation when heterogenous reduction occurs and is catalysed by the presence of lime particles. Coal combustion research has also revealed that nitric oxide formation is higher for coals that contain higher quantities of volatile compounds; nitrous oxide emissions are correspondingly lower (Jensen *et al.*, 1996). Since biomass fuels are characterised as being more volatile than coal, it is to be

expected that biomass combustion would produce higher nitrogen oxides emissions and it should be noted that gas phase nitric oxide formation originates from volatile compounds.

2.7.3 Sulphur oxides

Corrosion of metal throughout power plants and atmospheric pollution are both caused by sulphur oxides; the corrosive effect of sulphur was historically of prime concern before attention was given to anthropogenic environmental pollution. Sulphur is present in a wide range of forms in both solid fossil and biomass fuels, for example as pyrite mineral (FeS_2) in coal and hydrosulphides ($-\text{HS}-$) within vegetation (i.e. amino acids and proteins). The combustion of fuels containing sulphur leads to the production of sulphur dioxide which is further oxidised to sulphur trioxide. Sulphuric acid (a corrosive form of sulphur) is produced because of the high affinity for water by sulphur trioxide, although this route to sulphuric acid is only feasible at relatively low temperature; above 500°C dissociation occurs (Glassman & Yetter, 2008). Consequently sulphuric acid is most likely to form at the relatively cooler temperatures of the flue gas exit zone of a combustion plant, with sulphur oxides forming potentially at heat exchanger surfaces:



It is normal commercial practice to add limestone (continuously, at a feed rate concomitant with the fuel feed rate) to a fluidised bed combustor for effective control of sulphur dioxide emissions. Calculation of a calcium:(fuel) sulphur ratio is used often to monitor the minimum quantity of limestone required to achieve a specific reduction in sulphur dioxide. For example, a calcium:sulphur ratio of 3:1 is considered acceptable to achieve a sulphur dioxide absorption efficiency of 70 % for coal containing less than 2 % sulphur (Khan

& Gibbs, 1996). Other studies into sulphur dioxide absorption declare a calcium:sulphur ratio (e.g. Wolf *et al.* (2005), Xie *et al.* (1999)), however the kinetics of calcination and sulphation do not seem to be considered. Calcination is relatively fast, reaching completion after 50 seconds, whilst sulphation requires 1200 seconds to reach completion (Oka, 2004a); consequently residence time of fuel in the combustor is an important consideration as are the following additional parameters affecting sulphation:

temperature — high fluidised bed temperature increases sulphur dioxide emission;

limestone structure — older limestone rocks are more crystalline, inhibiting sulphur dioxide absorption;

limestone particle size — smaller particles reduces the volume of particle core where limestone remains unreacted, therefore smaller particles reduces the Ca:S ratio;

limestone porosity — the rate of calcination (and consequent sulphur absorption capacity) is most favourable for limestones with higher porosity;

fluidisation gas velocity sulphur dioxide emissions increase with gas velocity.

During fluidisation, limestone particles are exposed to both oxidising and reducing conditions due to the dynamic motion of particles and gases. The initial activation of limestone is thermolysis, to produce calcium oxide (lime) as a catalytic species which allows for the subsequent sulphation to occur, capturing sulphur oxides (equation 2.24). In the presence of chlorine, a likely scenario when combustion of MSW is considered, sulphur dioxide absorption is altered. Content of sulphur in the fly ash is increased, as is chloride in fluidised bed ash, the latter of which is due to molten calcium chloride penetrating the pores of lime particles to prevent chloride vapourisation. For a calcium-sulphur molar ratio of 2.5–3:1, the conversion of calcium oxide to calcium sulphate is estimated to be approximately 30–40 %, rising to 100 % in the presence of

hydrogen chloride (Xie *et al.*, 1999).

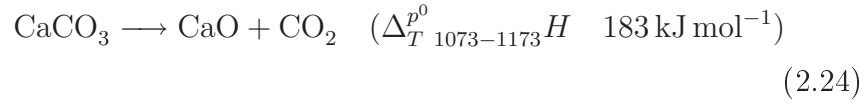
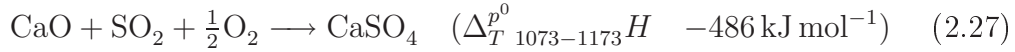
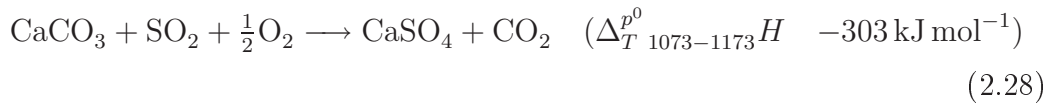
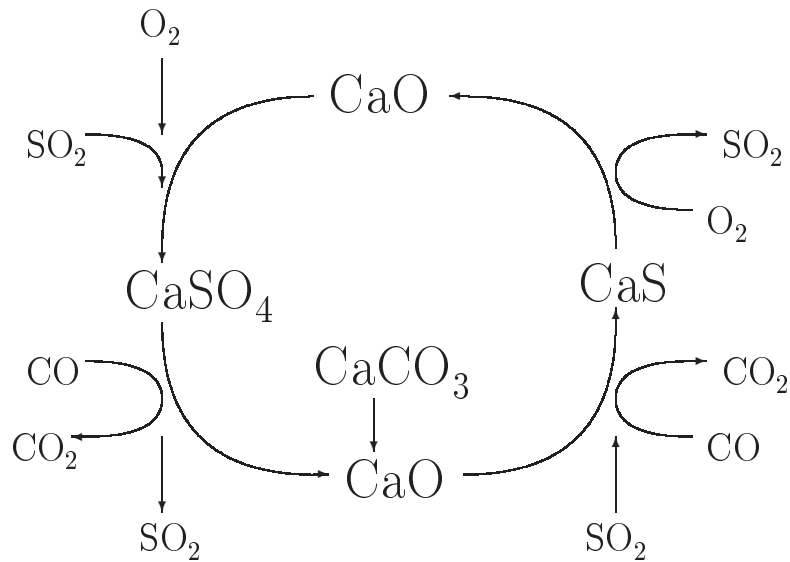


Figure 2.6: Schematic diagram of reactions of limestone particles with sulphur, adapted from Hansen *et al.* (1992)

2.7.4 Halides

Chlorine is introduced into biomass fuels during the growth stage of the original vegetation, via treatment with organo-chlorine fertilisers. Other halides such as bromine may be naturally present and will not be considered further.

Within the combustion zone, chlorine is converted to alkali salts and hydrogen chloride and at the regions of cooler temperatures, where condensation of these compounds occurs onto fly ash particles in the flue gas or heat exchanger surfaces (causing fouling and corrosion). Hydrogen chloride formation is problematic in contributing towards system corrosion and external emission to cause environmental damage by acid rain formation and toxicity to human health. The alkali salts affect the fuel ash characteristics by reducing the ash melt temperature, inducing agglomeration and hence defluidisation of the fluidised bed particles. As well as sulphur dioxide control, limestone is used to reduce emissions of hydrogen chloride:

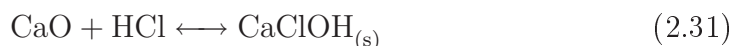
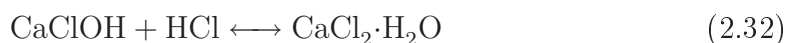
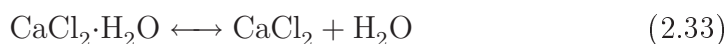


An importance consequence of this reaction (equation 2.29) is the effect on sulphur dioxide emissions, in which it has been shown that the presence of hydrogen chloride causes a reduction in the absorption of sulphur emissions (Julien *et al.*, 1996). The mechanism for this observation is that the formation of (liquid state) calcium chloride prevents sulphur capture by coalescence of lime particles, to reduce the surface area available for sulphation to occur. It is interesting to consider that calcium chloride has a melting point of 772 °C; at typical fluidised bed combustor temperatures molten calcium chloride would be present to interfere in sulphation. An inverse relationship between sulphur dioxide emission and hydrogen chloride has been demonstrated (Ferrer *et al.*, 2005), in that the addition of limestone during combustion of coal and RDF is not effective for hydrogen chloride capture when sulphur dioxide is present. Conversely, hydrogen chloride is removed by limestone when sulphur dioxide is absent; the conclusion is that sulphur absorption is more favourable than hydrogen chloride absorption.

It has also been proposed that contrary to general consensus limestone is not effective in absorption of hydrogen chloride, instead preferring formation of calcium chloride. This is especially favourable in the presence of water at levels normally experienced in fluidised bed combustors (Lawrence & Bu, 2000):



Clearly, this observation is in direct contradiction with equation 2.29, but appears plausible in consideration of the hygroscopic character of calcium chloride. Furthermore the aforementioned study cites the known observation that calcium chloride (presumably from equation 2.29) and calcium sulphate (equation 2.27) form a eutectic mass which melts at 723 °C, which has the effect of extending the sulphation of calcined limestone. This conclusion regarding limestone and ineffective absorption of hydrogen chloride is similarly demonstrated in the study of hydrogen chloride absorption in flue gases (Partanen *et al.*, 2005b), where calcium hydroxychloride is considered an important intermediate:



2.7.5 Metals

Excessive exposure to some trace metals is detrimental to both animal and plant lifeforms and therefore knowledge of the transport of trace metals during fluidised bed combustion is of interest to improve the efficacy of emissions controls. Various metals are naturally present in biomass, but increased bioaccumulation has occurred for some elements such as cadmium (from chemically treated wood) or chromium (metal alloys) due to combustion of fuels containing these pollutants. A number of studies have instead reported the behaviour of MSW with reference to emissions of metals (e.g. Sørum *et al.* (2004)). For non-sorted MSW, the transport of a number of metals has been investigated: It is evident from Figure 2.7 that for metals such as cadmium and mercury, the majority of emissions are expected to be in gaseous form. In contrast, other metals such as lead (similar to zinc) and iron/copper (> 90 %) are transported ultimately as bottom ash. Overall, on a material balance basis approximately 80 % of MSW is converted to gaseous matter. In a review of preceding work, it has been shown that some metals (cadmium, lead) react with chlorine present

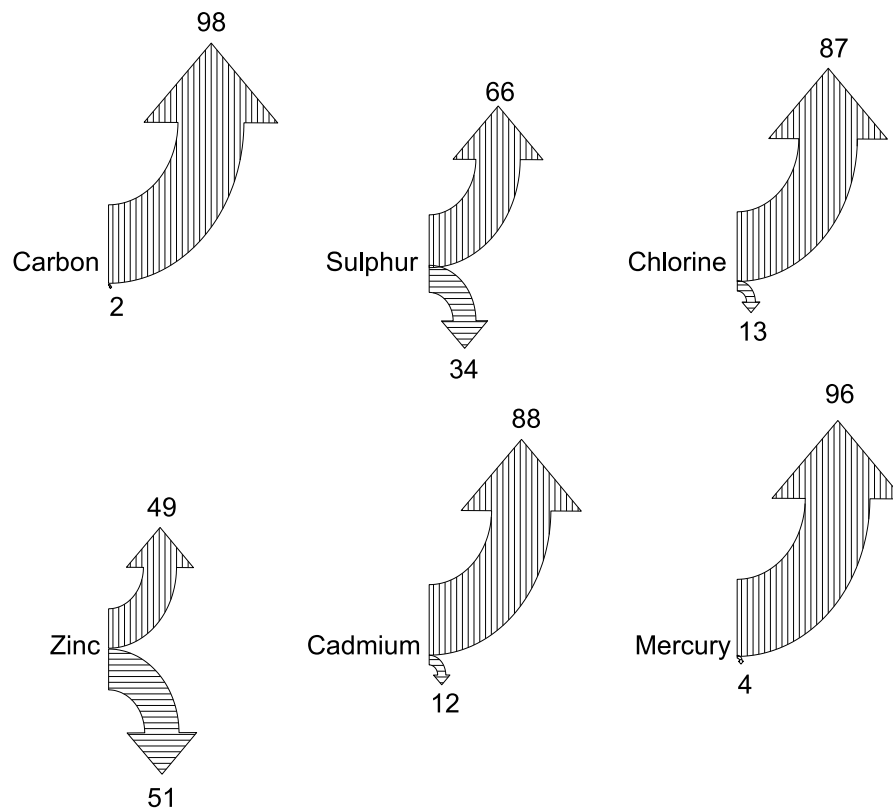


Figure 2.7: Material process flow ‘Sankey’ diagram to indicate flow of selected elements through an MSW combustor. Upward flow ($\Uparrow$) represents gaseous emissions including fly ash material and downward flow ($\Downarrow$) represents bottom ash. Adapted from Brunner & Mönch (1986)

in the fuel to form gaseous phase metal dichlorides (Manninen *et al.*, 1996). This occurs at temperatures between 600–900 °C and is therefore of relevance for a fluidised bed combustor.

The use of limestone to control sulphur dioxide emissions within a fluidised bed combustor has been shown to be a cause of increased metals emissions in the flue gas. Lead, cadmium and manganese were reported to show the largest increase, by a factor of 4–600 % compared to absence of limestone (Clarke, 1993). The mechanism is attributed to higher transport of particulate solids into the flue gas ('loading'), which was observed also and is most likely to be due to the higher friability of limestone compared to silica sand which is the usual fluidised bed material. To a lesser extent, limestones themselves contain metal carbonates, commonly of manganese, zinc and lead.

As well as the effects of chlorides as described in § 2.7.4, the behaviour of metals are also altered. Organic chlorides such as those prevalent in poly-vinyl chloride plastics has been observed to increase the proportion of metals (chromium, copper, cadmium, zinc) in the fly ash, whilst bottom ash metal content decreases (Wang *et al.*, 1999). In the absence of chlorine, metal oxides were formed in preference which condensed into the bottom ash; suggesting that removal of chlorine from the fuel supply will avoid gaseous emissions of metals pollutants.

2.7.6 Gaseous organic pollutants

The fuel mixtures investigated by Raini & Martti (1996) — RDF and wood chip — are most similar to this research project. For fuel mixtures ranging from 15–45 % RDF with wood chips, emissions of nitrogen oxides, sulphur dioxide, PCDD and PCDF compounds found to be were at levels within European Union limits (Figure 2.8). The limits for emissions of nitrogen and sulphur oxides within the EU are dependant upon power plant capacity, ranging from 400 mg N m⁻³ for nitrogen oxides and 850 mg N m⁻³ for sulphur dioxide, with reference to 50–100 MW_{th} plants co-incinerating waste in accordance with European Directive 2006/76/EC on incineration of waste (European Parliament,

Table 2.9: Flue gases concentrations (Raini & Martti, 1996)

Test/concentration	Test1	Test2	Test3	Test4	Test5	Test6	Test7	Test8
Flue gas temperature °C	112	123	124	127	137	130	105	140
O ₂ concentration %	4.84	4.69	5.29	5.52	5.23	5.70	6.09	5.40
CO ₂ concentration %	15.26	15.13	14.60	14.38	14.30	13.76	13.46	13.73
CO concentration mg N m ⁻³ , 11 % O ₂	1004	1379	1192	1615	951	2040	1675	1122
C ₂ H ₂ concentration mg N m ⁻³ , 11 % O ₂	1.67	1.86	1.32	2.60	3.99	2.09	9.38	3.41
NO ₂ concentration mg N m ⁻³ , 11 % O ₂	117	155	182	208	374	367	313	356
SO ₂ concentration mg N m ⁻³ , 11 % O ₂	9.0	26.5	41	76	273	239	259	285
Particles mg N m ⁻³ , 11 % O ₂ , dry gas	2.3	8.9	6.8	13.2	16.5	14.6	48	208
Heat input MW	3.6	3.5	3.5	3.5	4.3	3.4	2.6	4.8

2000). It should be noted that for the commercially active power system capacity used in this aforementioned study, these legislative emission limits are not applicable (European Parliament, 2000). This “capacity output” dependant emission limit is not provided for emissions of PCDD and PCDF compounds; a single limit of 0.1 ng Nm^{-3} is imposed. As can be seen in Figure 2.8, gaseous emissions of PCDD/F congeners are within statutory limits but emissions from fly ash material do breach the limit, for a fuel mixture of 85 % wood 15 % RDF. Combustion was considered to be difficult, because the presence of ex-

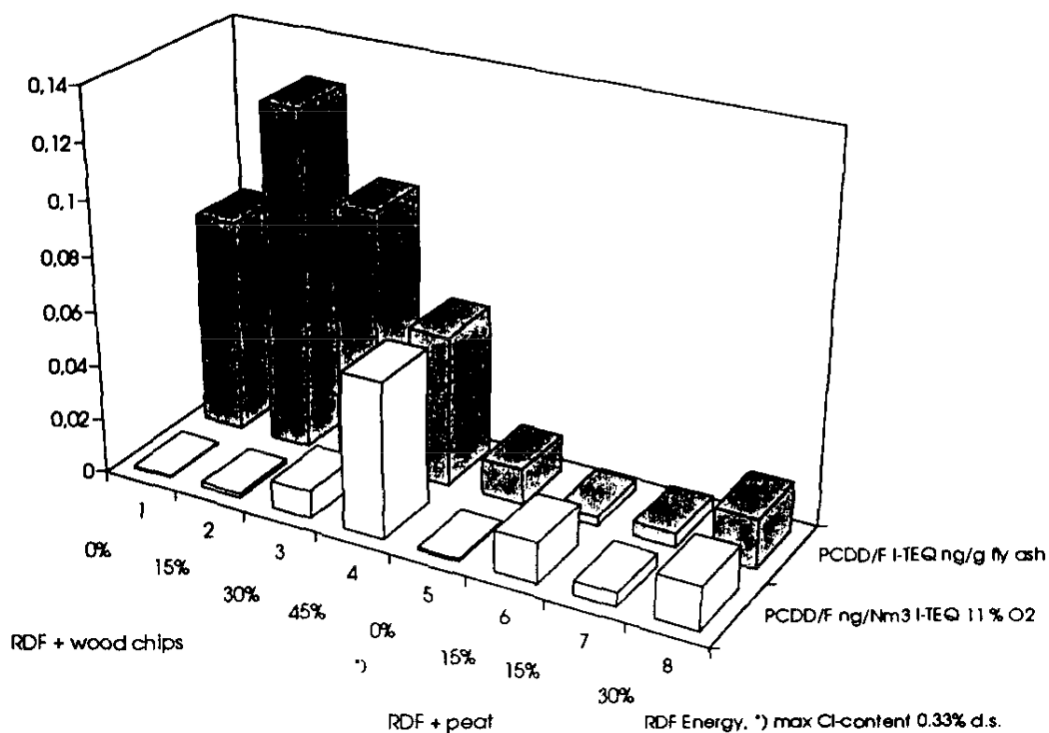


Figure 2.8: Emissions of PCDD and PCDF compounds (Raini & Martti, 1996)

cessive metals and physically obtrusive plastics prevented effective combustion, indicated by occasionally high carbon monoxide formation.

Another study (Hedman *et al.*, 2005) suggested that RDF may be more efficiently used for combustion than recycling, when the MSW is created in regions of low population density and consequently making transportation costs excessive. Main areas of interest are the (calorific) quality of the sorted waste (Table 2.10), combustion efficiency with biomass (reed canary grass) and the

extent of pollutant emissions. Emissions of the major flue gases, carbon, nitrogen and sulphur dioxides as shown in Table 2.11 were all indicative of efficient combustion. Dioxin emissions were significantly below the legal limits for some fuel mixtures of reed canary grass and RDF, although in the majority of analyses levels of specific PCDD/F congeners were above emissions limits.

Table 2.10: Waste fractions (Hedman *et al.*, 2005)

Material categories	%	Ash (%)	Cl (%)	Contribution to total Cl (%)
Uncoated paper	50	2.2	0.002	1.1
Coated paper	23	28	0.03	7.5
Paper packages ^a	13	6.5	0.03	3.4
Soft plastics	2.8	2.1	0.72	20
Hard plastics	1.7	6.4	3.4	58
Textile, leather	5.6	1.1	0.07	3.9
Wood	0.2	1.3	0.04	0.1
Remaining combustibles ^b	1.9	15	0.32	6.2
Glass, mineral	1.4	—	—	—
Metal	0.3	—	—	—

^a Incl. composite materials of paper and plastics/aluminum foil.

^b Incl. tissue paper.

Practical measures are outlined in one study (Obernberger *et al.*, 2006), that could be taken to minimise formation of PCDD and PCDF compounds. Such measures include ensuring complete combustion (whilst maintaining minimum excess air) of the fuel to avoid the flow of unburnt fuel particles in the freeboard zone. Activated carbon may be used as a secondary method of inhibition of these pollutants, applied to the flue gas flow.

2.8 Toxicity of PCDD and PCDF compounds

The term *dioxin* refers specifically to the compound 2,3,7,8-tetrachlorodibenzo-p-dioxin. Due to isomeric structural variation (based upon generic structures shown in Figure 2.9), there are 75 possible PCDD compounds and 135 PCDF compounds that may exist (Hester & Harrison, 1996). For a given mixture of these compounds — or congeners — there is a variation in chemical characteristics and as a consequence toxicities. Specific structural characteristics of each congener determines directly the relative extent of toxicity. One example of this observation is the position and degree of halogen substitution.

Table 2.11: Emissions of pollutants and elemental analysis (Hedman *et al.*, 2005)

Emissions from first run of full-scale combustion, including elemental analysis of dust (fly-ash particles after cyclone) and analysis of bottom ash and fly ash from cyclone

Parameter	Unit	Percent of RDF mixed with reed canary-grass					
		0% RDF		21% RDF		36% RDF	
<i>Flue-gas</i>							
O ₂	%	9.4	n.a.	8.4	8.9	9.1	9.5
CO ₂	%	11	n.a.	11	10	11	11
CO	mg/m _n ³	0.3	n.a.	1.7	0.6	1.6	0.2
NO	g/m _n ³	0.15	n.a.	0.17	0.16	0.16	0.15
NO ₂	mg/m _n ³	0.06	n.a.	n.a.	n.a.	n.a.	n.a.
NO _x	g/m _n ³	0.15	n.a.	0.17	0.16	0.16	0.16
SO ₂	mg/m _n ³	56	n.a.	0	0.01	62	56
TCDD-eq(1-TEQ)	ng/m _n ³	0.07	0.03	0.06	0.03	0.12	0.09
PCDD+PCDF	ng/m _n ³	3.5	1.9	4.6	1.9	9.5	7.0
PCDF/PCDD		1.7	0.9	1.9	0.7	0.9	0.7
HCl	mg/m _n ³	68		99		77	
HF	mg/m _n ³	0.69		1.8		2.0	
Dust	mg/m _n ³	54		42		47	
As	µg/m _n ³	3.0		4.4		6.9	
Cd	µg/m _n ³	3.4		11		20	
Cr	µg/m _n ³	10		11		15	
Cu	µg/m _n ³	48		133		244	
Mn	µg/m _n ³	98		27		23	
Ni	µg/m _n ³	4.3		4.6		3.6	
Pb	µg/m _n ³	78		167		221	
Zn	mg/m _n ³	1.6		3.2		3.6	
<i>Bottom-ash</i>							
Moisture content	%	0.2		0.2		0.1	
Unburned	% of DM	5.6		4.8		1.3	
Cl	% of DM	0.03		0.05		0.05	
Si	% of DM	35		46		30	
Al	% of DM	0.84		3.2		5.2	
Ca	% of DM	2.0		4.0		5.6	
Fe	% of DM	1.5		0.8		1.5	
K	% of DM	3.4		2.5		2.2	
Mg	% of DM	1.2		1.0		1.2	
Mn	% of DM	0.43		0.24		0.22	
Na	% of DM	0.25		0.35		0.48	
P	% of DM	1.6		1.0		0.9	
As	mg/kg DM	<11		4.9		4.8	
Cd	mg/kg DM	<0.4		0.2		<0.1	
Cr	mg/kg DM	81		51		148	
Cu	g/kg DM	0.45		1.5		0.39	
Hg	mg/kg DM	<0.1		<0.1		<0.1	
Pb	mg/kg DM	10		16		11	
Zn	g/kg DM	0.39		0.48		0.30	
<i>Fly-ash (cyclone)</i>							
Moisture content	%	76		73		51	
Unburned	% of DM	14		9.0		10	
Cl	% of DM	0.82		1.1		0.36	

The 10 rows at the top show values from duplicate sampling of dioxins and arithmetic mean values (geometric mean values for CO) of corresponding continuous measuring of inorganic gases.
n.a., not analysed due to instrument malfunction.

There is a very wide range of toxicity sensitivities amongst mammals; guinea

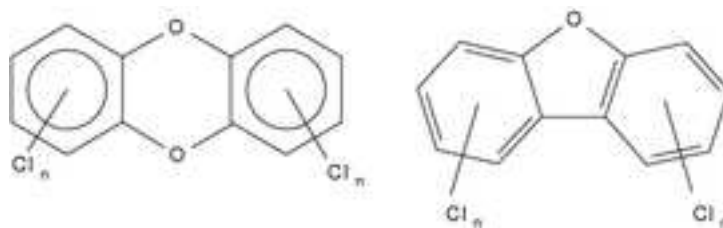


Figure 2.9: Dioxin & Furan generic molecular structures

pigs are most sensitive ($\text{LD}_{50}=1\text{ }\mu\text{g kg}^{-1}$) whilst hamsters are least sensitive ($\text{LD}_{50}=5000\text{ }\mu\text{g kg}^{-1}$, Poland & Knutson (1982) cited in Hester & Harrison (1996)), where “ LD_{50} ” is a formal measure of acute toxicity in terms of the Lethal Dose required to kill 50% of the sample population. The effects of toxic exposure of dioxins to animals are numerous, including: oedema; hyperkeratosis (skin lesions); endocrine dysfunction; for humans, the most well documented effect being chloracne.

Toxicity of PCDD and PCDF congeners are said to be achieved by causing changes in gene expression that control cellular differentiation and growth. These changes are made via chemical binding between the polyaromatic structure of the dioxin congeners and the aromatic hydrocarbon component of the (genetic protein) receptor (Hung *et al.*, 1996). Thus variation in toxicity may be attributed to the myriad of possible interactions between isomerically different PCDD and PCDF congeners, with genes of numerous animal species. As well as mammalian species being susceptible to dioxin poisoning, other animals that are dioxin sensitive include birds, fish and marine mammals (whales, seals). Recent research into the effects of dioxins upon a wider range of animals has resulted in a revision in assessing dioxins’ toxicities.

Evaluating the risk of exposure to PCDD and PCDF congeners is complicated by the dynamic nature of mixtures of these compounds; the chemical and physical characteristics have widely differing impacts. Toxic equivalent factors (TEF) are a measure of the relative risk of exposure to each congener, relative to the toxicity of the most toxic congener 2,3,7,8-tetrachlorodibenzo-p-dioxin.

A database of such toxicities calculated on the basis of TEF values has been published and submitted to the World Health Organisation (den Berg *et al.*, 1998).

2.9 Biological impact of trace metals

Trace metals — or more generally, trace elements — may be considered as those elements (65 in total) excluding macroelements, group 18 (inert, or noble gases) elements and radioactive elements. Macroelements, deemed essential to planetary life are generally accepted as those that exist within organisms at levels greater than 0.1 % concentration (Markert, 1994), these being: *a)* hydrogen, *b)* oxygen *c)* carbon, *d)* nitrogen, *e)* phosphorus, *f)* sulphur, *g)* chlorine, *h)* potassium, *i)* sodium, *j)* calcium, *k)* magnesium. Trace elements may also be classified by physiological impact. The definition of what constitutes a trace element is not clear; one author has suggested that classification of “generally essential” and “partially essential” elements as being arbitrary (Table 2.12, Markert (1994)). Other authors have made a more strict classification, based upon existing knowledge of those elements found to be essential. There are eight elements known currently to be essential to all plant life (Table 2.13), in that these elements: “...cannot be substituted by others [elements] for their specific biochemical roles...so that it [organisms] can neither grow nor complete some metabolic cycle.” (Kabata-Pendias & Pendias, 2001). Furthermore there are an additional nine elements that await new evidence confirming their essential status, either being essential only to some plant species or because the required concentration is very low ($\mu\text{g kg}^{-1}$ – ng kg^{-1}): *a)* Aluminium, *b)* Arsenic, *c)* Bromine, *d)* Fluorine, *e)* Iodine, *f)* Lithium, *g)* Nickel, *h)* Rubidium, *i)* Selenium, *j)* Strontium, *k)* Titanium, *l)* Vanadium.

Trace elements are involved in various biochemical processes including: respiration; photosynthesis; catalysis activation (via enzymes). If the supply of trace elements is interrupted, plant growth becomes abnormal and stunted. Conversely, plants are also susceptible to damage caused by excessive concentrations of trace metals. Individual elements may have particular impacts on

Table 2.12: Trace element arbitrary classification adapted from Markert (1994)

Generally essential	Partially essential
Boron	Arsenic
Cobalt	Chromium
Copper	Fluorine
Iodine	Lithium
Iron	Lead
Manganese	Selenium
Molybdenum	Silicon
Nickel	Tin
Zinc	Vanadium

Table 2.13: Trace elements known to be essential to plant life, adapted from (Kabata-Pendias & Pendias, 2001)

Boron	Manganese
Cobalt	Molybdenum
Copper	Silicon
Iron	Zinc

Table 2.14: Trace elements known to be essential to animal and human life (Haines, 2000)

Arsenic	Iron	Selenium
Cobalt	Iodine	Silicon
Chromium	Manganese	Strontium
Copper	Molybdenum	Vanadium
Fluorine	Nickel	Zinc

specific plants. For example nickel is involved in the metabolism governing nitrogen transport and is among the most toxic metals (such as mercury and lead) when in excess. Excessive concentration causes inhibited plant growth and stunted root development; cereal crops have a known sensitivity to excessive levels of nickel in the environment (Kabata-Pendias & Pendias, 2001). In general, plants are more tolerant of excessive concentrations of trace metals than deficiencies.

Animal (including human) organisms also have essential needs for trace elements (Table 2.14). For example chromium is necessary for insulin activity and thus is involved in metabolism of carbohydrates, lipids, proteins. Deficiency in chromium has been found to exhibit glucose intolerance and abnormal nitrogen metabolism; toxic exposure may result in anaemia, kidney damage, liver failure (FSA, 2003). A limited number of elements are classed as being non-essential due to a lack of evidence, even though they exist in body tissue (Boron, Lithium, Germanium, Rubenium, Strontium). However, cadmium, mercury and zinc are known to be toxic, attributed to their physiological effects even at low levels. Typical effects upon human health include: impaired mental activity; insomnia; headaches; renal damage; impaired haemesynthesis (Haines, 2000).

2.10 Chemical analyses of pollutants

Measuring the levels of pollutants emitted by an energy power plant is an essential legislative requirement in some geographic jurisdictions (European Parliament, 2000). Emission limits are explicitly stated as a legal means of promoting the safe operation of power plants and minimising environmental impact. As a result of low emission limits imposed, instrumentation must be accurate and sensitive to detect these chemical pollutants, often at levels of 10–0.1 mg kg⁻¹ and below. In general, either chromatography or spectroscopy are the instrumental methods used for environmental pollution analysis; they provide both qualitative and quantitative information, to a high accuracy and speed at reasonable cost. Such analytical techniques demand careful sample

preparation: *a)* concentration of the sample; *b)* minimisation/elimination of interferences; *c)* conversion of the sample into a form suited to the instrument (e.g. formation of an aqueous solution). The choice of instrumentation is most obviously determined to a large extent by the characteristics of the analyte(s) of interest; additional factors to consider are the expected concentration of the analytes, the number of analyses, the time to perform analysis, the cost of analysis. Specialist sample collection methods are required for PCDD, PCDF and PCB compounds. Assessing the risk of exposure to these pollutants is achieved using toxic equivalency factors. This TEF is a simplified measure, due to the common existence of these compounds in the environment as complex mixtures (Younes, 1995). To calculate mass concentrations, TEFs are used with individual compounds which are then used (as a sum of each TEF for each PCDD/F congeners) to compare actual emissions with the emission limit. From the relevant EU directive (European Parliament, 2000), the dioxin and furan emission limit is set at 0.1 ng m^{-3} , for a stated sample measurement period of between 6–8 hours. There are various sample collection procedures that may be deployed, in accordance with various geographic jurisdictions in USA (EPA, 1991) and United Kingdom (British Standards, 2006b). These regulatory controls exist to standardise the method of sample collection and analysis. The techniques stipulated are generally characterised as being cumbersome and laborious; the method described in this section offers significant advantages in speed, simplicity and as a consequence costs. For PCDD and PCDF congeners, GC-MS is the instrument of choice for analytical chemists. Similarly, for trace heavy metals ICP-OES is a popular tool to employ. Prior to analysis using these apparatus, the chemicals of interest must first be obtained and isolated.

2.10.1 Infra-red absorption spectroscopy

Within the electromagnetic spectrum, infrared radiation is caused by the inherent vibrational energy of chemical bonds of a molecule (Stuart, 2004). The radiation of the electromagnetic spectrum is characterised by a number of parameters, one of which is the wavelength of radiation. Radiation wavelength is

often expressed in terms of *wavenumber*, defined as the number of wavelengths of radiation per centimetre. Wavelength unit of measurement is cm^{-1} and this is useful in that wavenumber (w) is proportional to energy, in accordance with Planck's equation (equation 2.35):

$$E = h\nu = \frac{hc}{\lambda} \quad (2.35)$$

E = energy

h = Planck's constant

ν = electromagnetic spectrum frequency

c = speed of light

λ = wavelength

Each chemical bond between certain atoms will absorb a specific frequency of infrared radiation and so the chemical structure of compound that absorbs infrared radiation can be determined. There is one important restriction upon infrared spectroscopy in that only hetero-atomic molecules can be measured. Atoms do not contain chemical bonds and therefore do not possess vibrational energy, whilst homo-nuclear diatomic molecules such as nitrogen are of symmetrical chemical bond structure which prevents absorption of infrared radiation. The infrared range of the electromagnetic spectrum is defined as $400\text{--}13\,000\text{ cm}^{-1}$. A special method of infrared absorption detection is FT-IR spectroscopy which analyses infrared absorption within the range of $400\text{--}4000\text{ cm}^{-1}$ (often termed 'mid-infrared radiation'. This type of FT-IR is advantageous in terms of high sensitivity and speed of analysis (Smith, 1996).

2.10.2 Optical emission spectroscopy

Emission spectroscopy is the analysis of the phenomenon of absorption and emission of electromagnetic radiation caused by the excitation of atoms (Atkins, 1994). A classic demonstration of this behaviour is the burning of a solution of a metallic salt in a bunsen burner; radiation is emitted within the visible spectrum and characteristic colours are emitted depending on the metal concerned. For example sodium emits a yellow colour when burned, hence exploited in the

form of street illumination. Inductively coupled plasma atomic emission spectrometry (ICP-AES, also known as inductively coupled plasma optical emission spectrometry) is a specialised variation of this analytical technique, applicable to this project as a method of determining metal content within a matrix such as ash. It is an advantageous system in that: *a)* a wide range of detection, $0.1\text{--}1000\text{ }\mu\text{g ml}^{-1}$ is available; *b)* multi-elemental analysis is possible either in simultaneous or rapid sequential analysis mode; *c)* precision to 0.1–1% RSD (Mendham *et al.*, 2000). Although the limit of detection for ICP-OES is said to be three orders of magnitude less than that of the similar technique of inductively coupled plasma mass spectrometry, ICP-OES offers an advantage in being less susceptible to sample matrix interferences effects (de Hoffman & Stroobant, 2007). Samples are usually introduced to ICP-OES as a dilute aqueous solution, although some instruments are capable to create an aerosol from a solid sample for subsequent analysis using laser or electric spark ablation. Various methods may be used to create a suitable solution; for breakdown of complex organic compounds perchloric acid is a powerful oxidising agent, whilst nitric acid is appropriate for many other inorganic substances.

As far as ICP-OES is concerned, other techniques may also be used for sample preparation. The previously described method is an example “wet ash” method. Variations upon this particular method revolve around the choice of acid to perform oxidation and chemical breakdown. Perchloric acid, being a powerful oxidant, is appropriate for organic material such as plant tissue. It is dangerous to use on account of being potentially explosive, especially the condensed vapours of oxidation. Similarly for hydrofluoric acid which is useful for decomposition of silicates in samples; consequently, laboratory glassware (containers, fume cupboard windows, etc.) must not be used; specialist fume cupboards, free of glass, wood and ideally with isolated ventilation) are necessary for both hydrofluoric and perchloric acids (Radojević & Bashkin, 2006). Despite these safety concerns, these acids are used to determine *total* metal content for many environmental samples (plant tissue, sediment, soil) primarily because other acids are unable to decompose silicates and organic matter in their entirety. The use of powerful oxidising agents does not require the

use of auxillary equipment, however weaker acids are often used in combination with apparatus such as furnace ovens, microwave ovens or a hot water bath. With a furnace oven operating over a nine hour period and subsequent use of a nitric acid and hydrochloric acid mixture, “dry ash” formation may be achieved (Radojević & Bashkin, 2006). Similarly with microwave digestion, hydrochloric acid and hydrogen peroxide are added to the sample into a polytetrafluoroethene container, chosen to tolerate a pressurised environment. Pressurisation has the advantage of increasing digestion efficiency and in the microwave radiation chamber allows for faster decomposition such that microwave digestion can be achieved usually within sixty minutes.

2.10.3 Gas chromatography

Gas chromatography is a ubiquitous analytical chemistry technique, to separate a sample into chemical constituents. For determination of PCDD and PCDF compounds, gas chromatography — coupled with mass spectrometry to identify compounds in a gas chromatograph — is capable to detect to levels of $1\text{--}5\text{ }\mu\text{g kg}^{-1}$ in fly ash (Snyder, 2004). Further advantages of gas chromatography in addition to high sensitivity are: *a)* rapid analysis time usually in minutes; *b)* non-destructive, allowing further analysis such as mass spectrometry for component identification; *c)* highly accurate quantification with relative standard deviation 1–5%; *d)* low cost; *e)* simple to use and reliable (Miller, 1998).

One of the primary requirements for the condition of GC samples is that they must be volatile, to facilitate transfer to the GC capillary column. Sampling of PCDD and PCDF congeners from combustion flue gas sources is complicated by the observation that compounds often exist in both vapour and liquid forms, the latter as adsorbed onto substrates such as soot particles and other fine particulate matter formed during combustion. As such, a sampling method must be devised that is capable of both adsorption (of congeners in the vapour phase) and filtration (of the solid particles where PCDD and PCDF congeners have adhered). In the case of PCDD and PCDF compounds this can

be achieved by the thermal desorption sampling method the efficacy of which has been demonstrated (Stuart, 2003). The aforementioned compounds are trapped onto an adsorbent material by transporting flue gas through a tube containing the adsorbent(s). Moreover the sampling tube contains fine particle material to trap larger size particulate material containing the analytes. The PCDD and PCDF compounds are subjected to heat to desorb away from the adsorbent onto the GC column. This thermal desorption technique is the basis of an investigation in this PhD project into a method of analysing for the presence of dioxins and furans that have been performed (Whitworth *et al.*, 2002), an alternative to existing standard methods. The current regulatory-approved ‘method 23’ (EPA, 1991) is complex and very time consuming, requiring several days if not weeks to prepare laboratory apparatus, perform analysis and collect data for subsequent interpretation. This PhD project was an attempt to use this GC-MS thermal desorption technique, primarily due to the attraction of a claimed potential analysis time of as little as two hours (Whitworth *et al.*, 2002). The analytical technique is similar to methods applied in other studies, concerning measurement of airborne vinyl chloride (Hung *et al.*, 1996) and dioxins (Tsytisik *et al.*, 2008).

There are a wide range of adsorbents commercially available, which may be selected on the basis of selectivity for the target chemicals of interest. In the case of PCDD and PCDF compounds, suitable adsorbents would be activated carbon (Markert, 1994) and XAD-type (styrene divinylbenzene) porous polymer resins (Supelco, 2008). Adsorbents are classified according to physical characteristics such as surface area, particle and pore sizes. Thus, for example coconut-based activated carbon may be sold in terms of a specific surface area $800\text{--}1000\text{ m}^2\text{ g}^{-1}$ and mean particle size 20 nm (Markert, 1994).

European standards have been published to determine the mass concentration of PCDD and PCDF compounds. British standard EN 1948 (British Standards, 2006b) is the national implementation of this European standard and explains various methods to determine dioxin concentrations from combustion of organic matter, such as MSW combustors, to facilitate compliance with the EU directive governing waste incineration. The European standard has

stipulated three broad techniques that may be used: *a)* filter/condenser; *b)* dilution; *c)* cooled probe. Similarly, USA EPA method 23 (EPA, 1991) describes how dioxins and furans may be extracted from MSW combustors for subsequent laboratory analysis. In comparison to the aforementioned European standard, this USA standard stipulates only one particular method, that of heated filtration and cold condensation. Further restrictions include specified filter and condenser operating temperatures.

Chapter 3

Methodology

Apparent from the literature review was a scarcity of published methods for combustion of biomass combined with MRFR and therefore initial practical experiments were required to determine optimum combustion test conditions. The parameters to assess these optimum conditions are shown subsequently.

3.1 Fuels compositions

The following table (Table 3.1) shows the nominal compositions of the fuels that were tested and these data were used to plan experimental tests. With reference to DDGS in Table 3.1, data shown was extracted from analysis performed by the supplier of DDGS pellets (McGhee, 2008); data for miscanthus, wheat, willow, RDF with plastic extracted from the Phyllis database (van Doorn, 1999), samples identifications 1201, 2192, 1373, 1091 respectively. RDF (with plastic) was chosen as an equivalent to MRFR. Subsequent laboratory analysis of the fuels was performed at an independent laboratory (TES Bretby, Burton-on-Trent) using a series of certified laboratory test methods. The results of these laboratory tests are shown in Table 4.1.

Preparation of biomass was not necessary for DDGS (supplied via Mitsui Babcock, Renfrew), miscanthus (supplied with sodium hydroxide as binder, Sundown Products, Huntingdon) and wheat straw (Charles Jackson, Long Buckby) because these fuels were available in the form of regular sized pel-

lets, generally of dimensions 6–8 mm diameter, 20–30 mm length and readily suitable to be supplied to the fluidised bed combustor. Willow wood (Rural Generation, Londonderry) was available as chips and consequently care was taken to select manually wood pieces that did not contain long length branches, stems and similar matter which would likely cause blockages to the fuel feed system. A series of fuel mixtures was devised, for all combustion tests performed (Table 3.2).

As was expected, MSW was highly heterogenous and variable in composition, both heterogeneity and variability being affected by geographic location and seasonal time. For the purposes of this PhD research project to represent an example of non-recyclable residual MSW, a single source of MRFR was obtained from a local materials recycling facility which processes total waste volumes of 93 000 tonnes per annum. Seasonal variation occurs such that during the summer, volumes are at a minimum whilst peak volumes of processing are reached during the winter season (Cutts, 2007). One of the first practical tasks deemed necessary was the comminution of MRFR from the bulk material received initially. A laboratory scale cutting mill (model SM1, Retsch; Haan, Germany) was available to reduce the MRFR to an average particle size of 20 mm; considered necessary to facilitate effective combustion, minimise disturbance to the dynamics of the fluidised bed and promote satisfactory supply of fuel through the feeder system.

Table 3.1: Nominal compositions of analogous fuels used in experimental design of combustion tests. All values shown on “as received” basis.

	DDGS	Miscanthus	RDF	Wheat	Willow
Carbon	45.2	44.9	38	39	47
Hydrogen	6.2	5.4	6	5	5.6
Oxygen	34.1	40.3	31.6	34.5	41.9
Nitrogen	4.91	0.51	1.4	0.59	0.4
Sulphur	0.56	0.08	0.4	n/a	0.03
Chlorine	0.2	0.447	0.6	0.281	n/a
Fluorine	n/a	0.001	n/a	n/a	0.01
Ash	4.1	4.6	15	11.3	1.6
Moisture	4.9	4.4	7	9.4	3.5
Calorific value (gross, MJ kg ⁻¹)	19.3	18.2	18.4	15.3	18.9

Table 3.2: A table of the fuel mixtures of all combustion tests. Percentages values expressed by weight

Biomass component	Range of MRFR fractions in each test (%)				
DDGS	0	10	20	50	70
Wheat	0	10	20	50	70

3.2 Mass balance calculations

For the purposes of this research project, simple mass balance calculations were beneficial in advance of the combustion tests, to provide guidance of the anticipated gas emissions of major components and to preview experimental conditions such as the effects of air and fuel supply rates. Chemical composition of the fuel samples was not known prior to combustion test experiments and so approximations were used (Table 3.1) from data of similar fuels already published elsewhere in a ‘Phyllis’ database (van Doorn, 1999). An electronic spreadsheet was created and the type of data used within the ‘Phyllis’ database was “as received” data, for inclusion in the mass balance spreadsheet. Percentage weight values were then converted to mole values in the following procedure:

1. A single fuel type in the ‘Phyllis’ database was identified (e.g. RDF with plastic)
2. “As received” data (percentage weight) values were entered into an electronic spreadsheet
3. A fuel feed rate value was estimated and entered into the spreadsheet
4. Weight values were subsequently converted to mole values

This is evident in `massbalanceextract` which shows how the calculation was computed using a spreadsheet. The “formula bar” shows details of the calculation to convert “as received” percentage weight values to mole values. The cell reference ‘B\$126’ corresponds to a cell value where the fuel feed rate was entered. Since combustion tests most often consisted of a combination of biomass and waste fractions, the spreadsheet consisted of two arrays of compositional data, with a third array created to represent a total fuel composition (Table 3.4). The cell references ‘C6’ and ‘C48’ refer to the individual quantities of carbon for each of the two fuels that comprise the fuel mixture. Fuel feed rate values were obtained from each combustion test by summation of the total mass at the start, end and the total duration of each test. For each combustion

test, the following experimental measures were made during the course of each test:

- initial and final mass of fuel;
- duration of combustion test;
- air flow rates;
- air heater natural gas flow rate;
- extent of fluidisation (indicated by use of a micromanometer to monitor changes in pressure);
- combustor temperatures;
- flue gas composition;
- metal and organic gas sample total flue gas volume;
- collection of flue gas sample for subsequent laboratory analysis.

Table 3.3: An extract of the mass balance spreadsheet.

	A	B	C	D	E	F	G
1	pre-combustion composition fuel x			phyllis rdf plastic id 2192			
2			% wt	mol			
3	moisture	ar	7.00E+00	1.43E+01	mol h	2.85E+01	
4					mol o	1.43E+01	
5	ash	dry	1.50E+01				
6	c	ar	3.80E+01	1.16E+02			
7	h	ar	6.00E+00	2.18E+02	total including water	2.47E+02	
8	n	ar	1.40E+00	3.67E+00			
9	o	ar	3.16E+01	7.25E+01	total including water	8.67E+01	

	A	B	C	D	E	F	G
85	% fuel x	50 % fuel y		50			
86	total fuel mix compositions	% wt		mol			
87	moisture	ar	5.95E+00	1.21E+01	mol h	2.42E+01	
88					mol o	1.21E+01	
89	ash	dry	9.55E+00				
90	c	ar	4.16E+01	1.27E+02			
91	h	ar	6.10E+00	2.22E+02	total including water	246.35	
92	n	ar	3.16E+00	8.27E+00			
93	o	ar	3.29E+01	7.54E+01	total including water	87.47	

Table 3.4: An extract of the mass balance spreadsheet, showing computation of total fuel composition.

	A	B	C	D	E	F	G
85	% fuel x	50 % fuel y		50			
86	total fuel mix compositions	% wt		mol			
87	moisture	ar	5.95E+00	1.21E+01	mol h	2.42E+01	
88					mol o	1.21E+01	
89	ash	dry	9.55E+00				
90	c	ar	4.16E+01	1.27E+02			
91	h	ar	6.10E+00	2.22E+02	total including water	246.35	
92	n	ar	3.16E+00	8.27E+00			
93	o	ar	3.29E+01	7.54E+01	total including water	87.47	

3.3 Energy balance calculations

The mass balance spreadsheet was appended to include data to enable energy balance calculations to be made, ultimately to indicate whether a combustion test produces a total net increase in energy. Energy balances calculations are based upon the *principle of constant heat summation* otherwise known as Hess' Law:

$$\Delta H^0 = \sum(\Delta H_f^0(\text{products})) - \sum(\Delta H_f^0(\text{reactants}))$$

However, for complex fuels such as biomass and waste materials, obtaining enthalpies for these as reactants is not practicable and so the 'total enthalpy form' (Reklaitis, 1983) is more appropriate because enthalpies of elements can be used as an alternative. As a consequence, ultimate analytical data is required, to obtain elemental composition of the fuels. The following sequences demonstrates how the heat output of the combustion process is computed.

1. Enthalpies of formations of the elements are added to the mass balance spreadsheet, i.e.:

- Carbon (graphite), 0 kJ mol⁻¹
- H (g), 217.97
- O (g), 249.17
- N (g), 472.7
- S (g), 278.81
- Cl (g), 121.68

(Enthalpies data values from thermodynamic data tables (Atkins, 1994))

2. Molar heat capacities values are obtained for the combustion products
3. Total enthalpies are obtained for the corresponding molar flow rate of each element
4. Median combustion temperature (of the hot zone, fluidised bed sand, unit of measurement K) for the fuel is obtained

5. Total enthalpies are calculated using the molar flow rates declared in the mass balance spreadsheet
6. Heat output is calculated as the difference between total enthalpies values for products and reactants
7. Calculations were made with actual composition data obtained later of the fuels used and comparisons made with the spreadsheets (see § 5.1)

3.4 Fluidised bed combustion

Within the facilities available, the fluidised bed combustor system is most applicable to combustion of the fuels due to the advantages described previously (§ 2.5.1). The combustion zone is of cuboid shape, the sides being 300 mm length, height approximately 1600 mm and the composition of the internal walls is stainless steel type 310 (25 % by weight chromium). The fluidisation air distribution grid comprises nine vertical nozzles, each nozzle having 12 horizontal holes. The nozzles are arranged into three linear rows. This type of gas distribution grid has been described as a ‘nozzle standpipe’ style, considered to be recommended for most applications and capable of extended periods of operation (CSL, 2005b). Nozzles are created at the upper end of the pipes (Figure 3.4), to allow a volume *below* the nozzles to be static and consequently to form a thermal insulator for protection of the horizontal plate against thermal expansion. The physical dimensions of the fluidised bed combustion chamber are shown in subsequent diagrams (Figure 3.2–Figure 3.4).

The fuel feed is of Archimedes screw type, primarily tolerable of pelletised fuels and fuel chips less than 40 mm particle size. The nominal power input of this pilot-scale combustor is estimated at 50 kW, based upon supply of coal at a feed rate of up to 7 kg h⁻¹. Assessment of the efficiency of the combustor may be made in two ways: monitoring of carbon monoxide (to declare combustion efficiency); monitoring of flue gas oxygen content (indicative of the operational efficiency to use air as fuel oxidant). As such, low carbon monoxide emission was indicative of high combustion efficiency, in terms of complete combustion of

fuel. Operational efficiency is a useful measure of the quantity of air “wasted”; a high content of oxygen in the flue gas is indicative of excessive air being supplied to the combustor, i.e. energy is being wasted to heat excess air that is not required for combustion of the fuel.

The fluidised bed combustor chamber is itself part of a pilot-scale multi-fuel combustion system and is configured in series with a secondary combustion chamber designed to accept pulverised powder and fuels in liquid form (Figure 3.5 and Figure 3.6). The secondary combustion chamber is not used for this research project although the flue gas sampling location is positioned in this chamber, where flue gas is extracted for numerous analyses. A selection of gaseous emission measurements were conducted.

The general target control parameters for operation of the combustor were as follows: *a)* temperature 850 °C (to mimic the mandatory minimum temperature required for a combustor consuming MSW as a fuel); *b)* flue gas oxygen content < 10 % (to indicate operational efficiency); *c)* duration two hours (to obtain sufficient flue gas volume for measurement of gaseous pollutants). With respect to the target temperature, the European Directive on incineration of waste stipulates that the target temperature of 850 °C in a combustion chamber must be maintained for a minimum of two seconds, without any subsequent addition of combustion air (European Parliament, 2000). Temperature monitoring of the combustor was an essential requirement for operation of the fluidised bed combustor, for both operational safety and data interpretation reasons (e.g. Figure 4.3). A comprehensive review of the thermocouples installed was completed, to monitor various parts of the fluidised bed combustor (Figure 3.7). New data loggers (TC-08 thermocouple data logger, Pico Technology, Cambridge) and associated computer software were also installed and configured. Empirical data shown in Table 4.3 were recorded during operation of the combustor.

Prior to each combustion test, the fluidised bed combustor was prepared with new fluidised bed material and initial operation of the combustor occurred for approximately two hours in order to reach a minimum required temperature of 400–450 °C. At the start of each combustion test, a sufficiently

high temperature was attained initially using the biomass fraction only, e.g. wheat straw pellets were used to increase the temperature of the combustion chamber to a minimum of 450–500 °C before commencement of combustion of a wheat-MRFR fuel mixture. Failure of fluidisation within the combustor was an occasional occurrence during early combustion tests. Complete combustion data could not be obtained initially and was only possible during the second year of this project after installation and configuration of new monitoring equipment: thermocouples (Figure 3.7 and Table 3.5) and an FTIR gas analyser.

Initial use of precedent gas analyser equipment was generally unreliable. Data collection was constantly interrupted by the need to remove blockage of particulates to the flue gas flow into the gas analyser; the filter appeared excessively sensitive to particulate matter contained in the flue gas, evident in Figure 3.1. This behaviour did not occur after installation of the new gas analyser. Data manipulation was required to convert the data from the initial gas analyser (ADC MGA-3000) for measurement of carbon dioxide and oxygen. This analyser did measure carbon monoxide and sulphur dioxide but precise details of how to convert the data (recorded in units of millivolts) were not provided by the equipment manufacturer and therefore are not reported in this project.

The normal composition of fluidised bed material used in the fluidised bed combustor comprised silica sand (97% quartz, remainder tridymite, cristobalite; particle size 1–2 mm; Garside Sands, Leighton Buzzard UK) but due to expectations that agglomeration would occur, limestone (39% calcium, particle size 5 mm; Tarmac, Buxton) was substituted into the fluidised bed material, as indicated in Table 4.2. The primary objective of varying the composition was to minimise agglomeration and hence extend operation of the combustor for maximum collection of operational data. Where agglomeration did occur to an extent that fluidisation failed and combustion tests were stopped, fluidised bed material samples were collected for SEM-EDX analysis. Fluidisation was observed using a pressure gauge micromanometer (model MDG FC001, Furness Controls, Burgess), where the change in pressure was recorded contin-

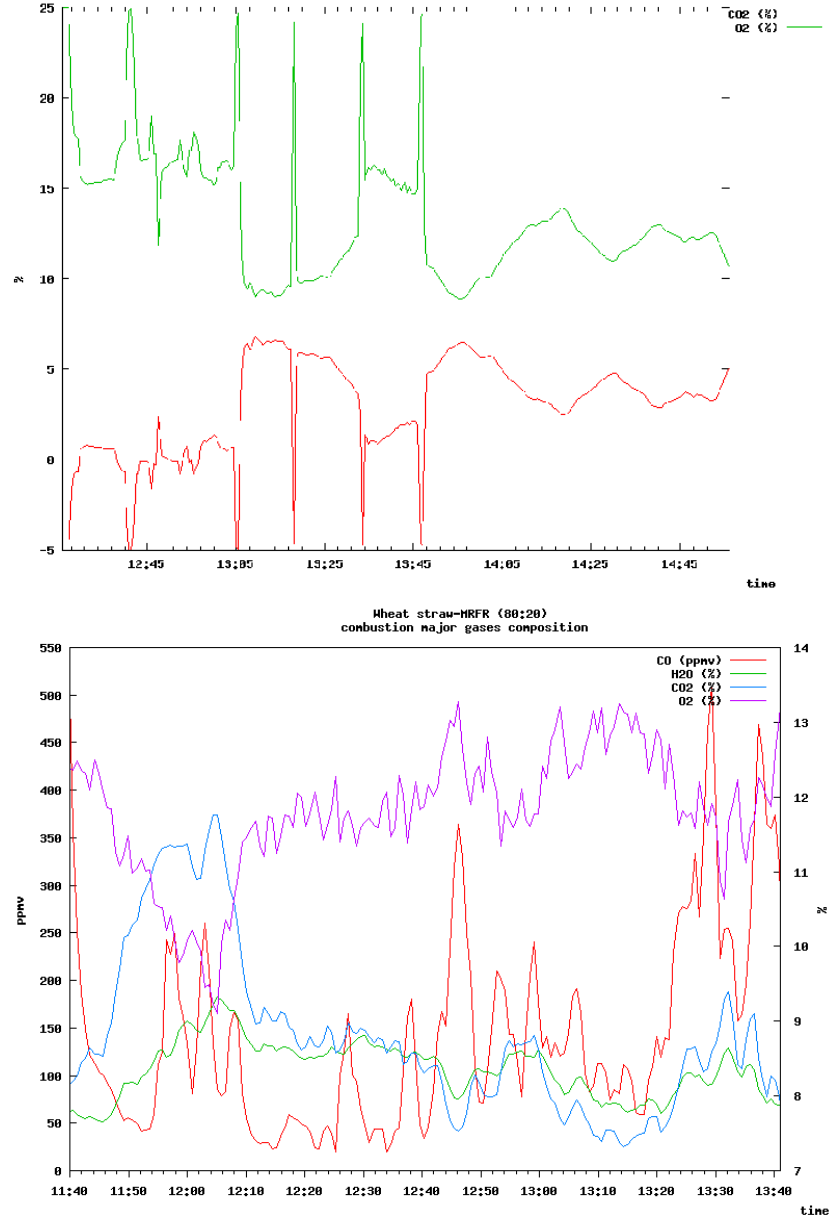


Figure 3.1: Comparison of flue gas measurement from gas analysers for combustion of wheat-MRFR (80:20). Preceding analyser (shown top) unable to measure water content and determination of CO content could not be confirmed.

uously in real-time, based upon monitoring the differential pressure caused by the dynamic motion of the fluidised bed particles to provide a measure of the agitation of the fluidised bed. The fluidised bed base (where air distribution nozzles are located) was packed with fluidised bed material and the initial mass of fluidised bed material was 22 kg, chosen by previous experience of technical personnel, but this was later revised to 25 kg.

Operations of power systems in the UK using waste as one of the primary energy sources are subject to compliance with European legislation governing waste incineration (European Parliament, 2000). The legislation demands control of various emissions of including:

Sulphur dioxide

Nitrogen oxides

Dioxins & Furans

Appendix A shows emission limits in more detail. It should be noted that some gases are not subjected to this legislation, but monitoring of such gases (e.g. carbon monoxide) is useful to assess efficient operation of the power plant.

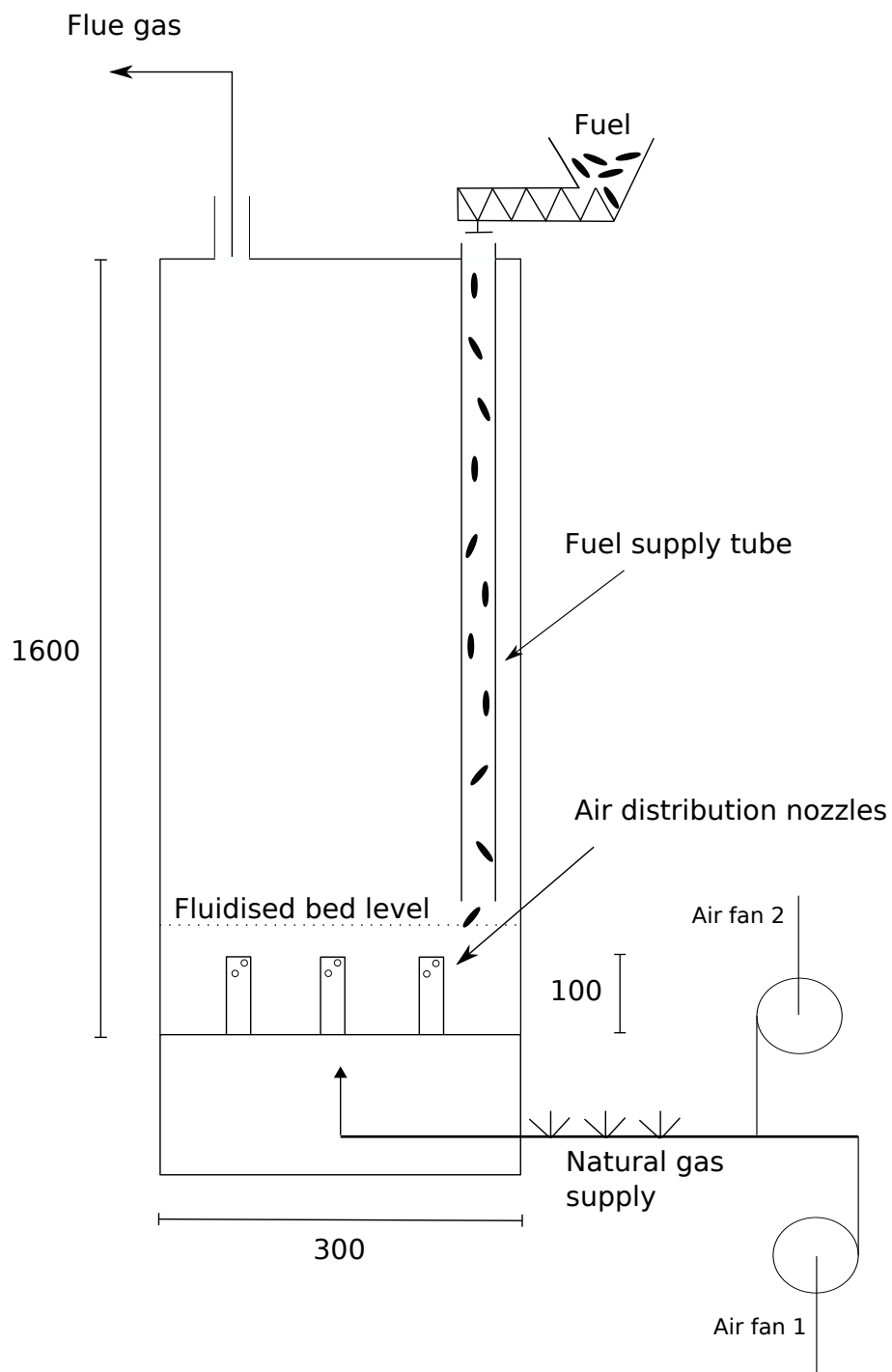


Figure 3.2: Schematic diagram of fluidised bed combustor. Unit of measurement, millimetre.

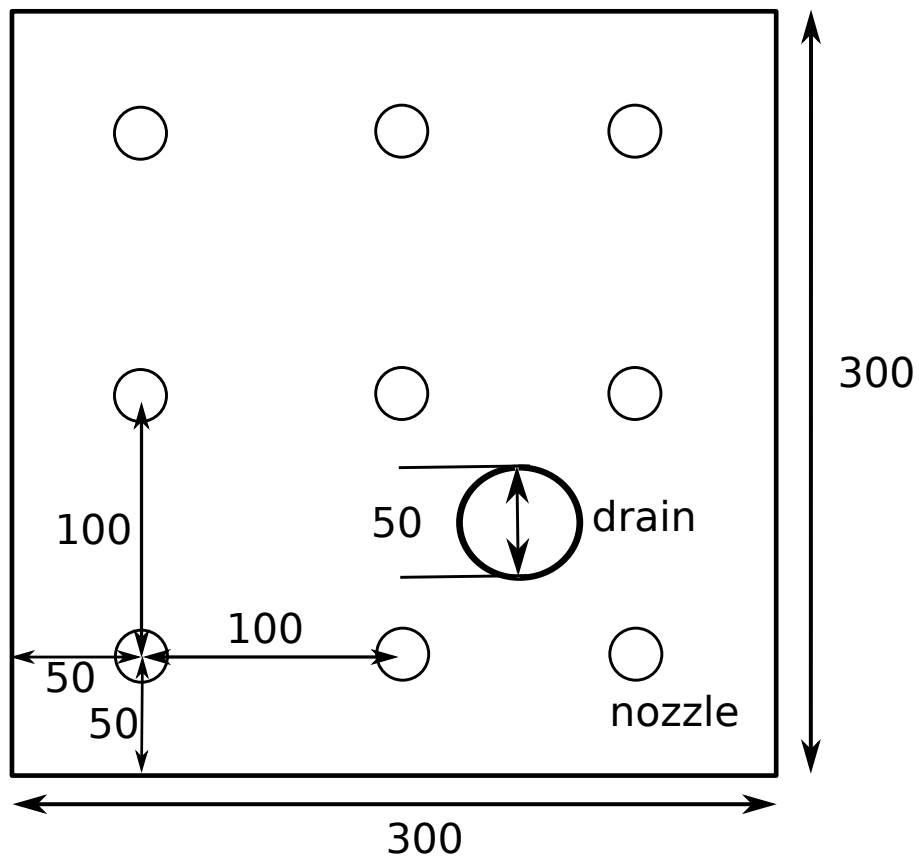


Figure 3.3: Fluidised bed base plan view. Unit of measurement, millimetre.

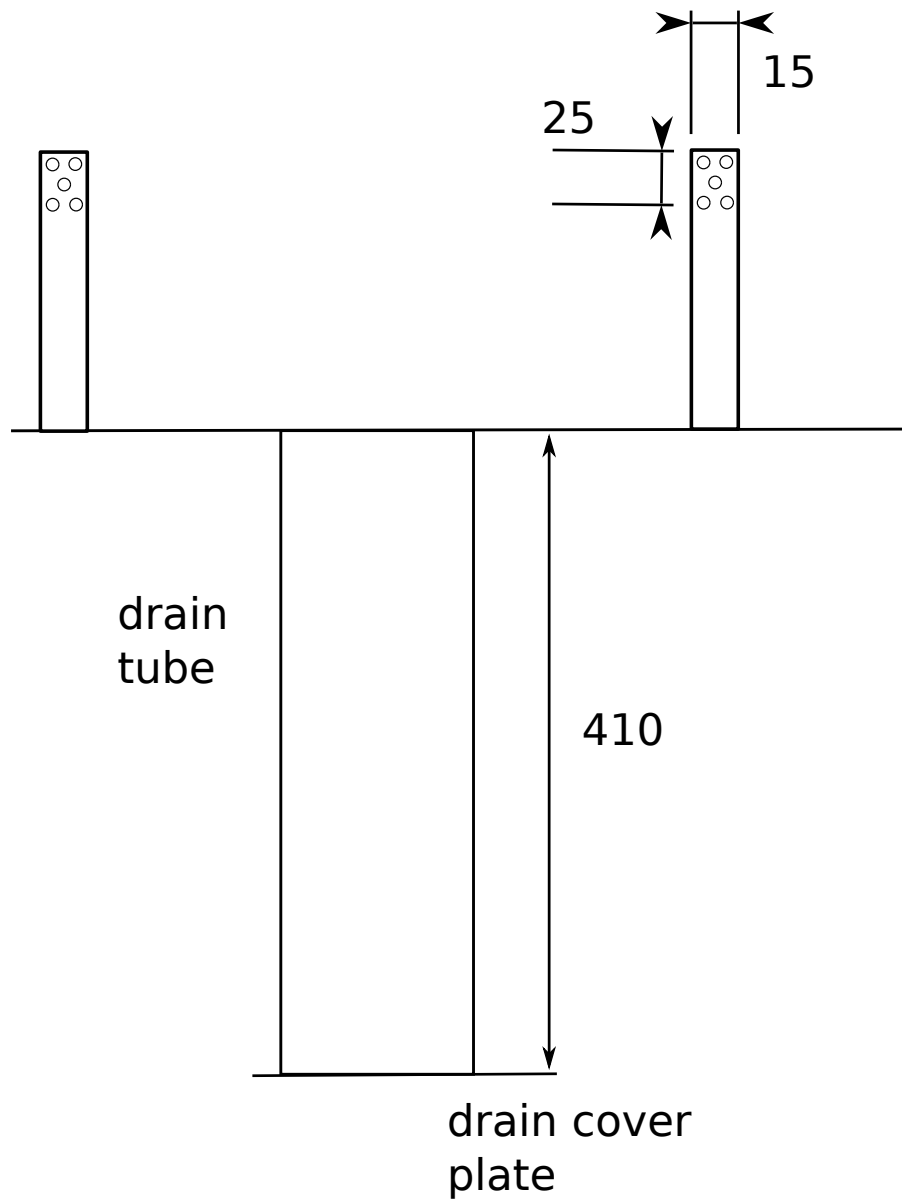


Figure 3.4: Fluidised bed base side view. Unit of measurement, millimetre.

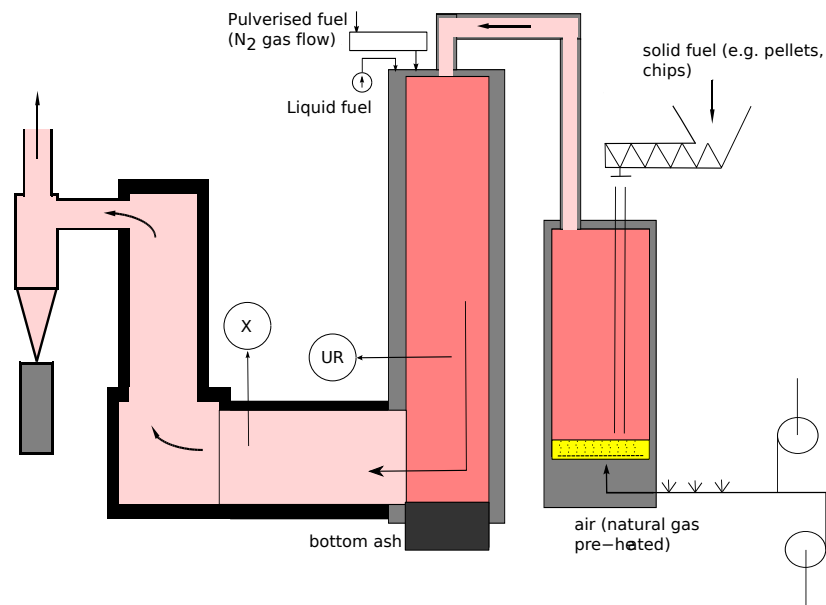


Figure 3.5: Multi-fuel combustor, including fluidised bed combustor. Flue gas analysis was performed during each combustion test (sampling point ‘UR’) and flue gas sample collection for subsequent chemical analysis (sampling point ‘X’).

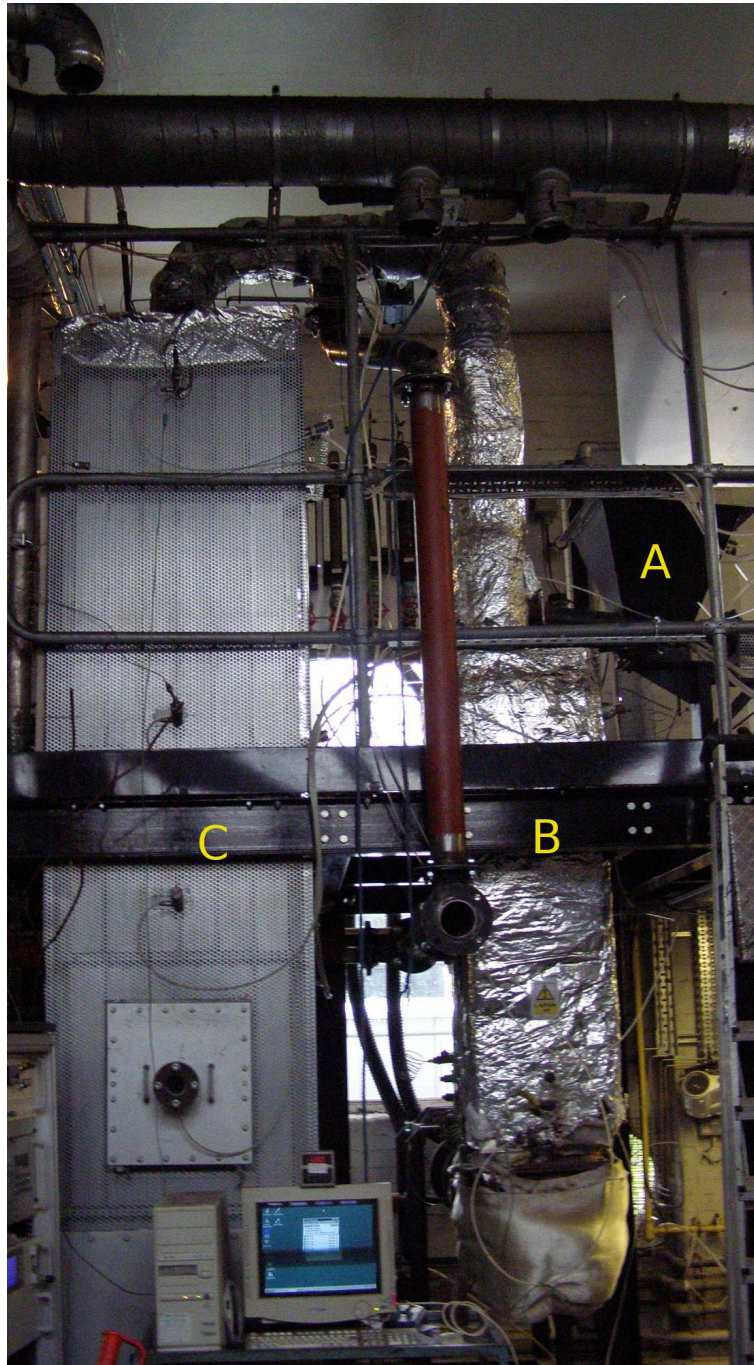


Figure 3.6: Photograph of multi-fuel combustor. The fuel hopper (A), fluidised bed combustor (B) and pulverised/liquid fuel combustion chamber (C) are shown for comparison with the preceding schematic diagram (Figure 3.5).

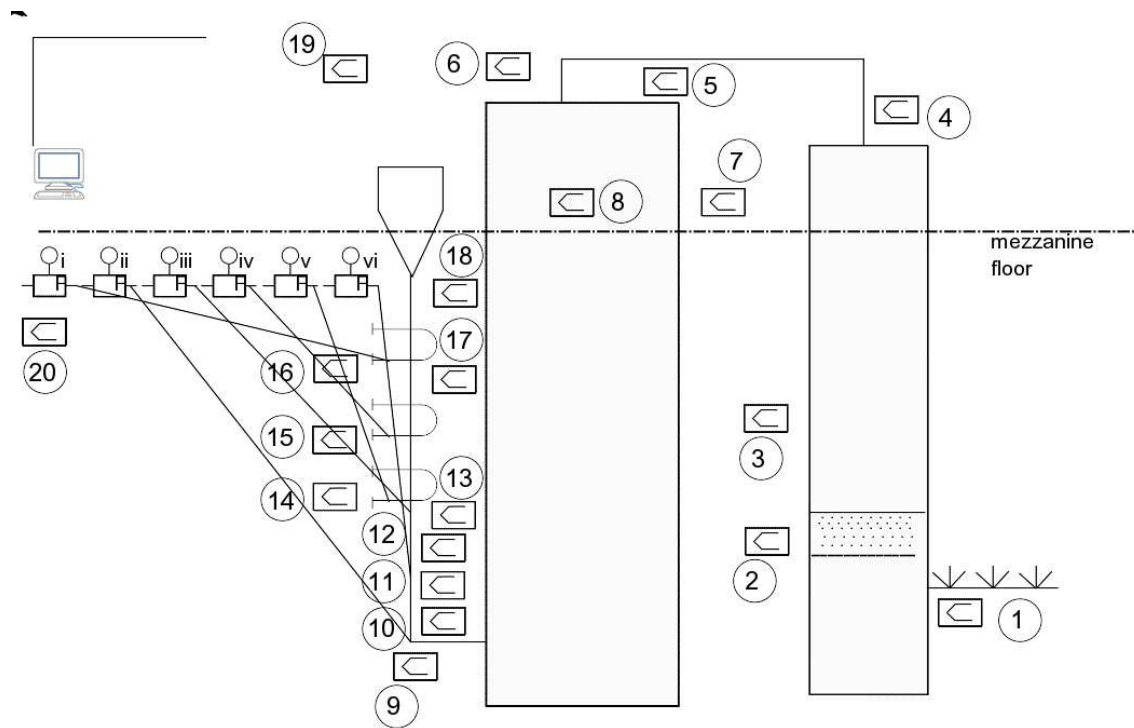


Figure 3.7: Schematic diagram of thermocouples (legend shown in Table 3.5)

Table 3.5: Legend for Figure 3.7

Legend:

Object number	Object name	Object number	Object name
1	Pre-heater gas	14	Hair pin 1
2	Fluidised bed (sand)	15	Hair pin 2 & 3
3	Fluidised bed (freeboard)	16	Hair pin 4 & 5
4	Fluidised bed (outlet)	17	Water cooled vertical
5	Gas combustor	18	Flue gas before cyclone
6	Gas fuel tube	19	TL2 ceramic
7	TL3 pyrotenox	20	Water cooler return
8	Gas temperature	i	Flowmeter hair pin 4
9	Water cooled corner	ii	Flowmeter water flow
10	Water flow (inlet)	iii	Flowmeter water cooled door
11	Water cooled corner	iv	Flowmeter hair pin 2 & 3
12	Water cooled flange	v	Flowmeter hair pin 1
13	Water cooled door	vi	Flowmeter water cooled corner

3.5 Chemical analysis

The pilot laboratory is fitted with appropriate data acquisition apparatus to enable immediate, or “real-time”, collection of data and hence dynamic observation of the process. The availability of continuous data compared to “snap-shot” data is advantageous in terms of a constant view of the process whenever changes occur. For example a classic test such as a titration gives information only at the time the test was conducted; changes to a process could occur between tests without being detected and information is averaged over time for the duration in which the sample was collected.

Trace-level pollutants such as transition metals and PCDD/F compounds are not produced during combustion at levels detectable instantaneously by existing analytical instrumentation and therefore continuous sample collection over a period of hours is necessary. European legislation exists for mandatory control of the emission of noxious pollutants; for dioxins, furans and metals, the relatively low levels of emissions demands sophisticated apparatus to be deployed. Traditional methods of chemical analysis for the detection of PCDD and PCDF compounds involve numerous laborious, time-consuming procedures. Congeners of PCDD/F pollutants are known to predominate in the flue gas adsorbed onto fly ash particles (Lindbauer *et al.*, 1992).

A “sampling train” is used to trap the compounds onto a suitable medium for subsequent solvent extraction, which must be performed for a minimum 12 hour period as a standard, validated method task (EPA, 1991). In contrast, a new method recently developed (Whitworth *et al.*, 2002) claims an analysis time of as little as two hours; seemingly based upon a type of “thermal desorption” gas chromatographic technique and this technique was the basis for devising apparatus to perform a similar method in this PhD project. Based upon these aforementioned methods, an alternative method was conceived to perform simultaneous collection of trace metals and gaseous organic pollutants emitted with the flue gas.

The principle of the apparatus was to act as a combined adsorption and filtration device to capture target analytes for direct instrumental analysis

without major sample analysis preparation involving solvent extraction. The apparatus, if successful, would have demonstrated a method of analysis that significantly reduces analysis time and solvent consumption and was devised to extract flue gas for organic compound and trace metal analysis, comprising ceramic tubing (pure alumina (Al_2O_3) AL23, Degussit, Hertford), glassware tubing and a pump to perform flue gas extraction. The glassware tube consisted of a GC inlet liner (SGE Europe, Milton Keynes) containing a range of adsorbent materials (all supplied from Sigma Aldrich, Poole): glass wool; activated carbon; and XAD-16 (a proprietary styrene divinylbenzene co-polymer). The glassware was intended to perform two functions; direct thermal desorption for subsequent GC-MS analysis, followed by analyte dissolution for ICP-OES analysis. A gas volume meter was utilised, to measure volumes of flue gas collected and to allow for subsequent calculation of flue gas component concentration levels. The standard method of gas sampling involves the use of an isokinetic extract of the flue gas (see Figure 3.9), but this requirement could not be met due to a lack of suitable pressure measurement devices.

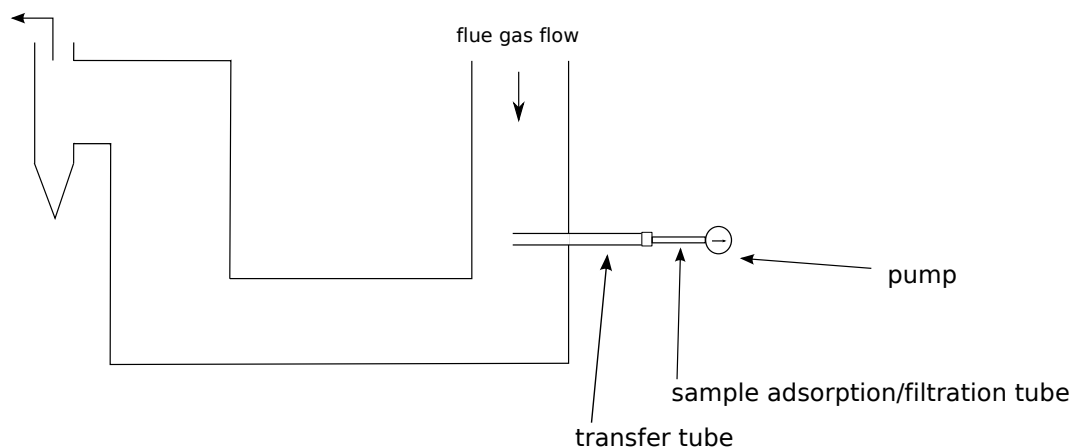


Figure 3.8: Schematic diagram of flue gas sample extraction system

3.5.1 FTIR

Major gaseous pollutant compounds are emitted in sufficient quantities to enable instantaneous, direct measurement using standard analytical equipment

such as an FTIR gas analyser. Flue gas analysis is able to monitor a range of analytes: *a)* carbon oxides; *b)* oxygen to determine combustion efficiency; *c)* nitrogen species; *d)* sulphur species to indicate potential pollution and corrosion. Nitrogen oxides and sulphur oxides are formed during combustion of fuels, and can cause photochemical smog and acid rain respectively; monitoring of these pollutant emissions is mandatory for operation of industrial scale generation of electricity and/or heat. As introduced in § 2.10.1, each component of the flue gas can be detected by the characteristic infrared radiation wavenumber of the chemical compound in the flue gas. A summary of analytes is shown in Table 3.6; vibrational motion is defined as molecular “stretching” along the axis of the chemical bond, whilst “deformation” indicates molecular bond motion transverse of the bond (Bellamy (1975) and Stuart (2004)).

Table 3.6: Characteristic infrared radiation wavenumbers of molecules.

Molecular bond vibration	Wavenumber (cm^{-1})
C=O	1690–1725
CN	1650
NO ₂	1610–1681
NH	3300–3400
acid halides (e.g. HCl)	1770–1815
OH (i.e. water)	3760
SO ₂ (deformation)	545–610
SO ₂	1151, 1361

3.5.2 ICP-OES

Heavy metals (defined as those with densities greater than 5 g cm^{-3} , Radojević & Bashkin (2006)), may be investigated using inductively coupled plasma optical emission spectrometry (ICP-OES). This technique allows simultaneous, multiple analyses of metals in samples, coupled with spectrometry for identifi-

cation. Whilst SEM-EDX is capable of quantitation to 0.1 % for agglomerated fluidised bed ash, significantly more accurate metal content of fly ash may be determined by ICP-OES. The inductively coupled plasma (ICP) is created by a fluctuating radiofrequency field, resulting in the ionisation of a hot gas (e.g. argon, or nitrogen) to produce ionised fluid (plasma) flame. An aqueous solution sample is injected into the plasma, where the high temperature conditions (5 000–10 000 K) cause aerosol formation and electronic excitation of atoms and potentially ions. Upon relaxation of these electrons to reach a more stable lower electronic state, characteristic visible radiation is emitted which is determined by the quantum energy levels between which electronic excitation occurred; the specific visible radiation is a manifestation of the original elements in the plasma. The wavelength of light radiation emitted corresponds to specific elements, to allow identification and total photon emission is directly proportional to analyte concentration. Light radiation is converted into electrical signals by a spectrometer and concentrations of elements in the analyte are computed by comparison with calibrated measurements of known reference element spectra. Optical emission spectroscopy coupled with ICP yields further information of isotopic composition of samples. Optical emission spectroscopy relies upon the need for ionised samples, which ICP conveniently provides, and then are subjected to a controlled magnetic field. Ionised compound fragments are detected as a function of the applied magnetic field. Commercial instruments are capable of detection of 20–30 elements within a few minutes and limits of detection for some elements may be as low as 1–10 ng l⁻¹ for elements such as cadmium, chromium and zinc (de Hoffman & Stroobant, 2007).

For this PhD research project a Varian ICP-OES instrument was used (model Vista-PRO, Varian UK, Oxford). The instrument was configured to analyse simultaneously a range of metal analytes with a horizontally orientated plasma torch generating a radio frequency field of 40 Hz. A library of reference spectra is referred to in the instrument software for each metal of interest, to produce output data of the sample. Samples were prepared from an aliquot of the fly ash, adsorption, and filtration media of the flue gas sample extraction apparatus followed by application of an acid digestion procedure originally suggested

for dissolution of metals in plant vegetation samples.

1. Sample aliquot transferred to a digestion flask such as a 50 mL Kjeldahl flask
2. Nitric acid concentrated (67–70 %) added (1 ml)
3. Sulphuric acid concentrated (98 %) added (1 ml)
4. Application of heat (e.g. using a hot plate) until vapour fumes appeared (less than 1 minute)
5. Solution filtered using filter paper and glass wool, into 100 ml volumetric flask and water added to volume mark

The practical tasks described above are a modification of suggested experimental methods (Radojević & Bashkin, 2006) and a consideration of the process of sample extraction in a validated method indicated by Figure 3.9.

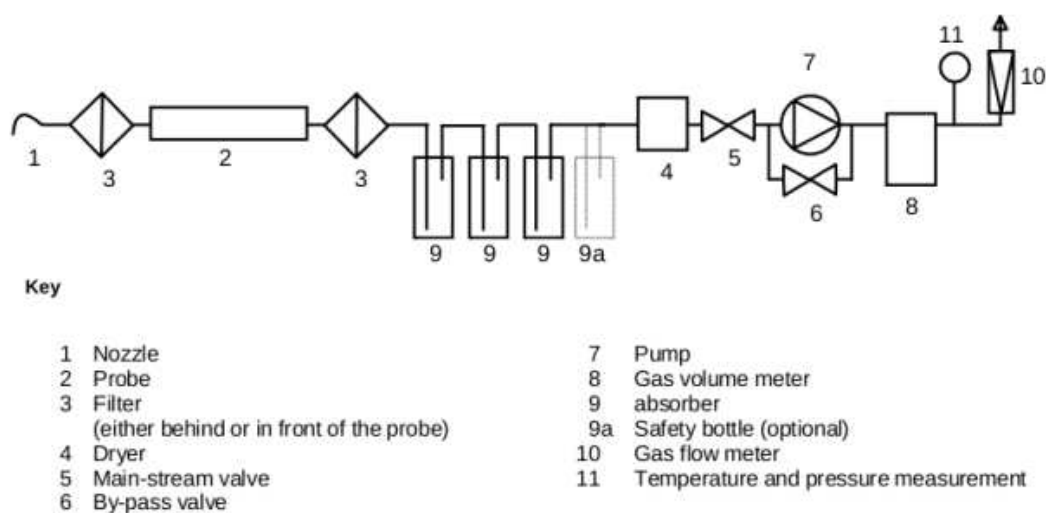


Figure 3.9: Single, main stream method for collection of metal analytes (extracted from (British Standards, 2004)).

3.5.3 GC-MS

Chromatography is a process of separating a substance into constituent compounds. Separation is achieved by specific interaction between a sample analyte, a solid phase and mobile phase; gas chromatography is defined by the use of a gas (commonly helium) as the mobile phase. In GC, samples (which must be volatile) are introduced into a tubular coiled column (typical dimensions 30 metres long, 0.25 mm internal diameter, made from fused capillary silica) using helium as the carrier mobile phase, where the internal surface of the column is coated with a stationary (either liquid or solid of typical film thickness 0.25 μm) polymer phase. The column is kept in a temperature controlled oven, where temperatures (0–400 $^{\circ}\text{C}$) are applied. Separation is achieved by partial equilibrium between the analyte compound, gas and stationary phases and differences in the relative vapour pressure of each compound. As the sample is carried by the gas phase through the column, the compounds exhibit different equilibrium coefficients and hence adhere to the stationary phase at different periods of time. In conjunction with mass spectrometry, each compound eluent can then be confirmed by isotopic mass determination. The mass spectrometer of a GC-MS system is the most popular device to use for identification of unknown compounds in complex mixtures (Powell, 2001).

For this research project, a low-resolution GC-MS was available for analysis of the combustion test samples (Autosystem XL GC coupled to Turbomass Gold MS; Perkin Elmer, Seer Green). A fused silica capillary column (BPX-5, length 30 metres, internal diameter 0.25 mm, stationary phase film thickness 0.25 μm ; SGE Europe, Milton Keynes) was used to perform the chromatographic separation. The instrument features a quadrupole mass analyser detector. The resolution of a mass spectrometer detector is a measure of the ability of the spectrometer to separate ions efficiently for accurate detection and may be calculated as follows (Powell, 2001):

$$R = \frac{m}{w_{5\%}} \quad m = \text{ion mass}$$
$$w_{5\%} = \text{width of mass peak at 5\% height}$$

It is on this basis that the quadrupole is classified as low-resolution (to unit mass for 1000 m/z) compared to other technology such as time-of-flight design which is high resolution and thus capable of determination of unknown analytes by confirmation of elemental composition (Masucci & Caldwell, 2004).

The original experimental design for measurement of PCCD/F congeners was utilisation of a thermal desorption type of GC-MS sample preparation technique. Although a chromatogram was produced, this technique was found to be not practical with the GC-MS used specifically. Temperature control of the injector port was not fully automated in terms of a rapid cooling facility, with the result that samples could not be analysed efficiently due to the time required to allow the injector port to cool to ambient temperature sufficiently low for manual handling, i.e. replacement of each sample inlet liner tube. In addition, there was a concern expressed by technical personnel of the risk of fouling of the injector port, to cause contamination of future analyses. As a consequence, the sample preparation technique was altered, to use a pressurised fluid extraction laboratory instrument (Accelerated Solvent Extractor model 200; Dionex UK, Camberley) to perform solid-liquid extraction of the analytes in the ash and adsorption media into a liquid solvent. This enabled faster analysis of a number of samples using the autosampler apparatus of the GC-MS.

The total-ion current (TIC) chromatogram (Figure 4.97) was the initial chromatogram produced by the GC-MS. It is a “general” type of chromatogram created by configuration of the mass detector to a “full-scan” mode where all molecular masses for a given mass range (typically 50–500 Da) are scanned by the mass detector continually during the chromatographic process. Therefore at any point in time during chromatographic elutions, the mass analyser will scan the mass range and record the relative intensity of detection of each mass value at that time. The sum of the intensities gives the *total ion* intensity which is then used to produce the total-ion current chromatogram. A mass chromatogram — also known as a selected ion chromatogram — is produced by measurement of the mass range scan for a single, specific ion. Thus, of the total-ion current (TIC) chromatogram previously mentioned, the

mass chromatogram for an ion of mass-charge ratio (m/z) 252 is subsequently shown (Figure 4.98). An assumption is made that ionisation of the gas chromatogram eluants prior to mass spectrometer analysis produces single-charge ions (Masucci & Caldwell, 2004) so that the m/z ratio is indicative of molecular mass. For example an m/z value of 252 was selected because it corresponds to the molecular mass for dichloro-dibenzo-p-dioxin. The molecular masses of a range of PCDD/F congeners was deduced as shown in Table 3.7 and used to obtain mass chromatograms from the GC-MS software (Turbomass; Perkin Elmer, Seer Green) based upon these molecular masses. For reference, mass chromatograms for standard fly ash are presented here (i.e. Figure 4.98 & Figure 4.100). The intensity of the total-ion current chromatogram (declared as 3×10^{10} in Figure 4.97) was compared to that of a mass chromatogram of interest (e.g. relative intensity of 3×10^9 in Figure 4.98) and it was interpreted that detection of a mass chromatogram of relative intensity fewer than two orders of magnitude than the TIC chromatogram constituted a significant eluant for subsequent mass spectrum investigation. Therefore the mass spectrum for the eluant mass chromatogram m/z 252 was obtained from the GC-MS software and compared to the corresponding mass spectrum in the NIST reference library to judge if the spectra were in any way similar (in this case, Figure 3.10). As a result of this process of investigation, it was concluded that since no mass chromatograms for the combustion test samples were of a sufficient relative intensity compared to the TIC chromatograms shown (e.g. Figure 4.105), no significant quantities of PCDD/F congeners was produced during any of the combustion tests.

As a result of the low resolution capability of the GC-MS available, only qualitative analysis of fly ash for PCDD/F congeners was anticipated to be possible. These compounds were isolated initially by the simplified apparatus described previously (Figure 3.8). A certified matrix reference material was obtained, to assess the ability of the method used in this project for detection of PCDD/F congeners. This matrix reference material was BCR-615 fly ash (Institute for Reference Materials and Measurements; Geel, Belgium) and certification provided with the material confirmed the quantities of *inter alia*

a range of compounds as shown in the following table (Table 3.8). A blank sample was created, such that the sample tubes comprised matrix material, adsorbent and filtration media but was not subjected to combustion flue gas exposure. The resultant chromatogram was subsequently produced using the GC-MS, to act as a reference for comparison with chromatograms of combustion test samples. Samples were not taken for combustion of biomass only (i.e. 100 % DDGS, 100 % wheat straw) because legislative monitoring of emissions of PCDD/F congeners is mandatory only for combustion of the waste fraction in a fuel. The GC-MS was configured with the following analytical method program:

- carrier gas, helium (1 ml min^{-1});
- injector port temperature , 330°C (15 minutes duration);
- splitless injection;
- column oven temperatures:
 - initial temperature 120°C , 1 minute duration;
 - temperature increase rate $20^\circ\text{C min}^{-1}$ to stage 1 temperature 200°C , 1 minute duration
 - temperature increase rate 2°C min^{-1} to stage 2 temperature 300°C , 20 minute duration
- mass spectrum analyser source temperature, 330°C ;
- ionisation mode, electrical ionisation;
- electron energy, $\pm 70 \text{ V}$.

A “library” of mass spectra data is stored within the GC-MS software system; the NIST/EPA/NIH Mass Spectral Library is produced by numerous mass spectrometrists within the respective USA government agencies National Institute of Standards and Technology, Environmental Protection Agency, National Institutes of Health. The library was searched from within the GC-MS to obtain

spectra of specific analytes — shown in Figure 3.10 and Figure 3.11 — from which comparisons could be made with spectra from combustion test analytes.

Table 3.7: Relative molecular masses (RMM) of PCDD/F congeners.

PCDD congener	RMM (g mol ⁻¹)	PCDF congener	RMM (g mol ⁻¹)
C ₁₂ O ₂ Cl	218	C ₁₂ OCl	203
C ₁₂ O ₂ Cl ₂	252	C ₁₂ OCl ₂	236
C ₁₂ O ₂ Cl ₃	286	C ₁₂ OCl ₃	272
C ₁₂ O ₂ Cl ₄	322	C ₁₂ OCl ₄	306
C ₁₂ O ₂ Cl ₅	356	C ₁₂ OCl ₅	340
C ₁₂ O ₂ Cl ₆	390	C ₁₂ OCl ₆	374
C ₁₂ O ₂ Cl ₇	426	C ₁₂ OCl ₇	409
C ₁₂ O ₂ Cl ₈	460	C ₁₂ OCl ₈	444

Table 3.8: Certified (matrix) reference material, PCDD/F congeners in fly ash (Emons, 2007). Only a selection shown of the 17 total congeners, to indicate the range of concentrations.

Compound	Certified value
2,3,7,8-T ₄ CDD	27 ng kg ⁻¹
2,3,7,8-T ₄ CDF	86 ng kg ⁻¹
O ₈ CDD	1.75 µg kg ⁻¹
1,2,3,4,6,7,8-H ₇ CDF	0.75 µg kg ⁻¹

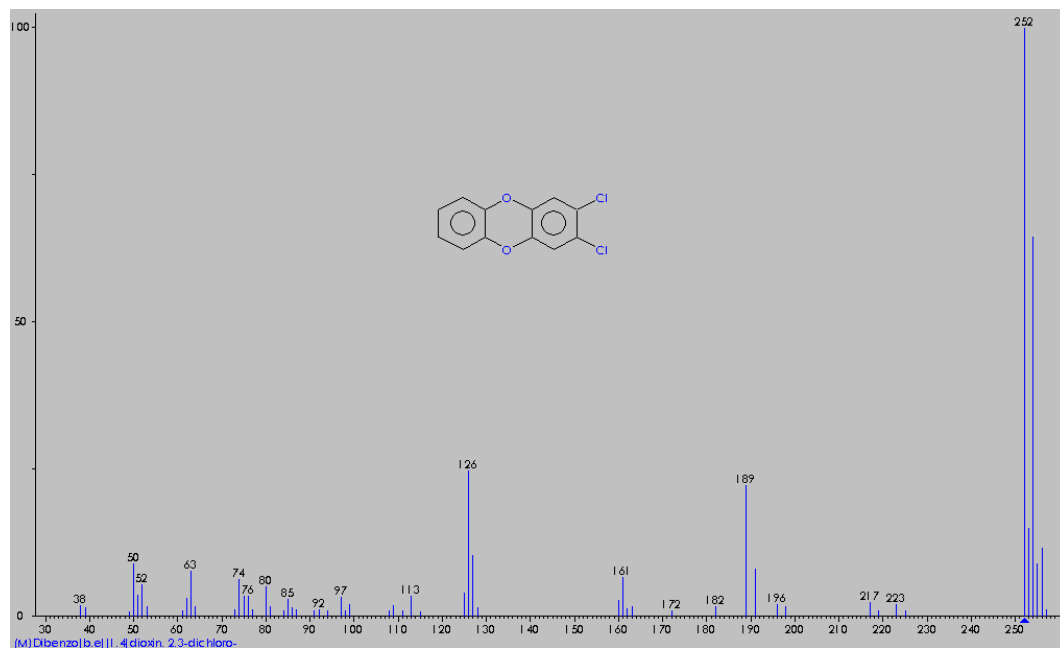


Figure 3.10: Reference mass spectrum, dichloro-dibenzo-p-dioxin.

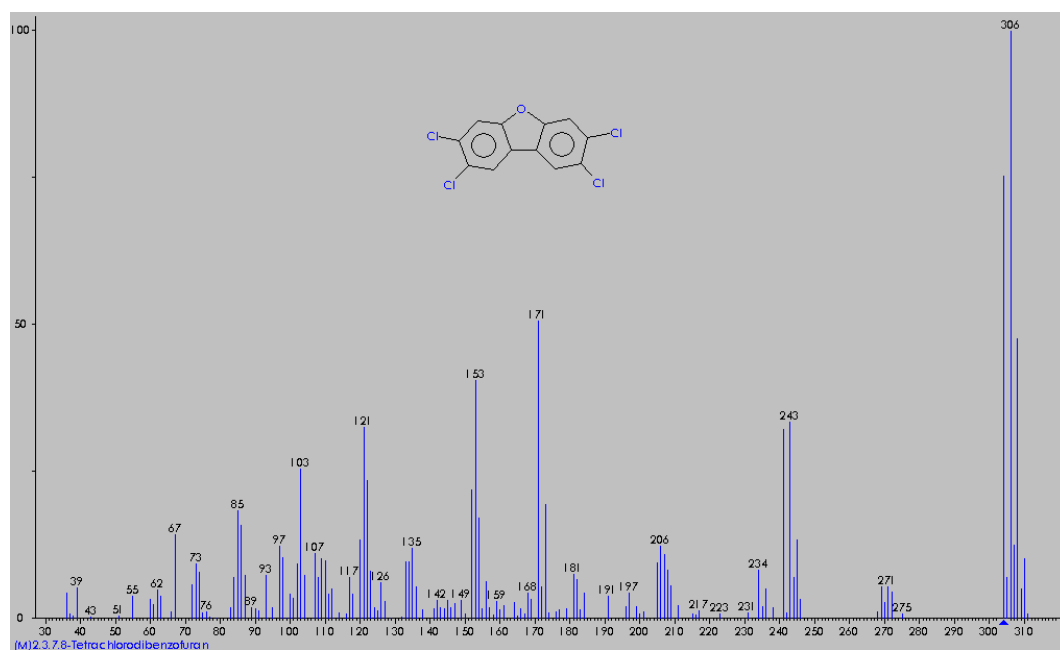


Figure 3.11: Reference mass spectrum, tetrachlorodibenzofuran.

Chapter 4

Experimental results

4.1 Fuel preparation

4.1.1 Composition of fuels

As stated earlier in §nominalfuels, laboratory analysis of the fuels was performed at an independent laboratory (TES Bretby, Burton-on-Trent). Laboratory test methods (developed internally by the laboratory) were performed to independently certified standards and the results of these laboratory tests are shown in Table 4.1. Compositions of the biomass fuels was in the form of densified pellets, of dimensions 6–8 mm diameter and 30 mm length. The bulk composition of the MRFR fuel fraction selected for this experiment was predominantly 90 % plastics 10 % fibres (paper, cardboard, wood). The material was comminuted to an average particle size of 20 mm using a laboratory scale cutting mill (Retsch; Haan, Germany). The chemical compositions of other fuels used during the process of assessing optimal combustor operation conditions are also shown in Appendix § Table D.1. All compositions values are shown on an ‘as received’ weight percentages basis. It should be noted that the quantity of chlorine in MRFR is approximately half of that typically expected in RDF type fuels, such as 0.6 % chlorine as shown in Table 3.1.

Table 4.1: Chemical compositions of the fuels.

	DDGS	Wheat	MRFR
Carbon	45.2	38.9	39.8
Hydrogen	6.2	4.9	5.2
Oxygen	34.1	36.7	27.2
Nitrogen	4.9	1.5	0.9
Chlorine	0.2	0.2	0.3
Sulphur	0.6	0.1	0.1
Ash	4.1	7	18.4
Moisture	4.9	13.5	8.5
Calorific value (gross, MJ kg ⁻¹)	19.3	16	22

4.1.2 Biomass fuels

Supply of fuel to the fluidised bed combustor is limited by the particle size of the fluidised bed material, fluidisation gas velocity and the dimensions of the fuel feed mechanism, all of which favour fuel particles less than 40 mm or so in size. As described earlier, the biomass fuels tested were available in the form of densified pellets (diameter 6–8 mm) and thus preparation was not necessary; however the MRFR fraction required significant size reduction.

4.1.3 Comminution of MRFR

Whilst the biomass fuel was readily available in the form of pellets and therefore fuel preparation was not necessary, the MRFR waste fraction required laborious size reduction tasks. Only a laboratory scale cutting mill (models SM1 and SM2000, Retsch, Haan, Germany) was available, suited for preparation of sample material prior to chemical laboratory instrument analysis. Over a twelve day period, approximately 60 kg of material was prepared by this process. It was apparent from the literature review that heterogeneous



Figure 4.1: DDGS pellets

waste particles are difficult to burn in a stable manner and therefore this laborious task was deemed to be justified. In addition, the dimensions of the screw feed system of the fluidised bed combustor prevented any bulk fuels from being supplied into the combustion zone. A single consignment of bulk sample MRFR (total mass 289 kg) was obtained from a local materials recycling facility and individual items from the bulk sample were selected manually, on the basis of being suitable for comminution by the cutting mill. A mixture of materials were chosen to represent the heterogeneous composition, which was dominated by plastics and fibres (cardboard, papers, textiles), whilst non-combustible fractions such as glass and metal items were not chosen because of specification of the types of materials that can be cut by the laboratory device. The approximate composition of the MRFR waste fraction is summarised below:

- polyethene (natural);
- polyethene (coloured);
- polyethene terephthalate (mixtures of various co-polymers);

- Other non-polyvinylchloride plastics, such as high density polyethene, films, caps, etc.;
- non-recyclable fibres (laminated papers, magazines, cardboard).

(Cutts, 2008)



Figure 4.2: Comminution of MRFR. Photographs shows selected material before and after size reduction using the laboratory cutting mill.

4.2 Fluidised bed combustion system operation

A total of twenty-five combustion tests of various biomass-waste fuel mixtures were completed with statistical reproducibility being demonstrated by repetition of the combustion of wheat-MRFR 90:10. Subsequent results correspond to combustion tests shown in Table 4.3 and results for the remainder combustion tests are shown in the appendix (§ Appendix D). The results of the supplementary combustion tests were not within the original scope of this PhD research project, being primarily concerned with agglomeration of the fluidised bed material, but are included in the appendix for the benefit of future research.

It is normal industrial practice to measure fuel composition and then determine a specific quantity of limestone to be fed continuously into the combustion chamber, concomitant with the fuel feed rate. In this study, the excessive limestone content of the fluidised bed composition (Table 4.2) was applied, to avoid the need to perform chemical composition laboratory analysis on each fuel mixture prior to a combustion test, which was not practically feasible. Occasionally, extra limestone may have been added to the combustor during operation, to avert agglomeration. This is evident in Figure 4.3, where the two instances of rapid decline in temperatures (specifically fluidised bed sand) were due to addition of approximately 2 kg of limestone.

Table 4.2: Characteristics of fluidised bed material during operation of combustor. Fluidised bed composition expressed by weight.

Fuel mixture	Fluidised bed total mass (kg)	Fluidised bed (SiO ₂ :CaCO ₃) composition	Fluidisation rate (mm H ₂ O)
DDGS	22	50:50	30
DDGS-MRFR (90:10)	22	50:50	25
DDGS-MRFR (80:20)	22	50:50	15
DDGS-MRFR (50:50)	22	50:50	5
DDGS-MRFR (30:70)	22	50:50	25
Wheat	25	50:50	30
Wheat-MRFR (90:10)	25	50:50	20
Wheat-MRFR (80:20)	25	50:50	15
Wheat-MRFR (50:50)	25	50:50	15
Wheat-MRFR (30:70)	25	50:50	> 100

Table 4.3: Summary of operation of fluidised bed combustor. Median values shown for combustion temperature and flue gas data.

Fuel mixture	Fuel feed (kg h ⁻¹)	Inlet air (l min ⁻¹)	Combustion temperature (fluidised bed sand, °C)	Flue gas content CO ₂) (% vol.)	Flue gas content O ₂) (% vol.)	Duration (hours)
DDGS	6	1400	848	8.6	11.1	2
DDGS-MRFR (90:10)	5	1400	861	7.9	12.0	4
DDGS-MRFR (80:20)	5	1400	844	8.9	11.4	3
DDGS-MRFR (50:50)	4	1400	803	7.3	12.6	3
DDGS-MRFR (30:70)	7	1400	796	9.5	10.3	3
Wheat	7	1300	773	8.2	11.6	3
Wheat-MRFR (90:10)	5	1400	787	9.9	10.6	3
Wheat-MRFR (90:10), repeat 1	8	1400	823	10.6	10.6	2
Wheat-MRFR (90:10), repeat 2	7	1400	853	9.3	10.8	2
Wheat-MRFR (80:20)	4	1400	839	8.3	12.1	2
Wheat-MRFR (50:50)	4	1400	760	7.7	11.0	2
Wheat-MRFR (30:70)	5	1300	817	8.9	11.0	3

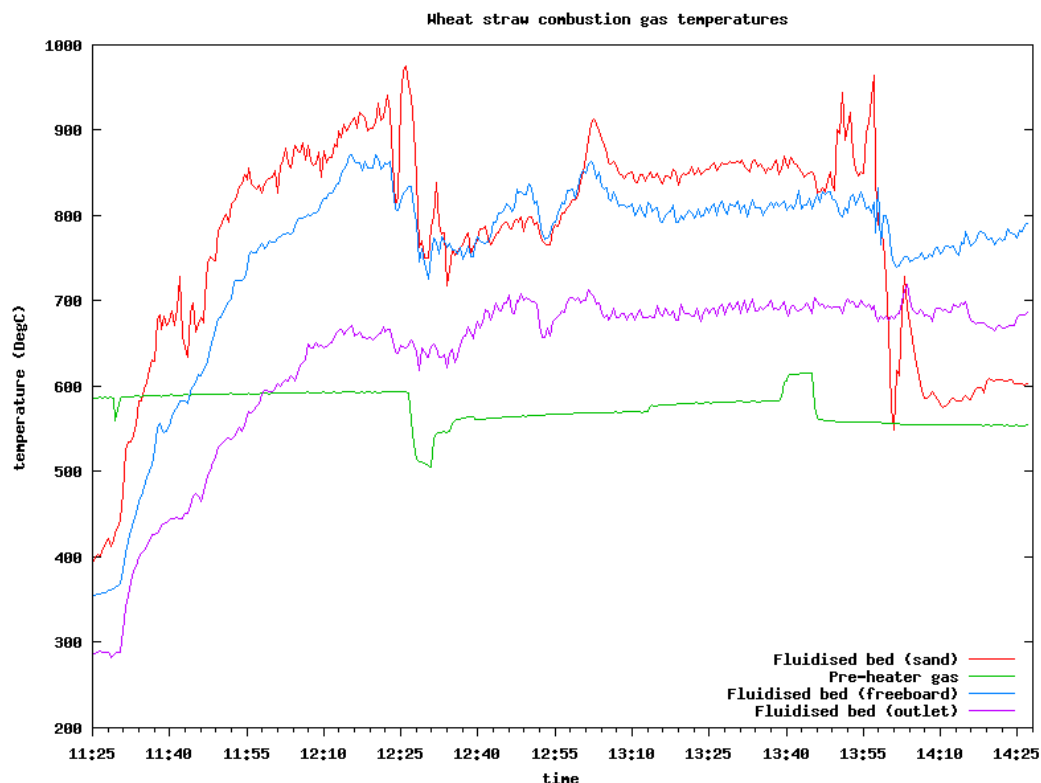


Figure 4.3: Time series profile of temperatures during combustion of wheat straw.

4.3 Gaseous emissions

Analysis of the flue gas using the FTIR instrument yielded detailed information about the chemical composition for each combustion test. The gas analyser (Protea Protir 204M) reports data in a readily accessible format and for a wide range of gases. Figure 4.4 is an example of a graphical representation of the data recorded by the new gas analyser.

The extent of major components (excluding nitrogen) of the flue gas composition for each combustion test is summarised in Table 4.4. Correlation between carbon monoxide and carbon dioxide during combustion tests was investigated, with the results shown in Figure 4.6 and Figure 4.7. The variation

Table 4.4: Variation in major gas composition of fuel gas in relation to change in fuel mixture composition (median values shown).

Fuel mixture	Flue gas content CO ₂ (% vol.)	Flue gas content O ₂ (% vol.)	Flue gas content H ₂ O (% vol.)
DDGS	8.5	11.2	9.0
DDGS-MRFR (90:10)	8.3	11.6	8.5
DDGS-MRFR (80:20)	8.8	11.5	9.4
DDGS-MRFR (50:50)	6.9	13.0	7.0
DDGS-MRFR (30:70)	10.2	9.7	9.4
Wheat	8.0	11.8	9.9
Wheat-MRFR (90:10)	9.8	10.6	9.3
Wheat-MRFR (90:10 repeat 1)	11.4	10.3	8.9
Wheat-MRFR (90:10 repeat 2)	9.3	10.8	8.9
Wheat-MRFR (80:20)	8.3	12.1	8.3
Wheat-MRFR (50:50)	9.3	11.4	7.8
Wheat-MRFR (30:70)	8.1	11.9	7.6

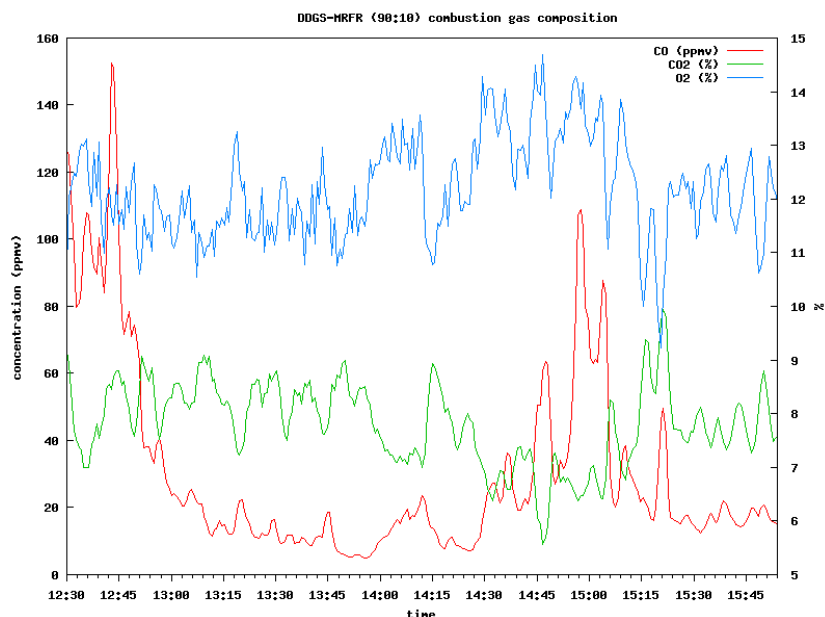


Figure 4.4: Carbon oxides and oxygen emissions, DDGS-MRFR (90:10)

in emissions of a selection of minor flue gas components, in accordance with change in content of MRFR in the fuel mixture is shown in Figure 4.9 and Figure 4.10 as examples. Of the biomass fuels tested, DDGS showed highest emissions of nitric oxide, the dominant form of nitrogen. Similarly, sulphur dioxide emissions were also highest from DDGS as the biomass fuel component; median emissions 91 ppmv for 100 % DDGS with fluidised bed material $\text{SiO}_2\text{-CaCO}_3$ 50:50. In comparison, median SO_2 emissions for Willow-MRFR (90:10) was 2.5 ppmv with fluidised bed material $\text{SiO}_2\text{-CaCO}_3$ 20:80 (further details of gaseous pollutants for combustion of willow are shown in Figure D.3). The following graphs summarise emissions data obtained for the fuels tested; all subsequent graphs (i.e. Figure 4.17–Figure 4.91) shown in this section correspond to periods of each combustion test where only stable combustion conditions were obtained. Classification of stable combustion conditions was a subjective task considering the following general factors: *a*) temperatures of the fluidised bed combustor; *b*) combustor temperatures relative to pre-heater gas temperature; *c*) variation in emissions of carbon oxides. This is represented

graphically in Figure 4.5; areas shaded by vertical lines were excluded from the data sets used to plot any subsequent graphs.

The impact of temperature upon gas emissions is dependent upon the gas species; some pollutants increase with temperature whilst others show a negative correlation. The following graphs in Figure 4.14–Figure 4.15 are presented here as a consequence, where the data corresponds to the *entire* duration of the combustion tests with the fuel mixtures. Similarly for nitrogen oxides and sulphur dioxide, Figure 4.10 and Figure 4.12 shows how emissions of these pollutants changes with temperature. Only data for combustion of pure fuels (i.e. DDGS 100 % and wheat 100 %, without any MRFR waste fraction) is shown, since the combustion tests for these fuels started at relatively lower temperatures and so the variation between combustion temperature and gas emission is more evident. When combustion tests involved the inclusion of an MRFR fraction, fuels were not added to the combustor until a higher temperature had been attained to facilitate combustion of less volatile components of the MRFR fraction, such as dense plastics.

Interactions between various components of the combustion flue gas during each test are shown in the following graphs (Figure 4.17–Figure 4.91), made possible using simultaneous data recorded by the FTIR flue gas analyser. These graphs are characterised in general as three-dimensional projections of the relationships between three variables measured by the gas analyser and where temperature is one of the three variables, thermocouples' dataloggers. The axes of each 3-D projection are labelled accordingly and the relationships between variables is represented by the “surface” of the three-dimensional plot of these types of graphs. The legend of each 3-D projection corresponds to the range of the z-axis which is the axis of vertical orientation relative to the ordinate and abscissa, such that all axes are perpendicular to each other at the origin, to form a right-hand triad. Thus, in the graph of Figure 4.21, emissions of carbon monoxide are at a maximum of approximately 2000 ppmv, which occurred where hydrogen chloride levels (greater than *circa* 22 ppmv) and temperatures (approximately 860 °C) were highest.

The relationships between emissions of hydrogen chloride and carbon monox-

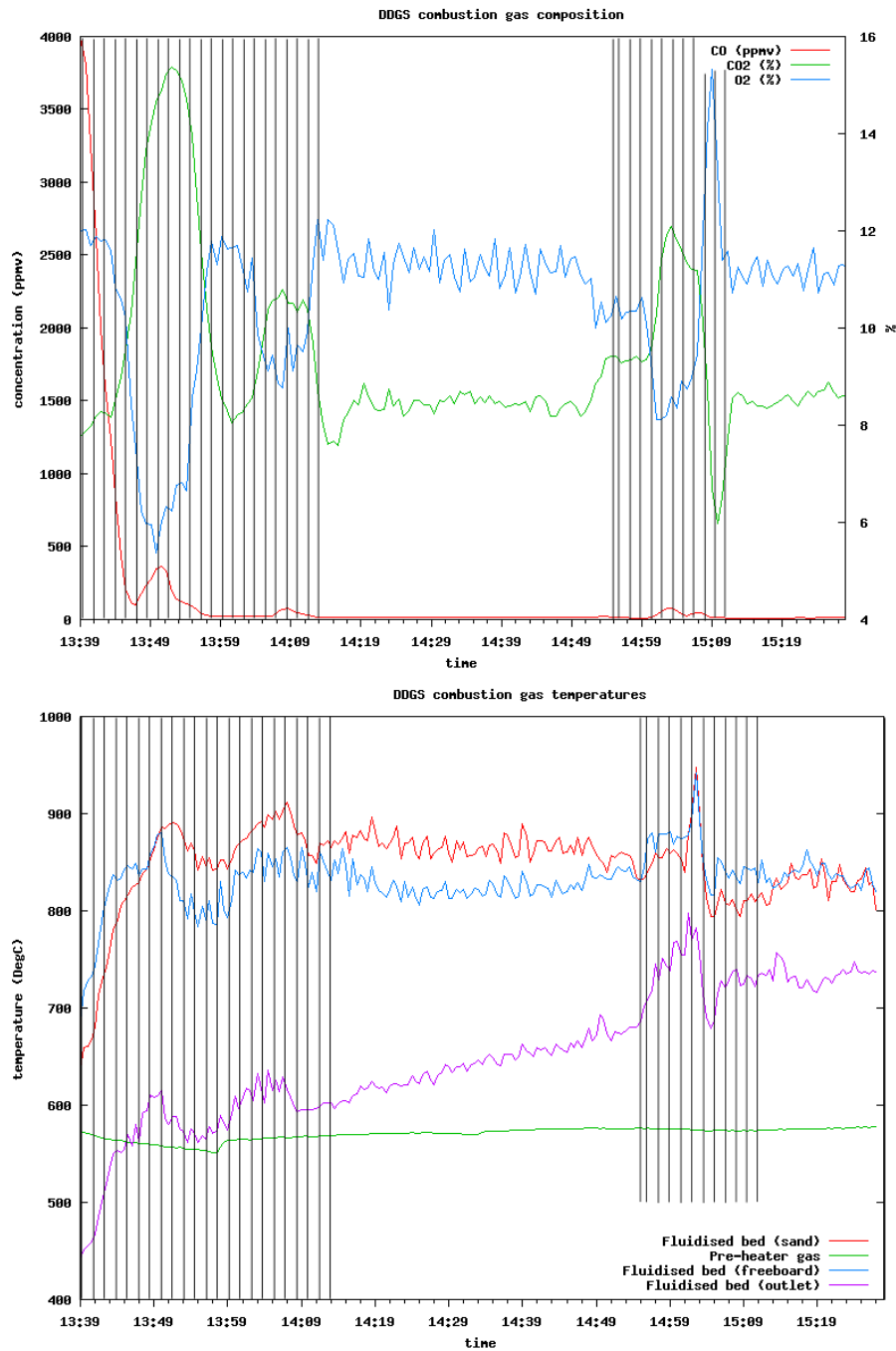


Figure 4.5: Example of stable combustion identified from a test, combustion of DDGS.

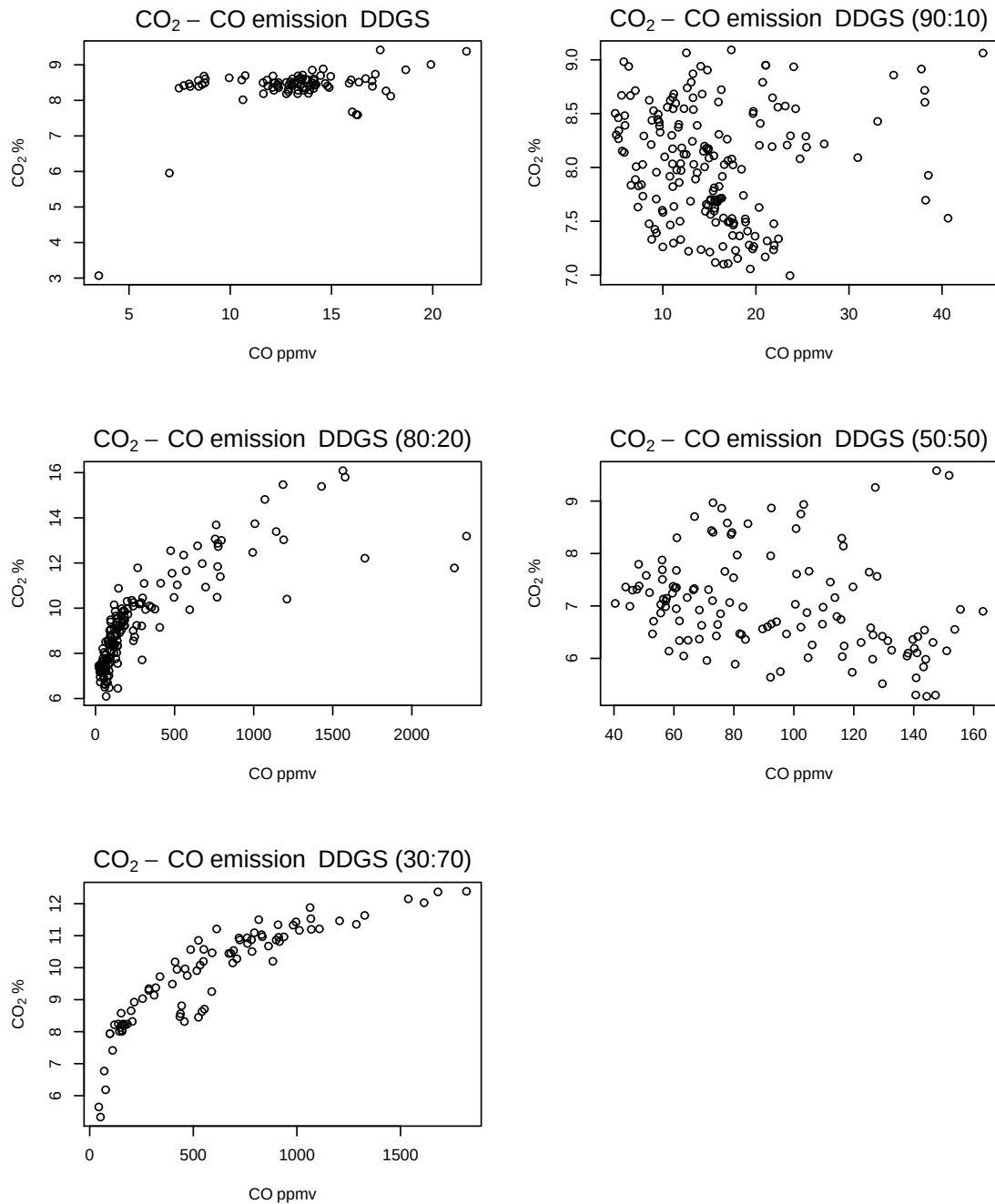


Figure 4.6: Relationships between carbon oxides emissions for combustion of DDGS.

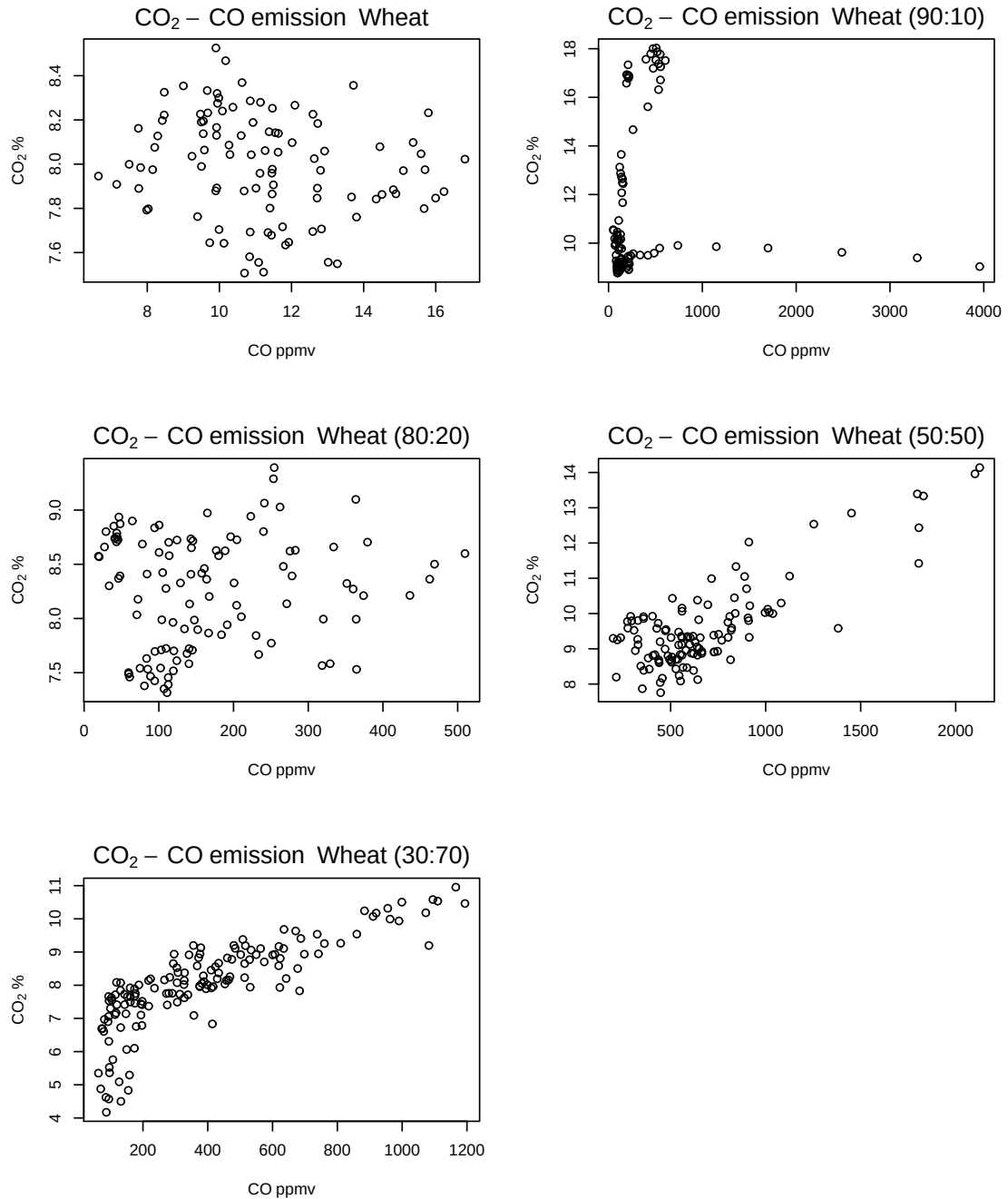


Figure 4.7: Relationships between carbon oxides emissions for combustion of wheat straw.

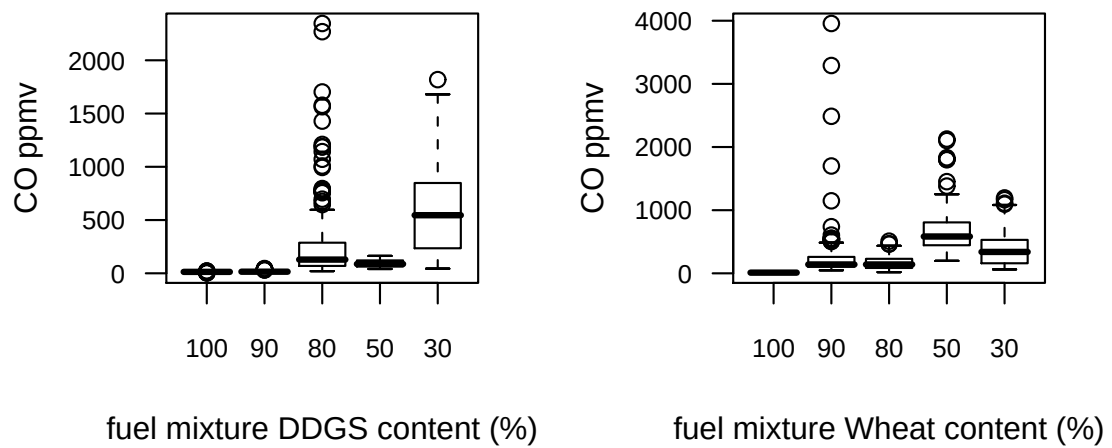


Figure 4.8: Variation in flue gas CO content.

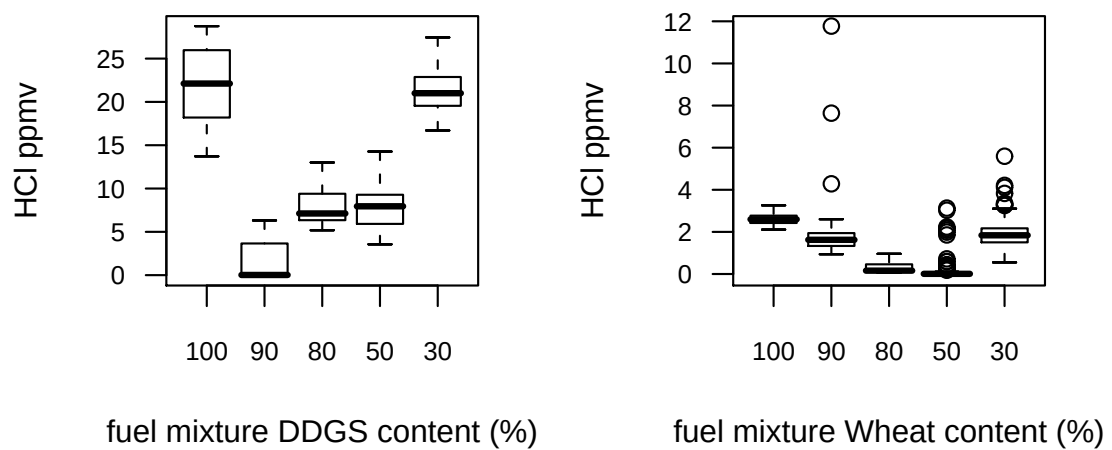
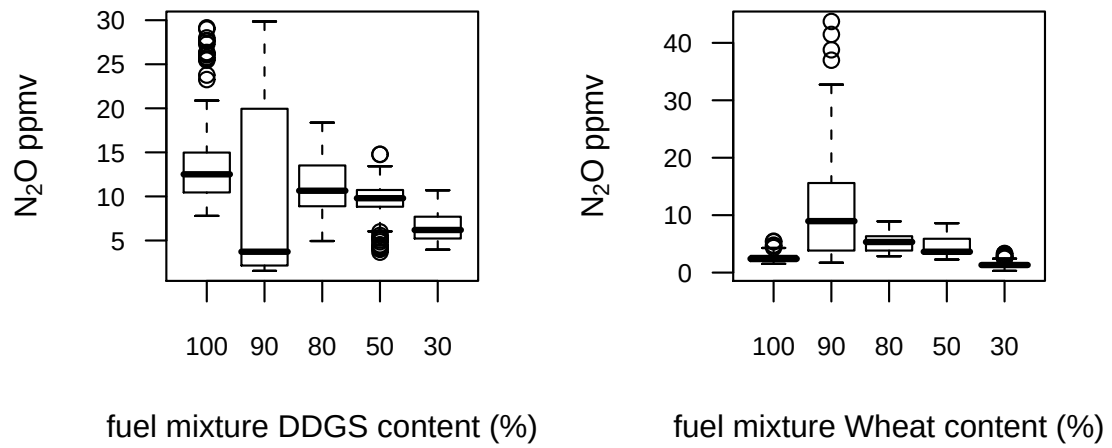
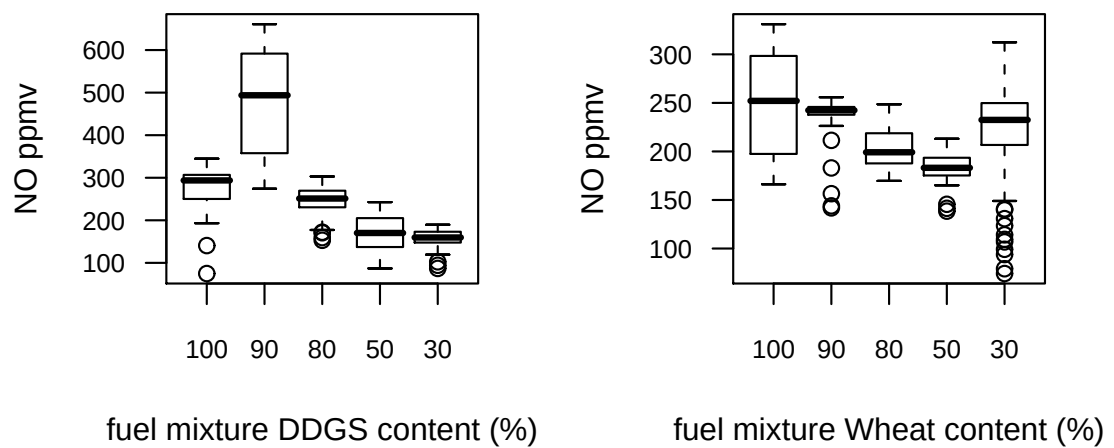
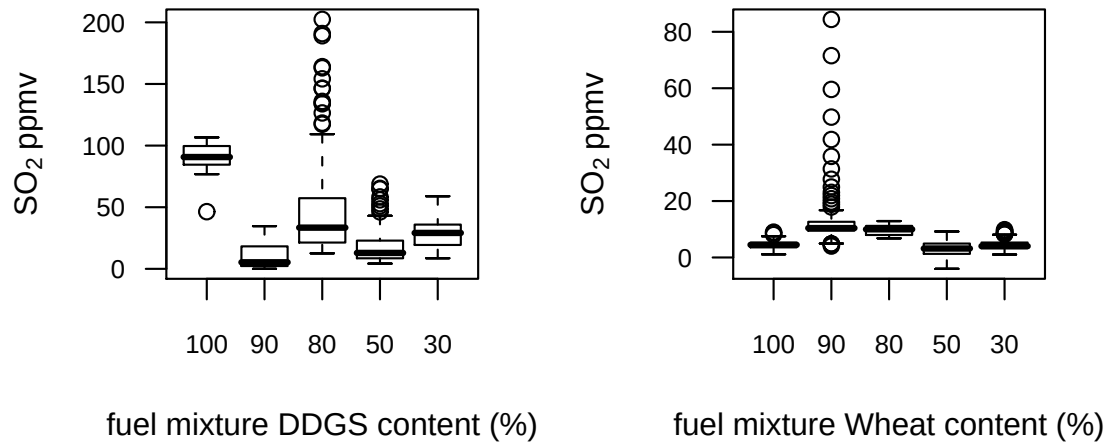


Figure 4.9: Variation in flue gas HCl content.

Figure 4.10: Variation in flue gas N_2O content.Figure 4.11: Variation in flue gas NO content.

Figure 4.12: Variation in flue gas SO_2 content.

ide with respect to combustion temperature are shown in Figure 4.17–Figure 4.26. The effect of combustion temperature upon emissions of carbon monoxide and nitric oxide are shown in Figure 4.27–Figure 4.36, similarly for sulphur dioxide, carbon monoxide and combustion temperature (Figure 4.37–Figure 4.46).

Emissions of hydrogen chloride, nitric oxide and carbon monoxide are indicated in Figure 4.47–Figure 4.56 with interactions between hydrogen chloride, sulphur dioxide and carbon monoxide are shown in Figure 4.57–Figure 4.66.

Hydrogen cyanide, ammonia and nitrous oxide emissions are compared in Figure 4.67–Figure 4.76, followed by comparison of hydrogen cyanide, ammonia and nitric oxide emissions in Figure 4.77–Figure 4.86. Finally, the relationships between emissions of sulphur dioxide, nitric oxide and carbon monoxide are demonstrated in Figure 4.87–Figure 4.96.

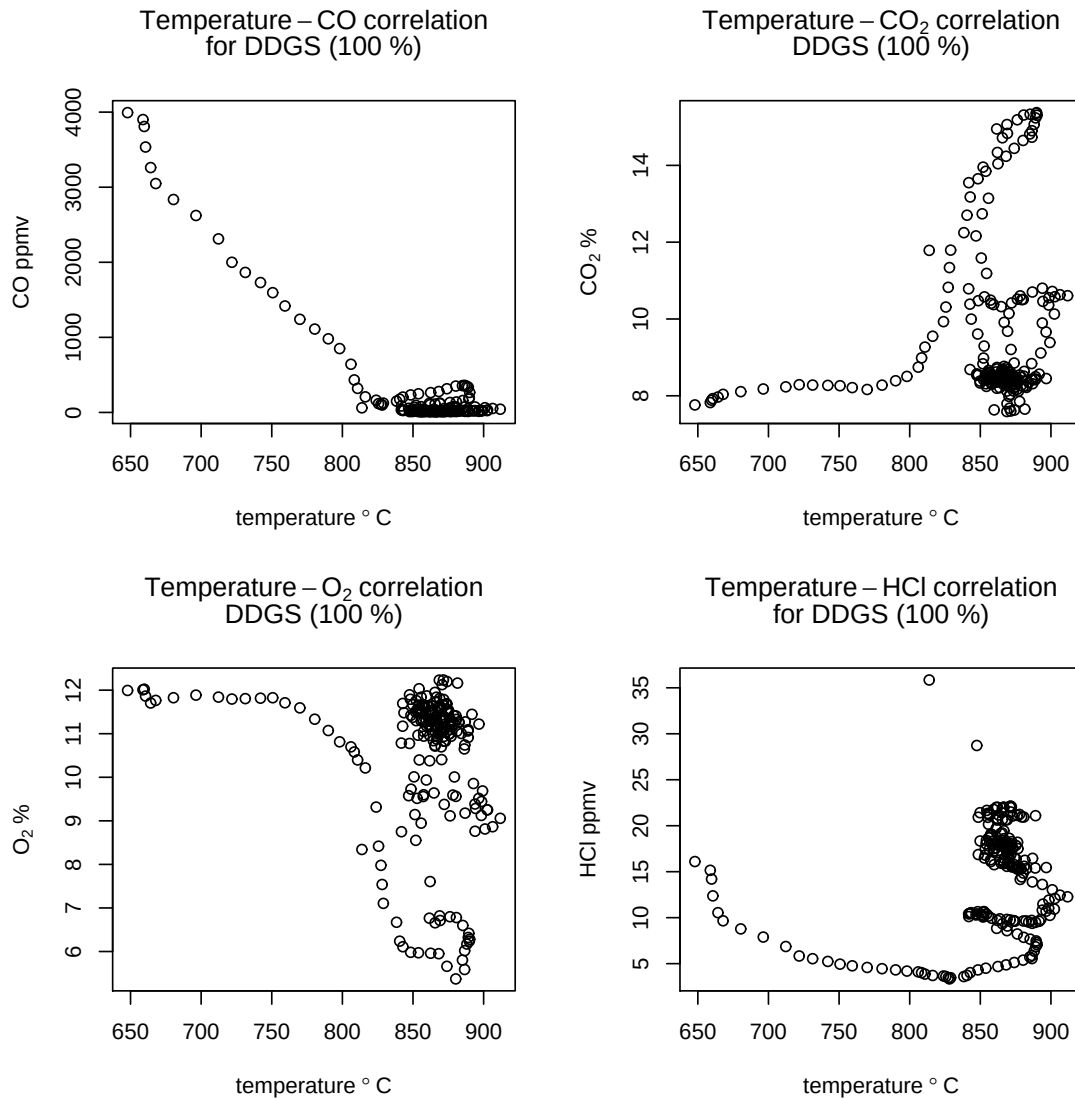


Figure 4.13: Correlations between combustion temperature (fluidised bed sand), carbon oxides, oxygen & hydrogen chloride for DDGS (100 %).

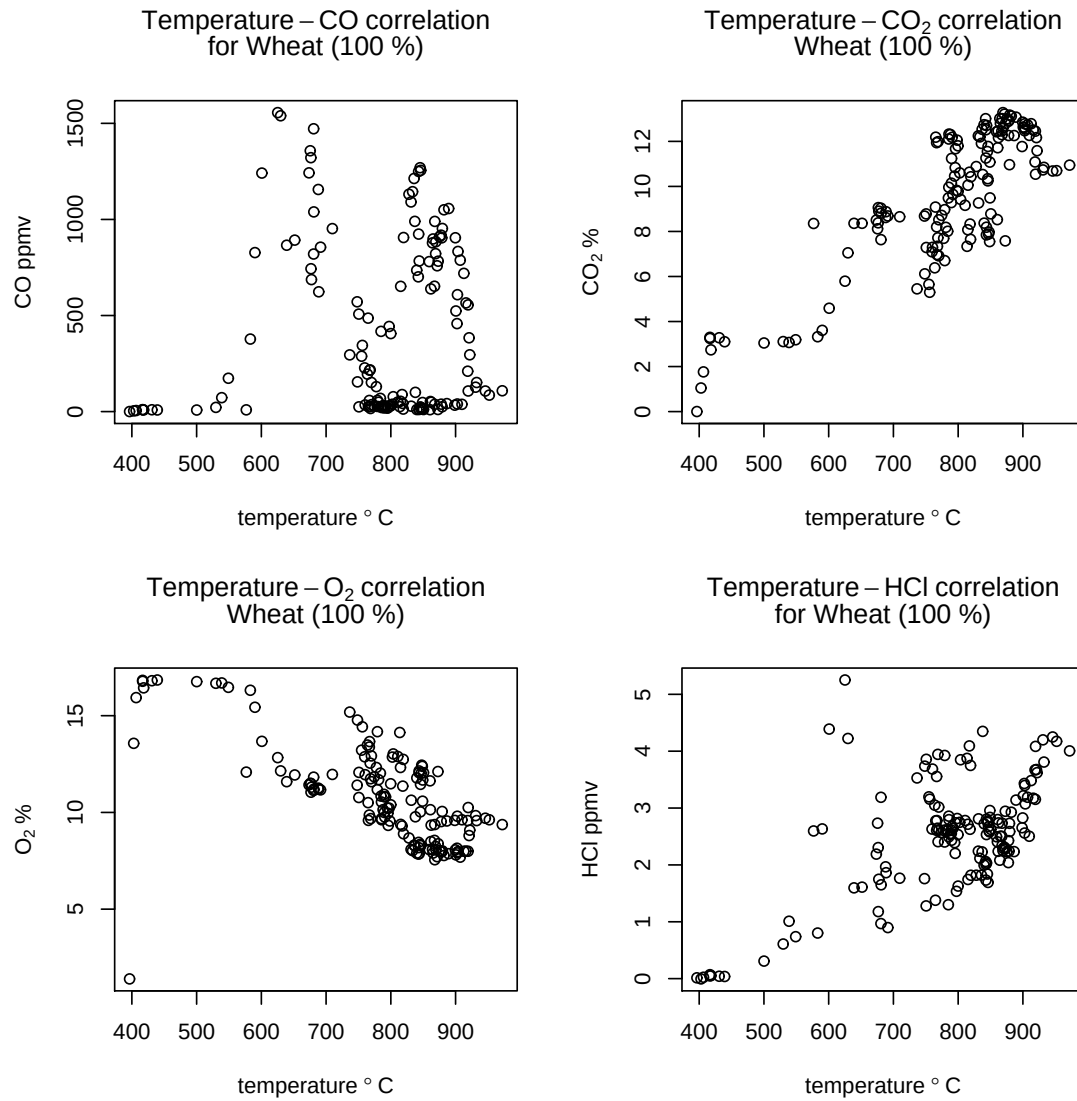


Figure 4.14: Correlations between combustion temperature (fluidised bed sand), carbon oxides, oxygen & hydrogen chloride for DDGS (100 %).

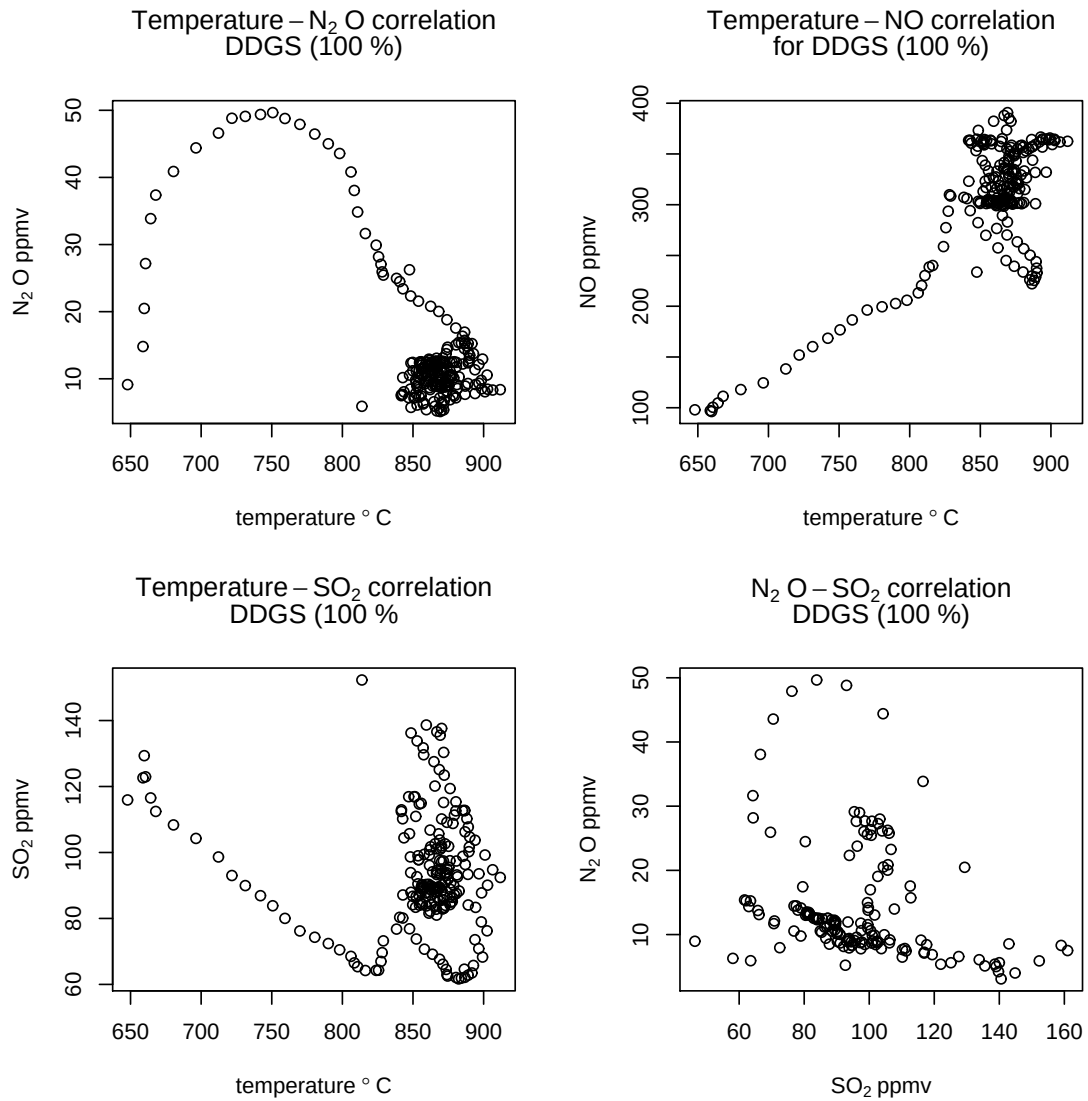


Figure 4.15: Correlations between combustion temperature (fluidised bed sand), nitrogen and sulphur oxides for DDGS (100 %).

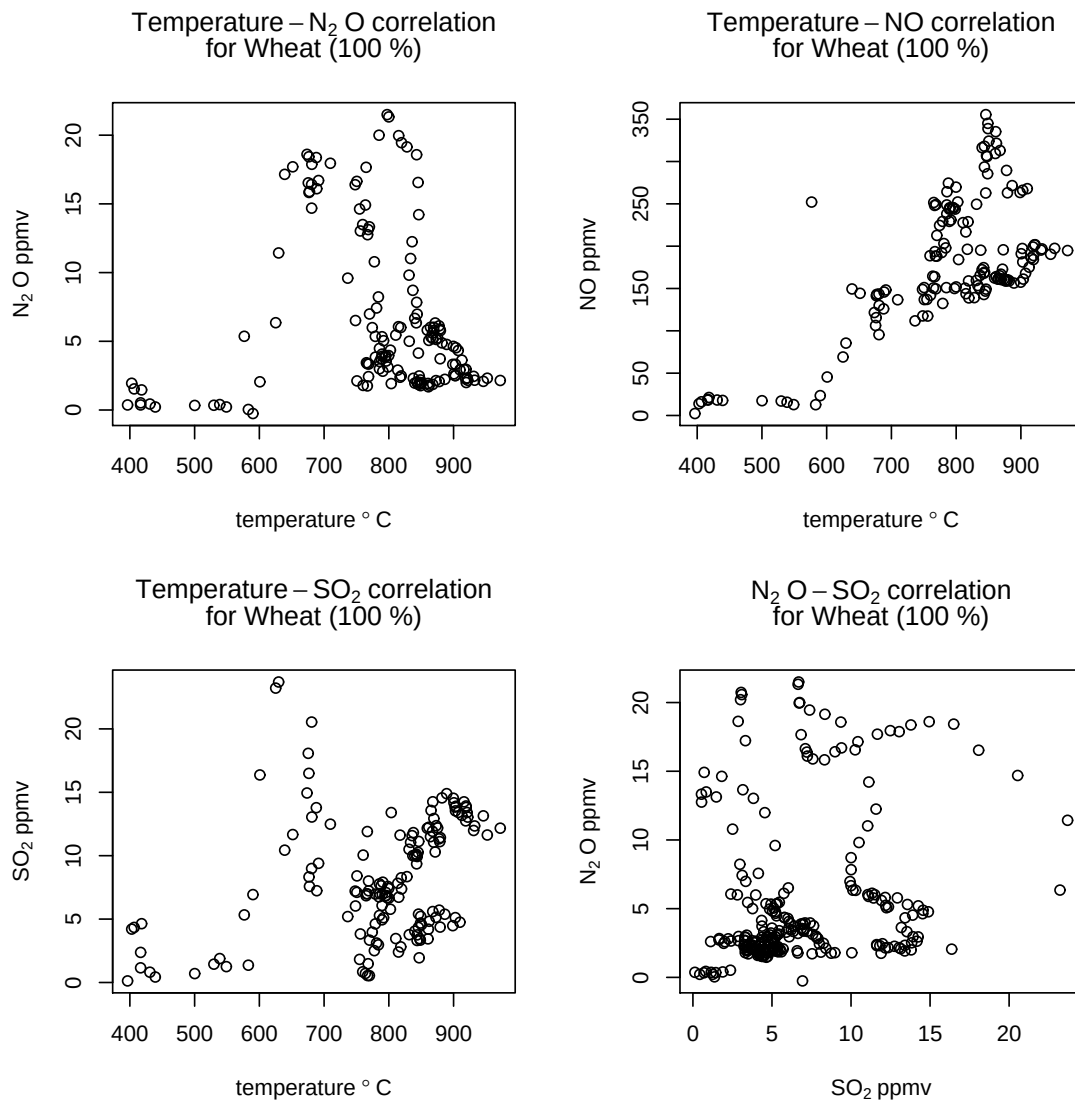


Figure 4.16: Correlations between combustion temperature (fluidised bed sand), nitrogen and sulphur oxides for wheat (100 %).

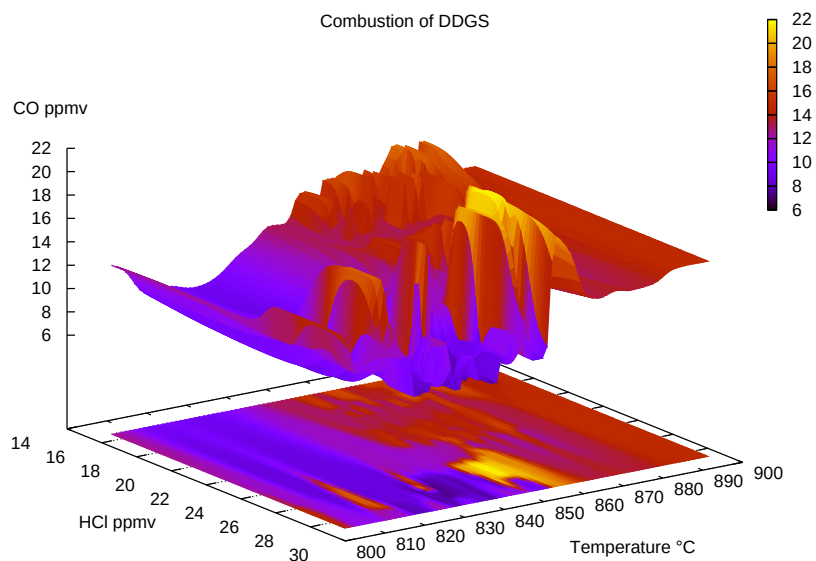


Figure 4.17: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of DDGS 100 %.

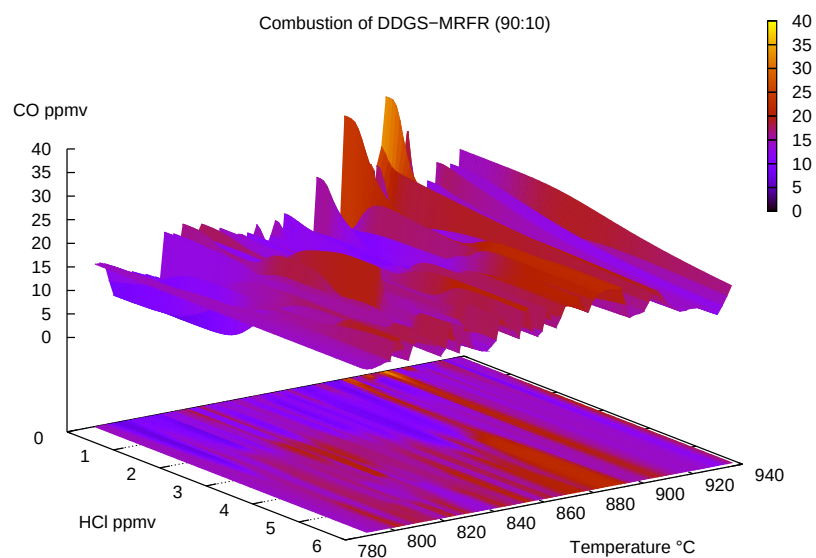


Figure 4.18: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

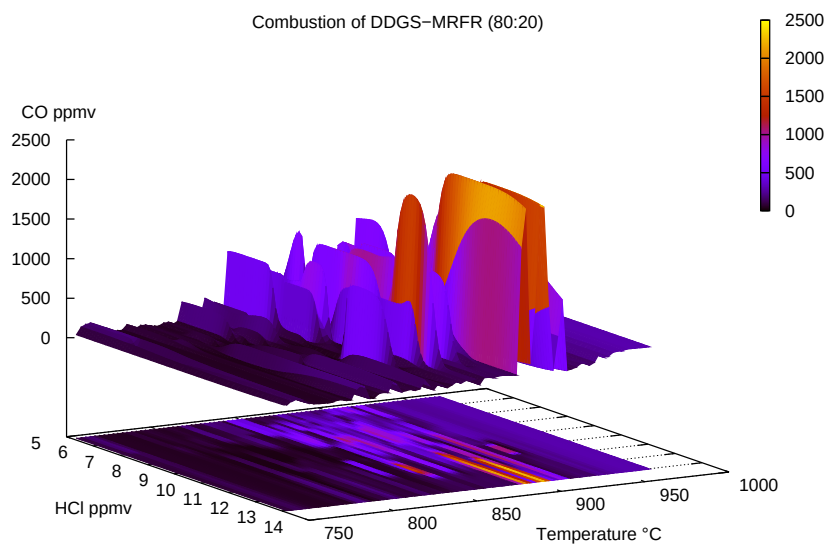


Figure 4.19: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

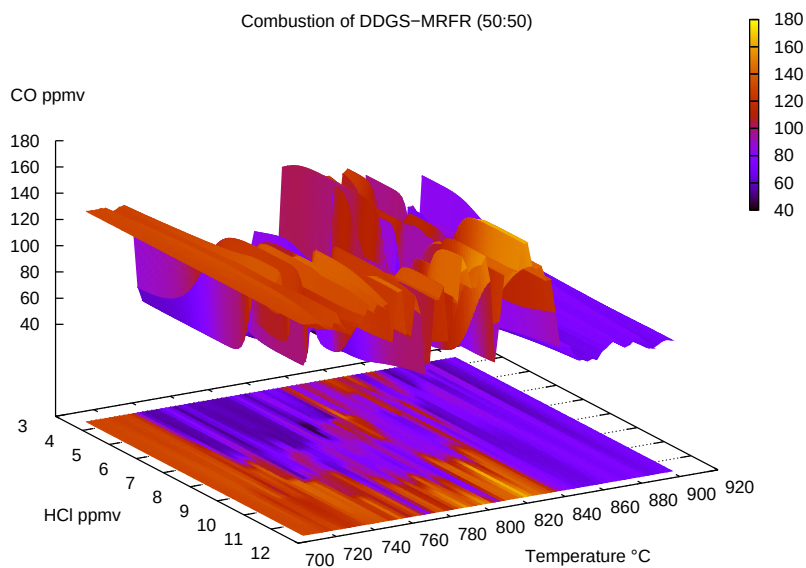


Figure 4.20: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

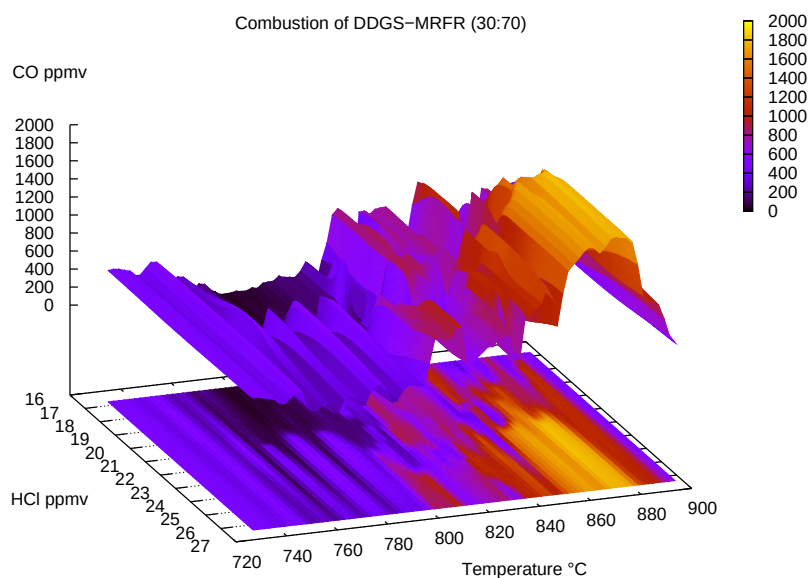


Figure 4.21: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

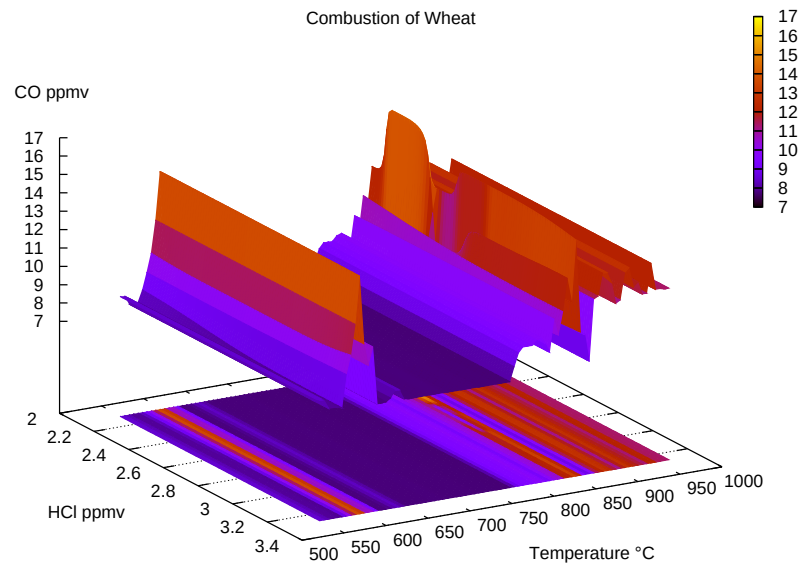


Figure 4.22: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of wheat 100 %.

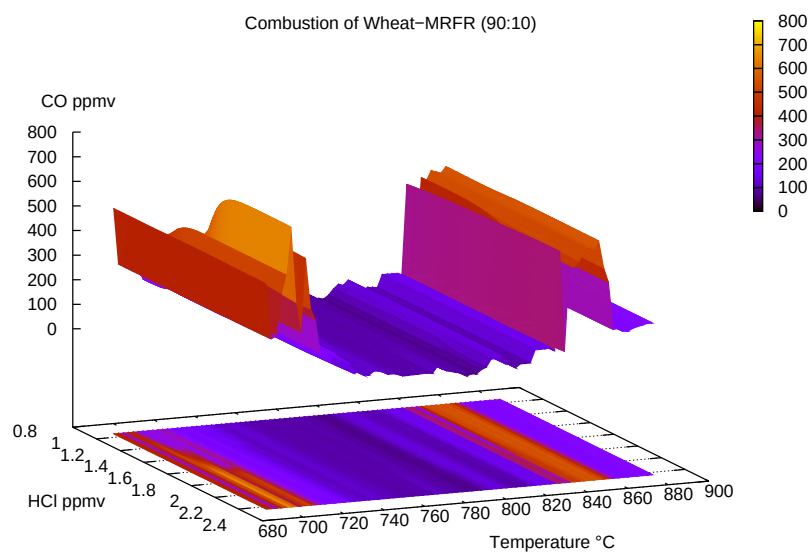


Figure 4.23: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

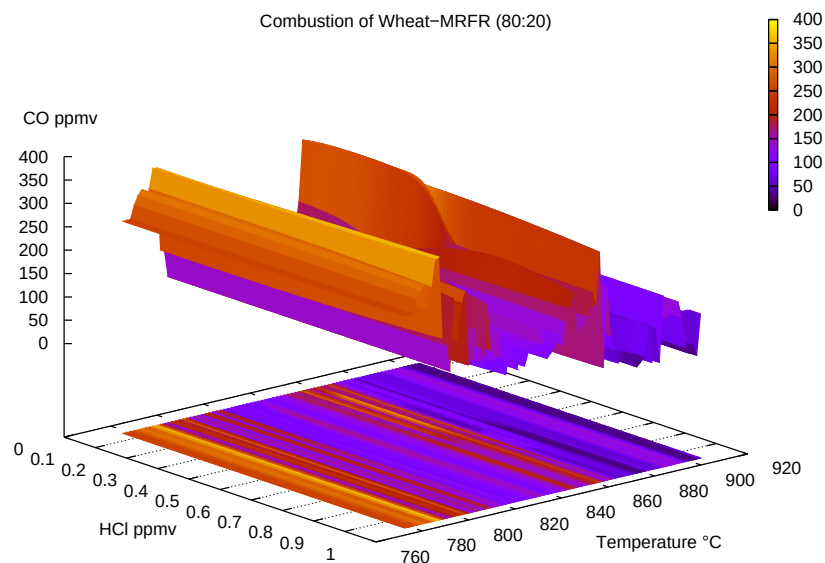


Figure 4.24: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

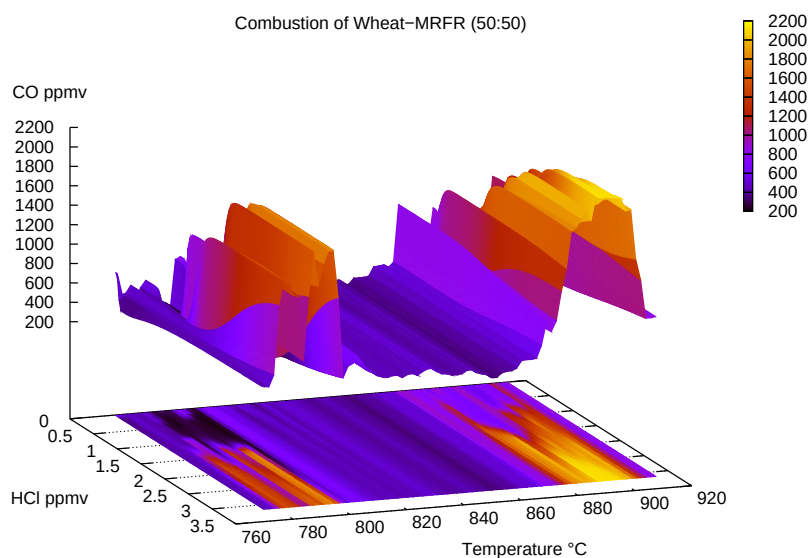


Figure 4.25: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

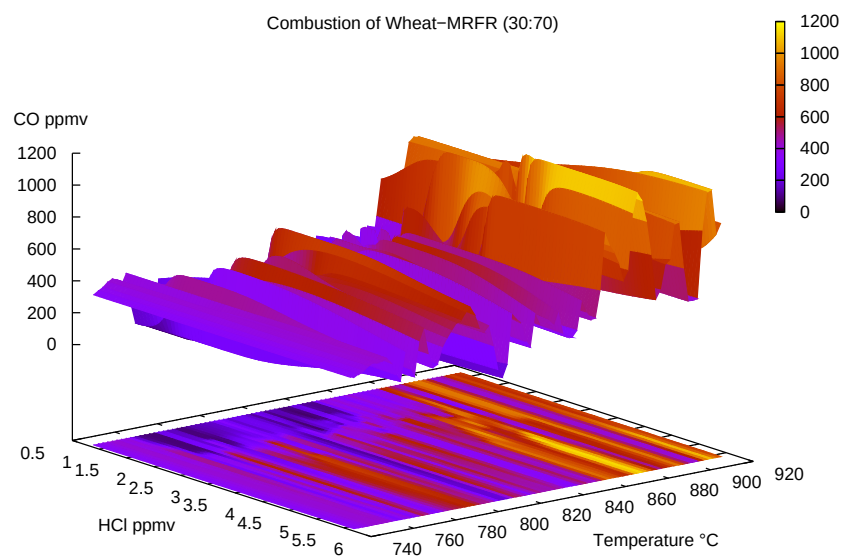


Figure 4.26: Relationship between simultaneous emissions of HCl and CO for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

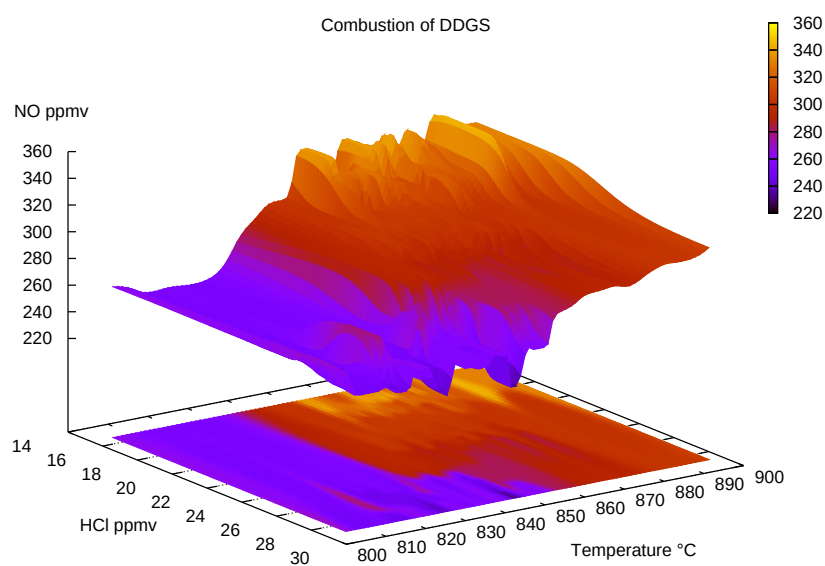


Figure 4.27: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of DDGS 100 %.

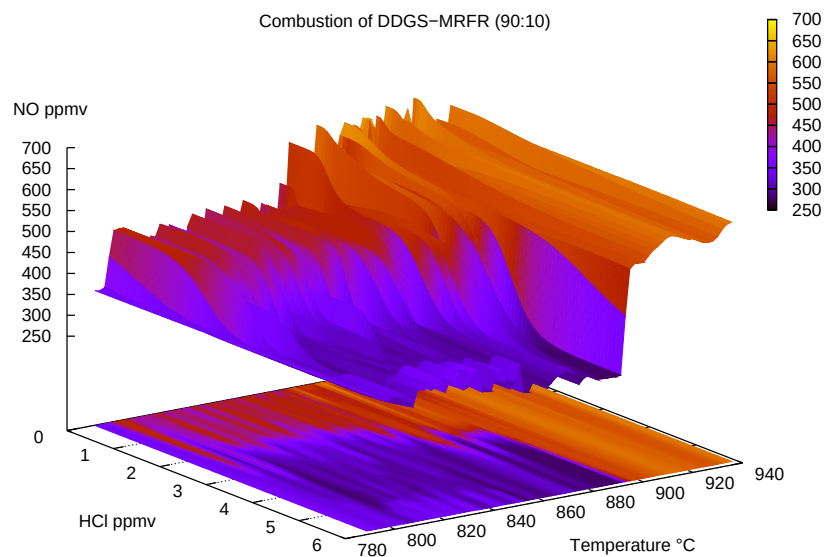


Figure 4.28: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

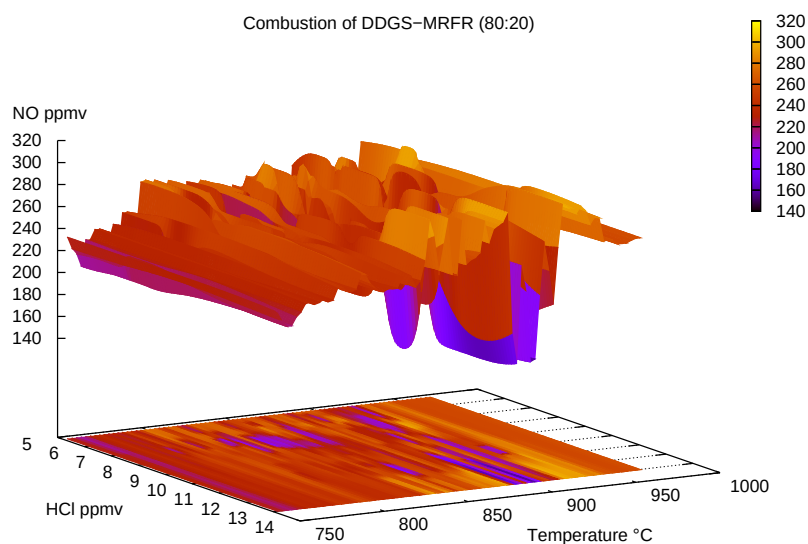


Figure 4.29: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

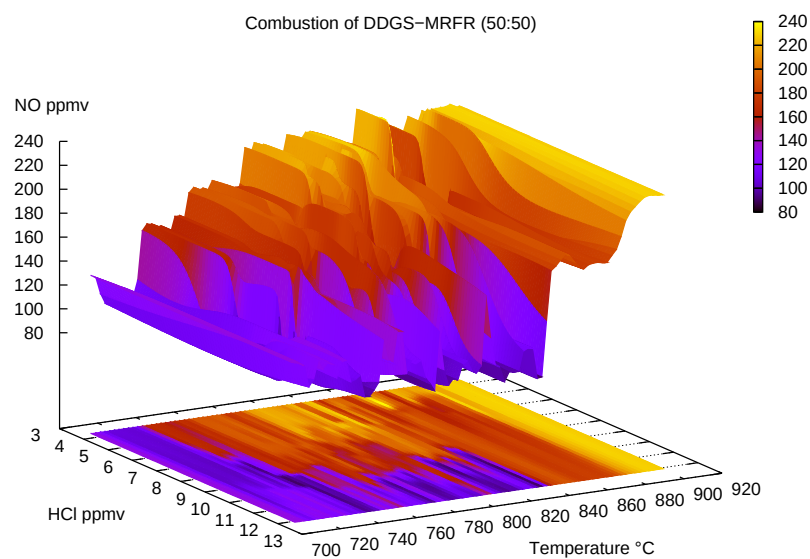


Figure 4.30: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

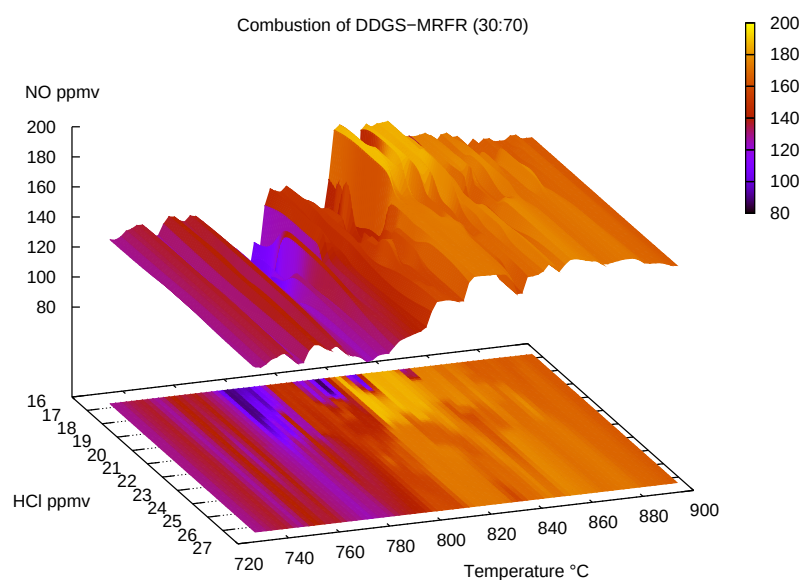


Figure 4.31: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

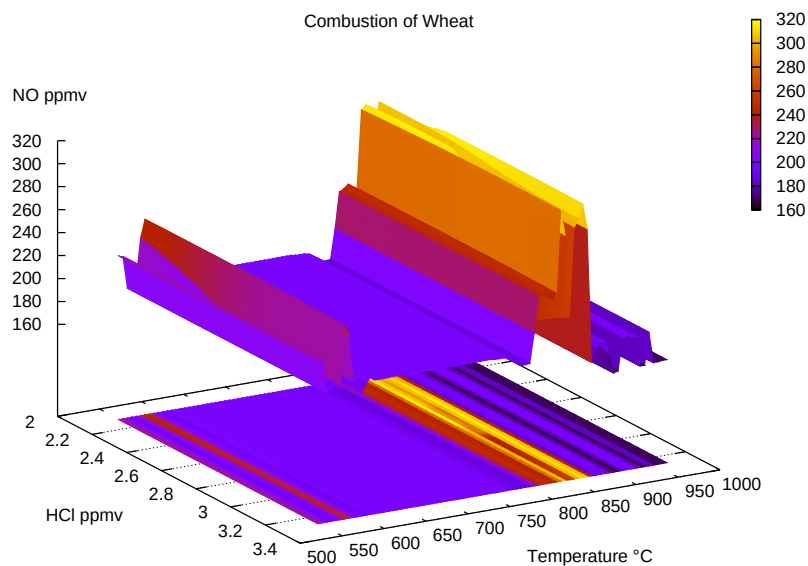


Figure 4.32: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of wheat 100 %.

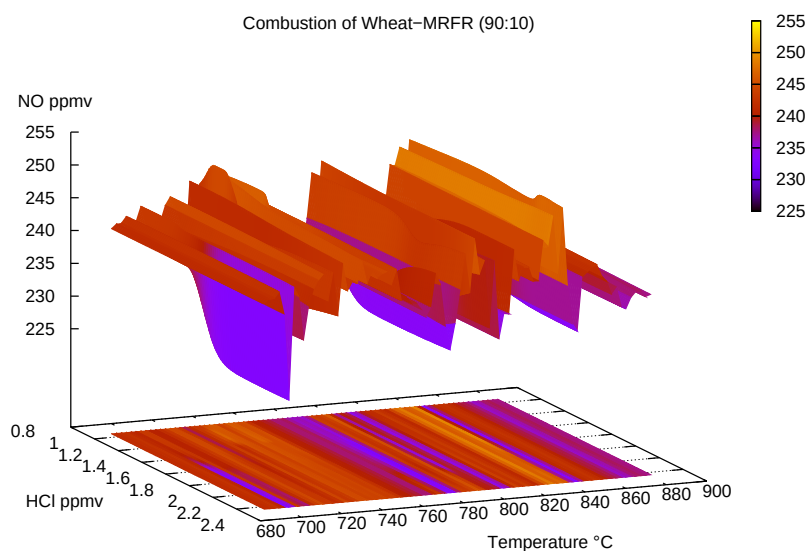


Figure 4.33: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

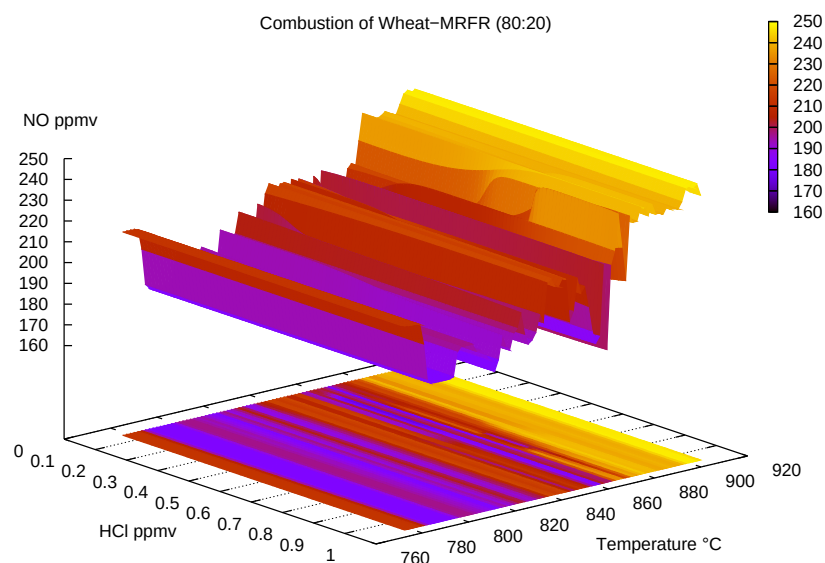


Figure 4.34: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

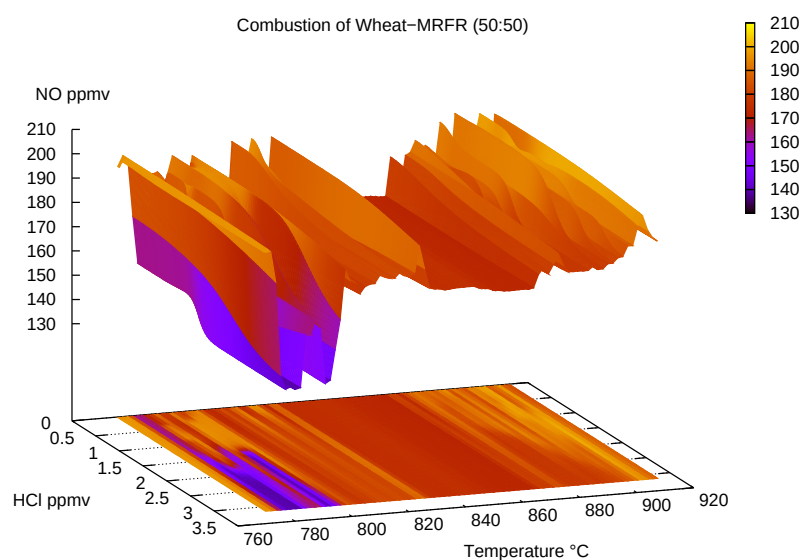


Figure 4.35: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

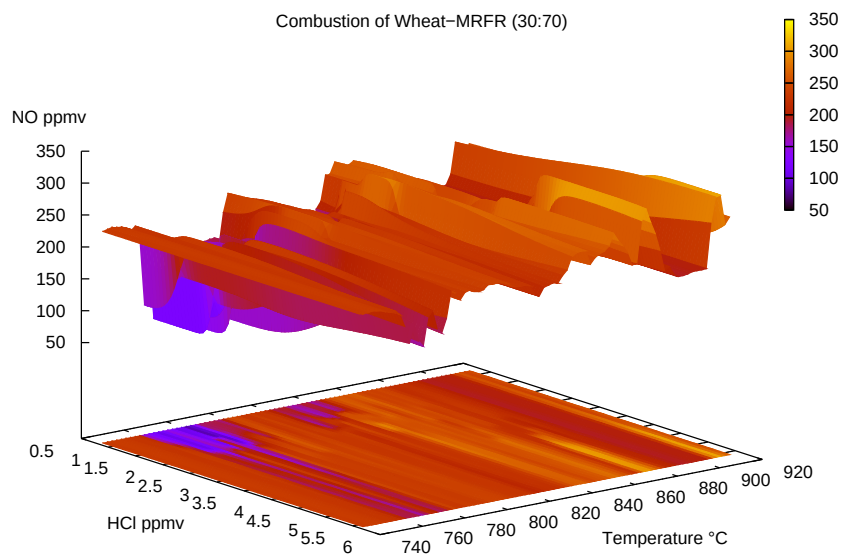


Figure 4.36: Relationship between simultaneous emissions of HCl and NO for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

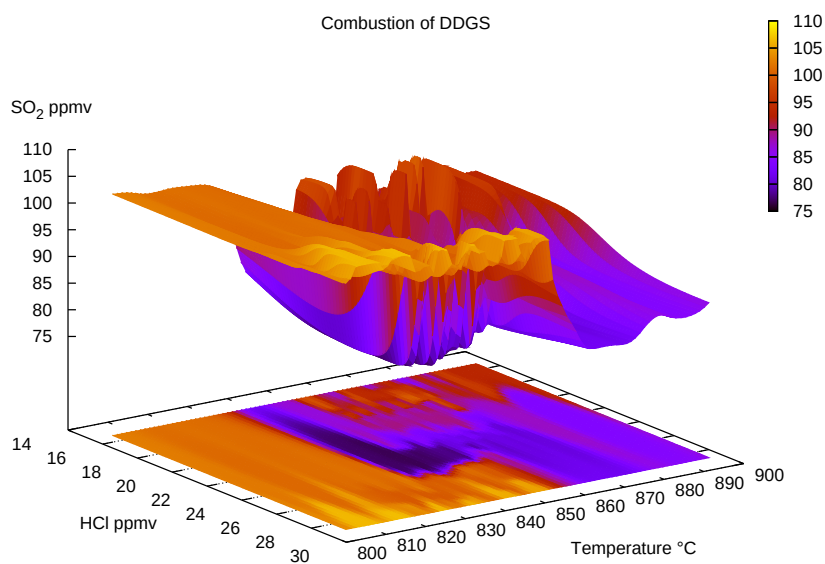


Figure 4.37: Relationship between simultaneous emissions of HCl and SO₂ for a range of combustion temperatures; combustion of DDGS 100 %.

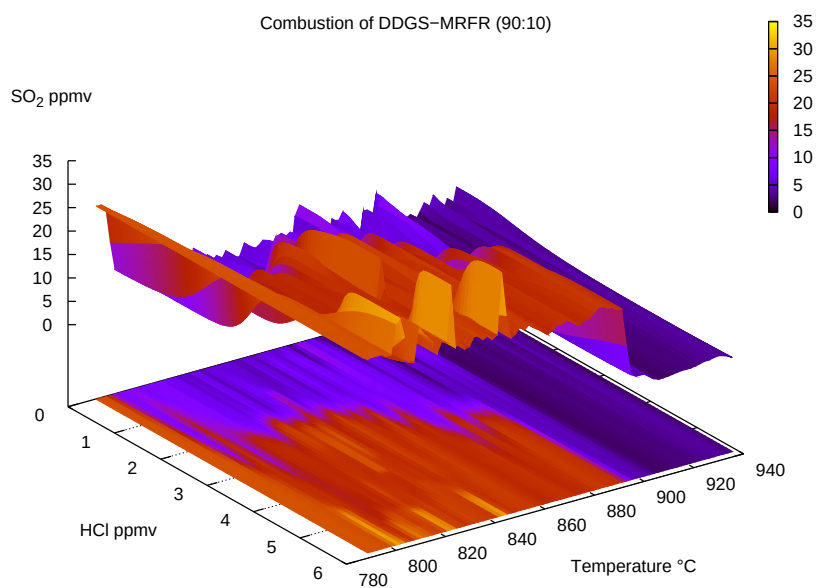


Figure 4.38: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

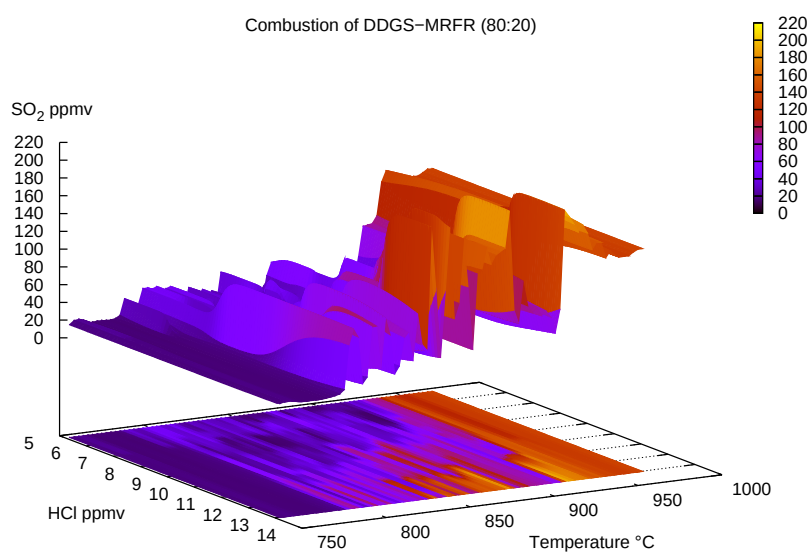


Figure 4.39: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

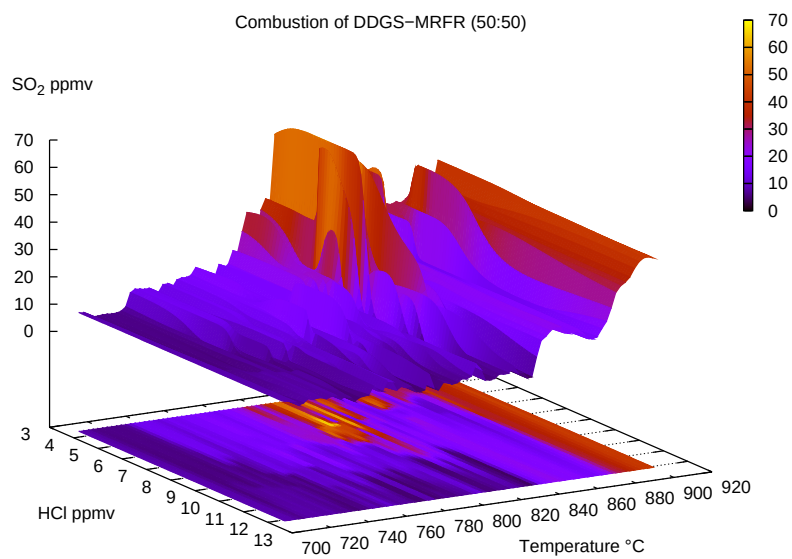


Figure 4.40: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

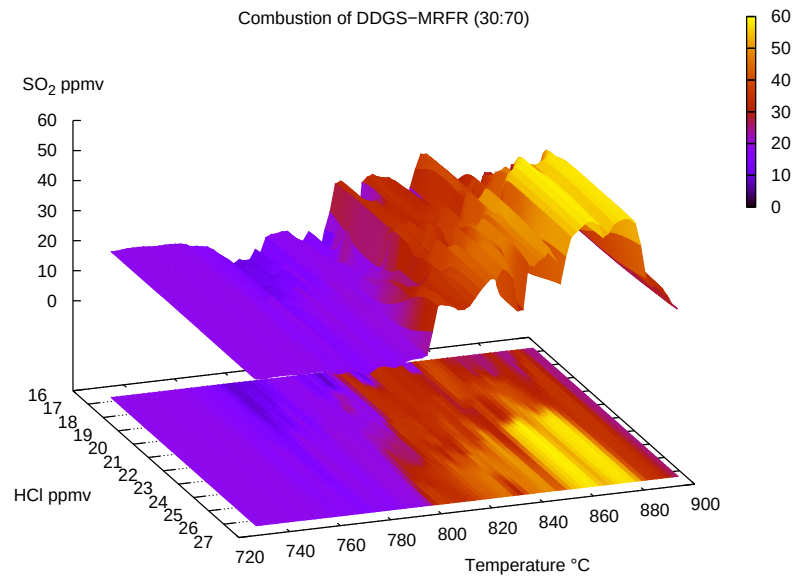


Figure 4.41: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

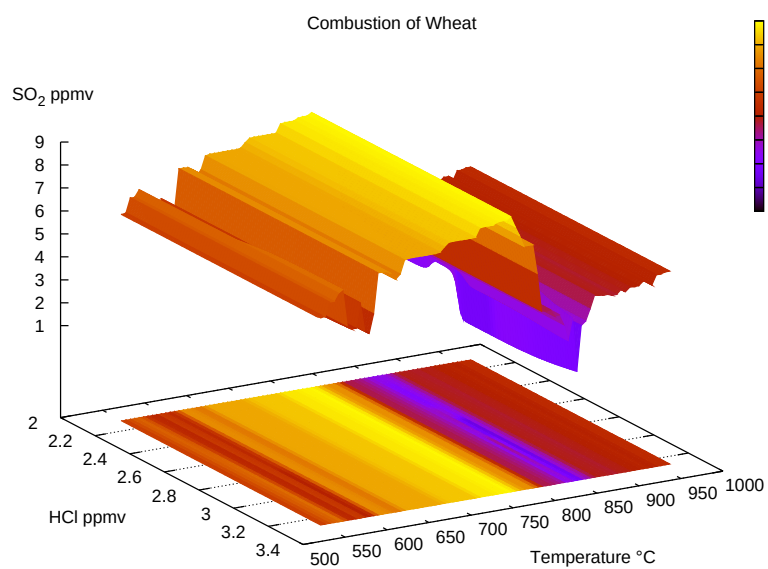


Figure 4.42: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of wheat 100 %.

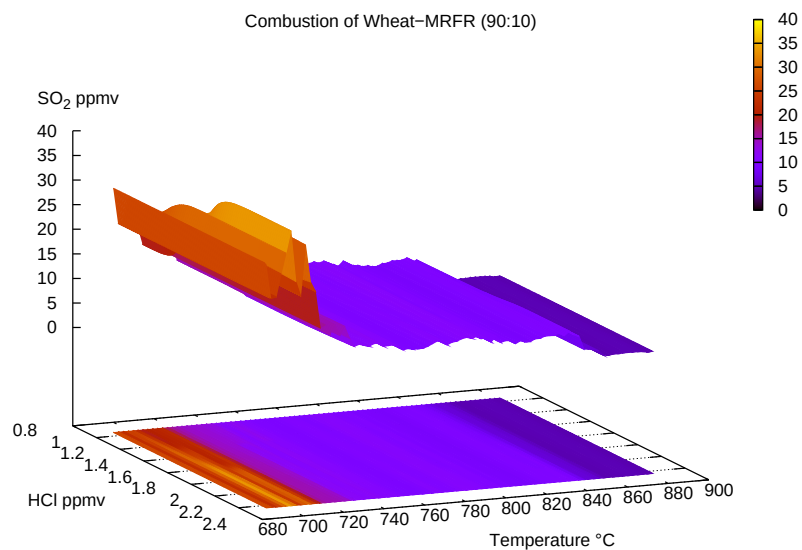


Figure 4.43: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

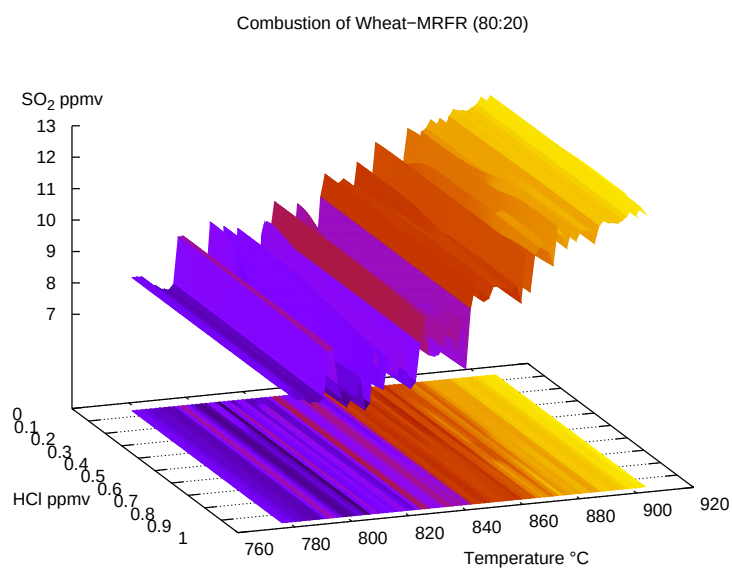


Figure 4.44: Relationship between simultaneous emissions of HCl and SO_2 for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

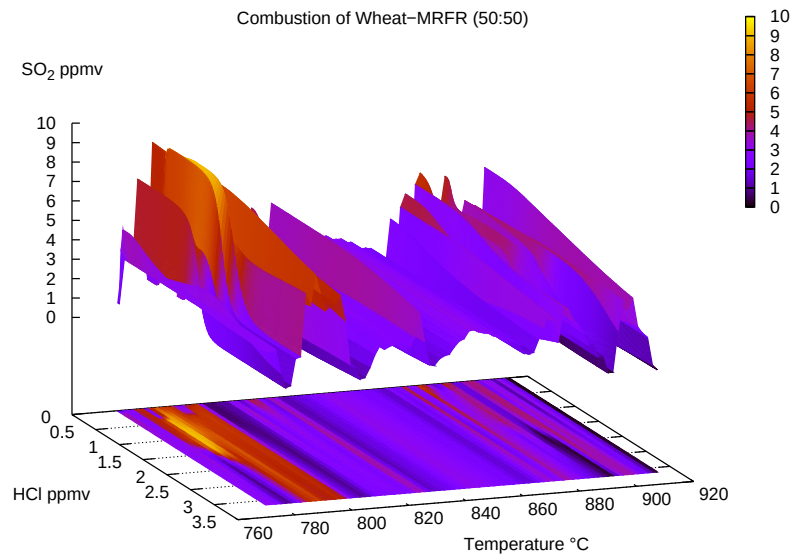


Figure 4.45: Relationship between simultaneous emissions of HCl and SO₂ for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

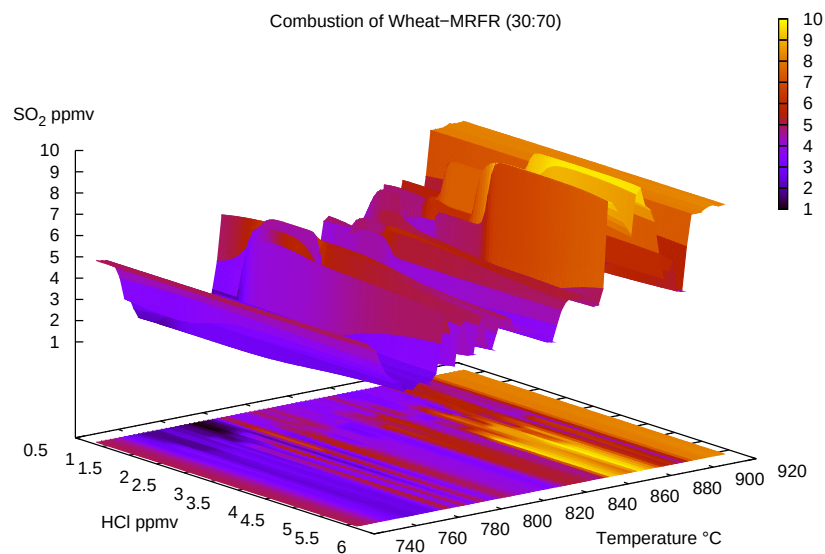


Figure 4.46: Relationship between simultaneous emissions of HCl and SO₂ for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

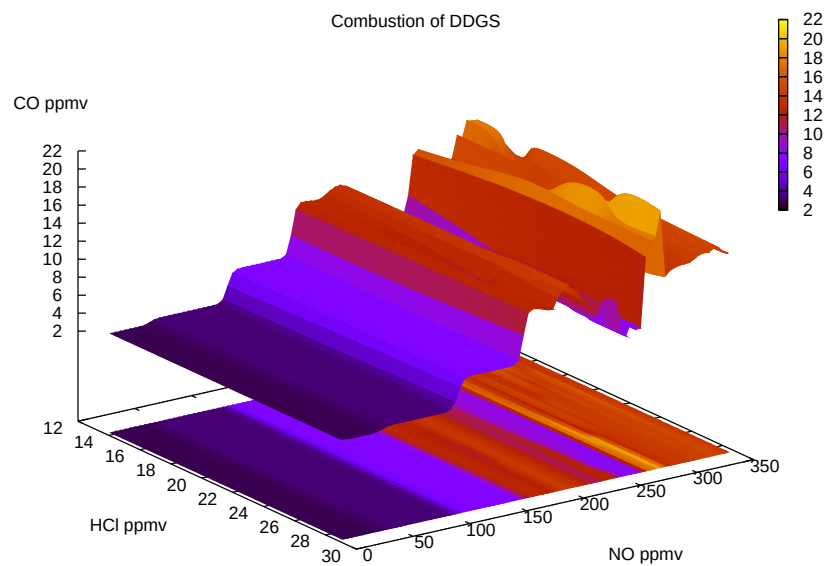


Figure 4.47: Relationship between simultaneous emissions of HCl, NO and CO; combustion of DDGS.

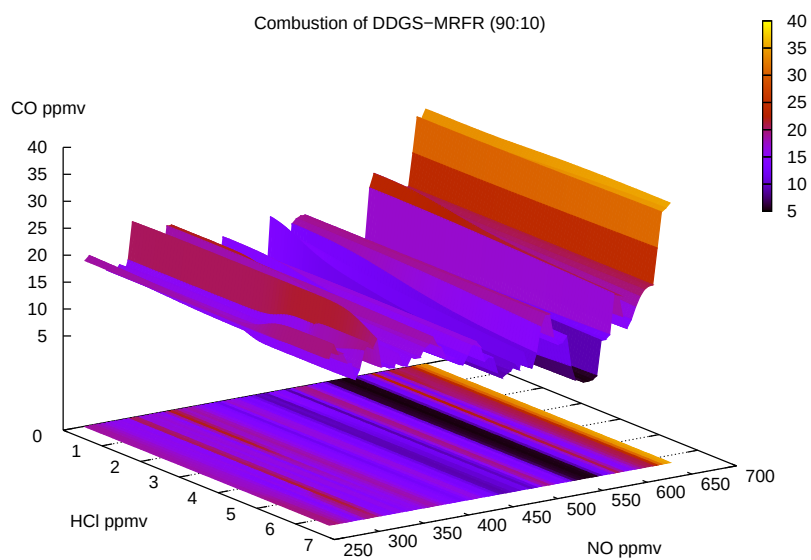


Figure 4.48: Relationship between simultaneous emissions of HCl, NO and CO; combustion of DDGS-MRFR (90:10).

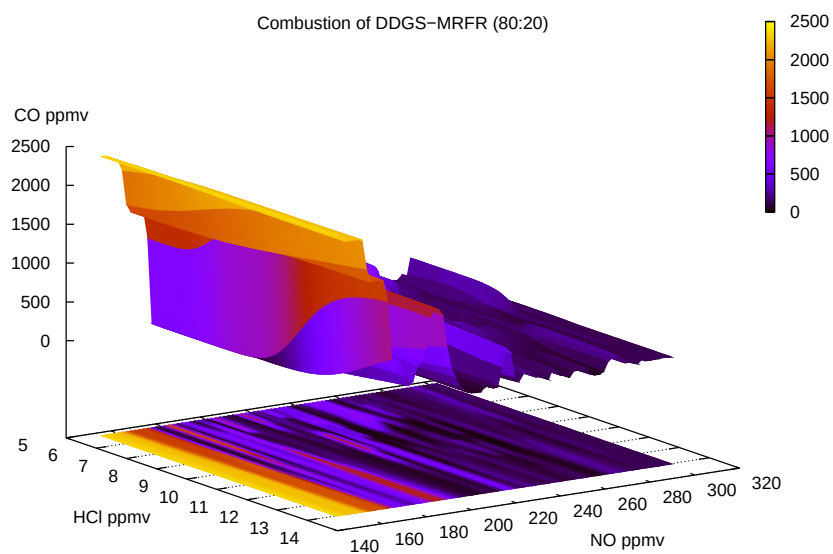


Figure 4.49: Relationship between simultaneous emissions of HCl, NO and CO; combustion of DDGS-MRFR (80:20).

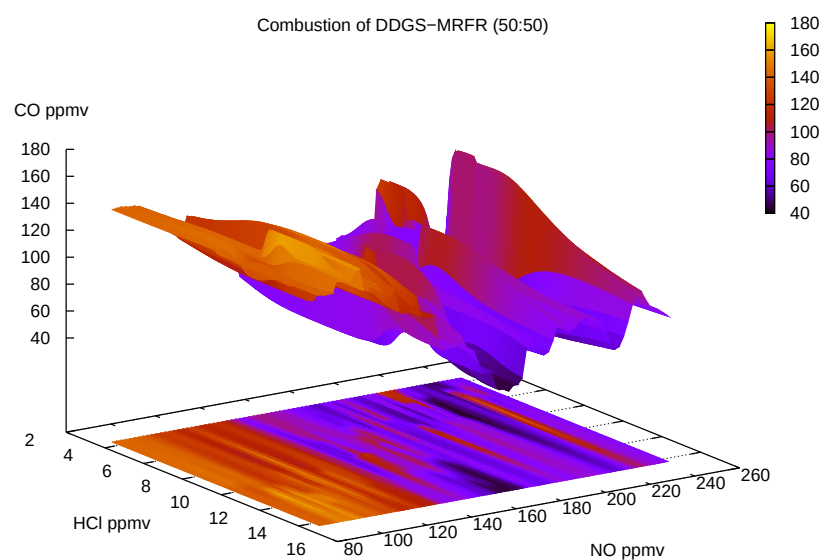


Figure 4.50: Relationship between simultaneous emissions of HCl, NO and CO; combustion of DDGS-MRFR (50:50).

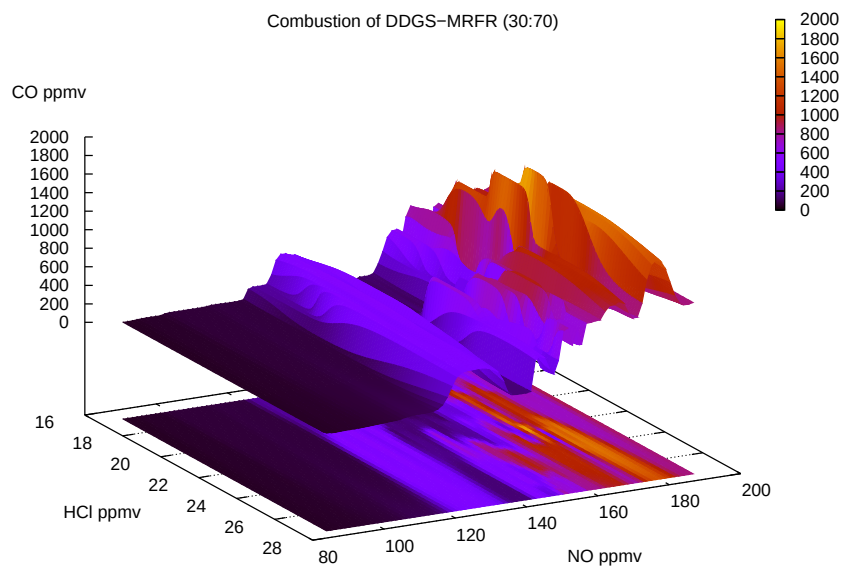


Figure 4.51: Relationship between simultaneous emissions of HCl, NO and CO; combustion of DDGS-MRFR (30:70).

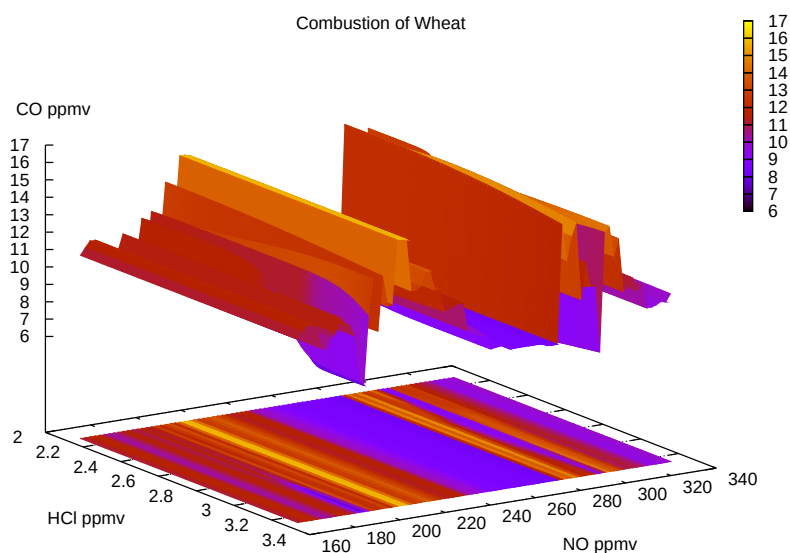


Figure 4.52: Relationship between simultaneous emissions of HCl, NO and CO; combustion of wheat.

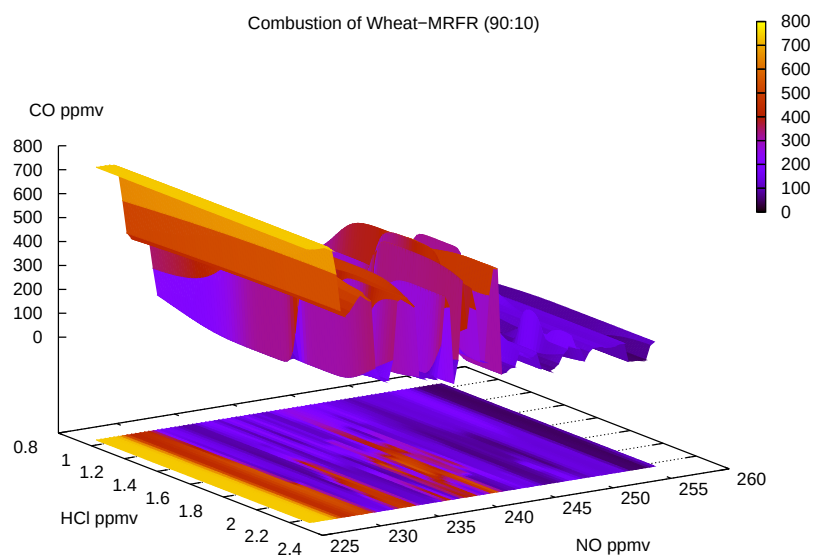


Figure 4.53: Relationship between simultaneous emissions of HCl, NO and CO; combustion of wheat-MRFR (90:10).

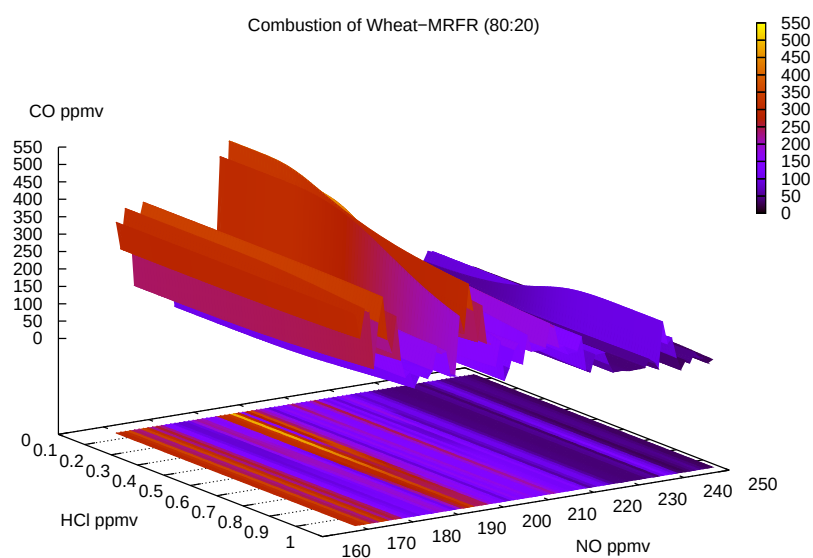


Figure 4.54: Relationship between simultaneous emissions of HCl, NO and CO; combustion of wheat-MRFR (80:20).

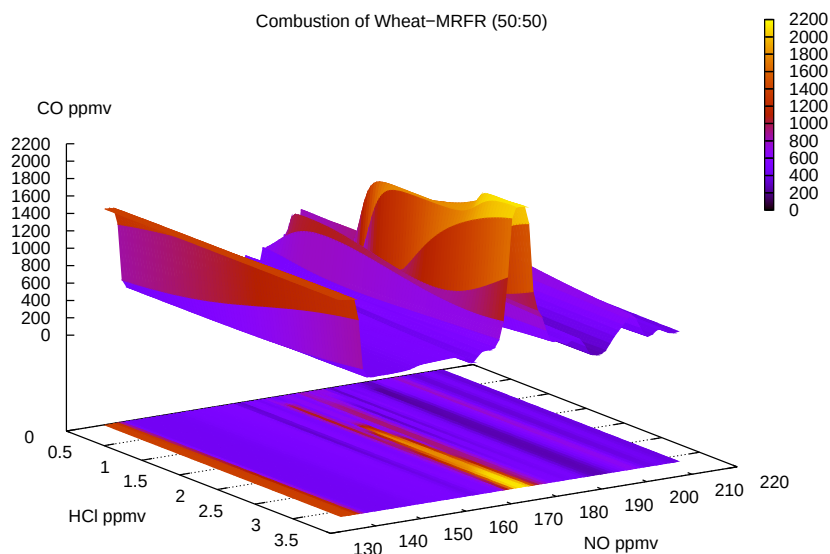


Figure 4.55: Relationship between simultaneous emissions of HCl, NO and CO; combustion of wheat-MRFR (50:50).

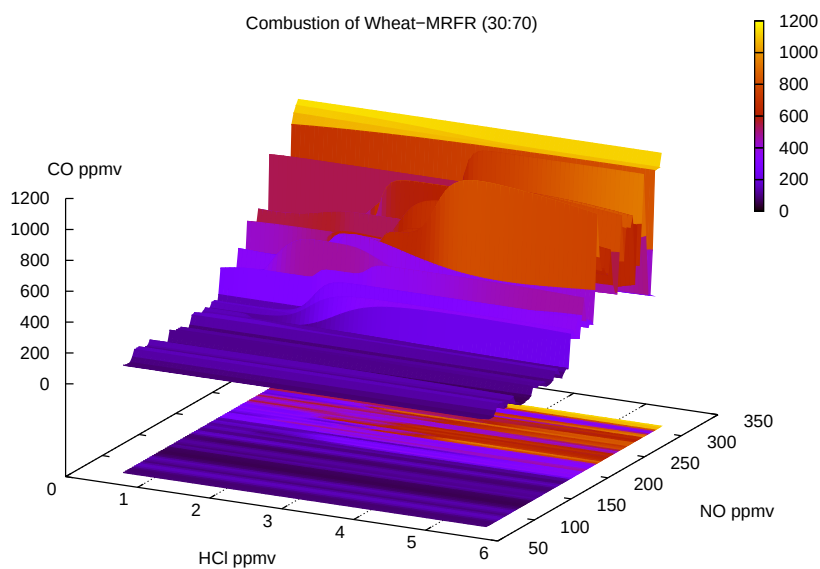


Figure 4.56: Relationship between simultaneous emissions of HCl, NO and CO; combustion of wheat-MRFR (30:70).

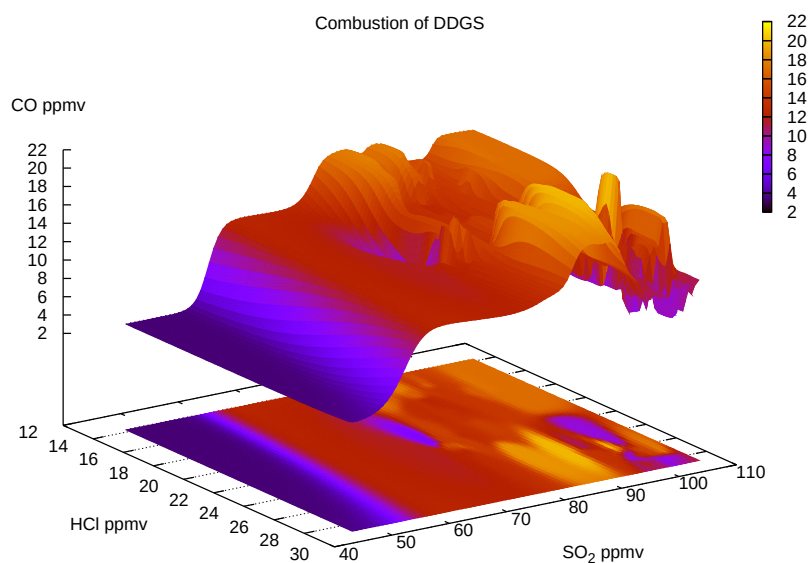


Figure 4.57: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of DDGS.

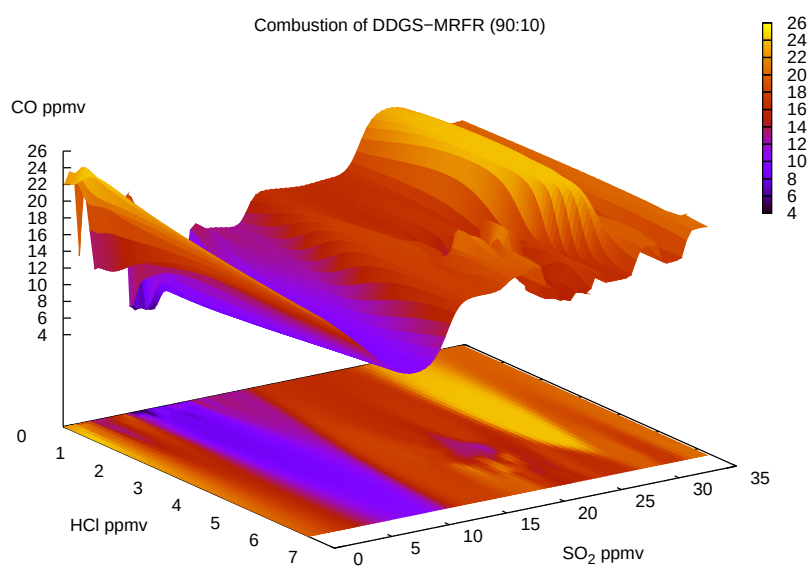


Figure 4.58: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of DDGS-MRFR (90:10).

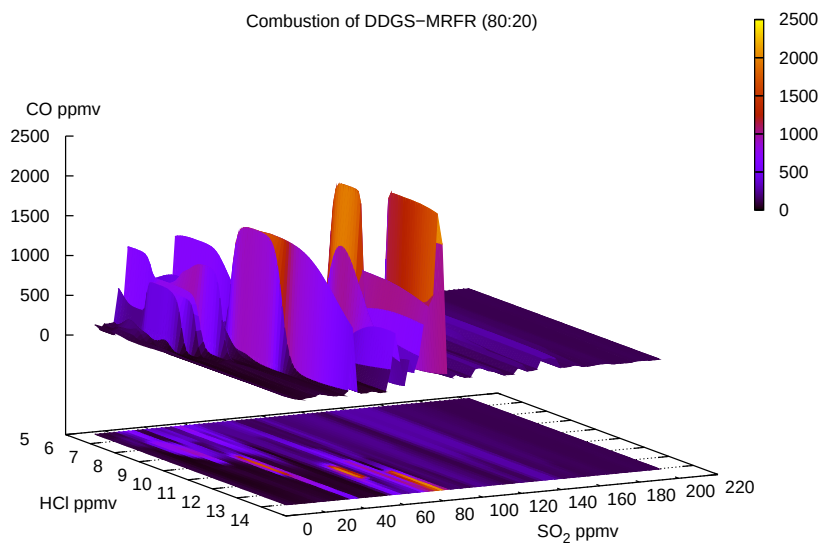


Figure 4.59: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of DDGS-MRFR (80:20).

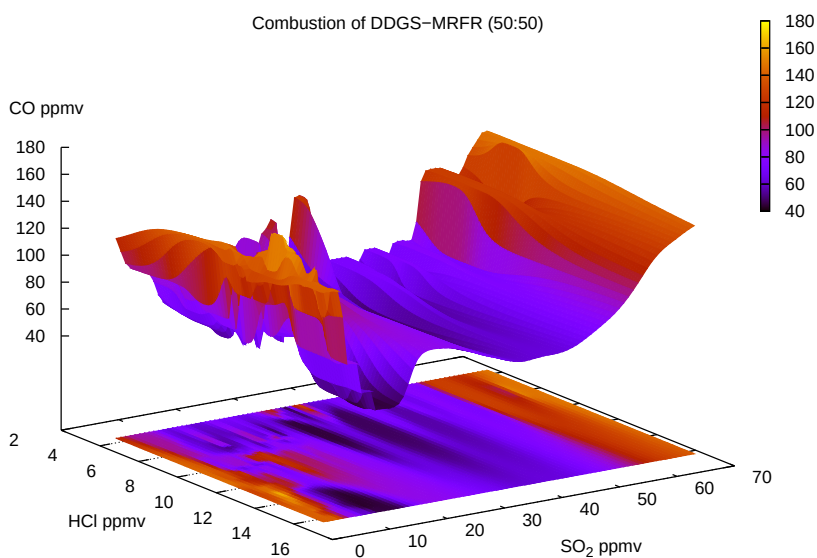


Figure 4.60: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of DDGS-MRFR (50:50).

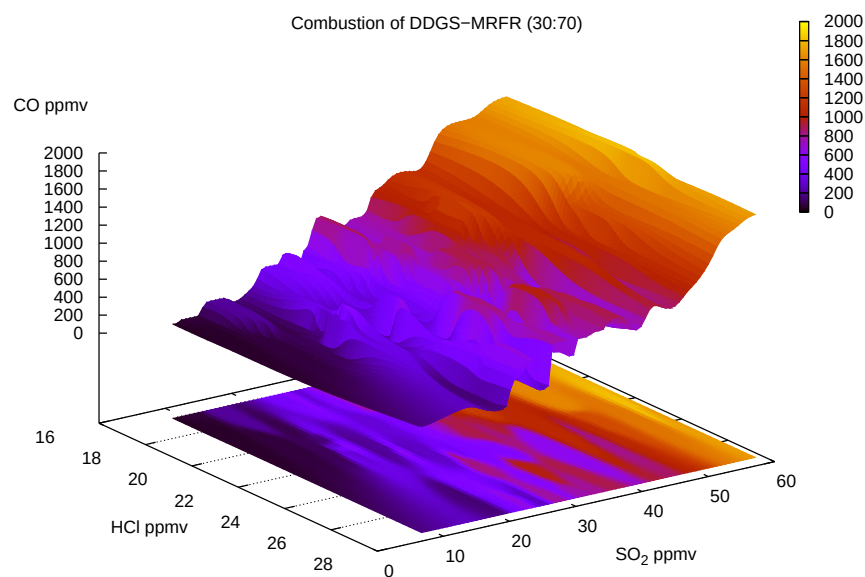


Figure 4.61: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of DDGS-MRFR (30:70).

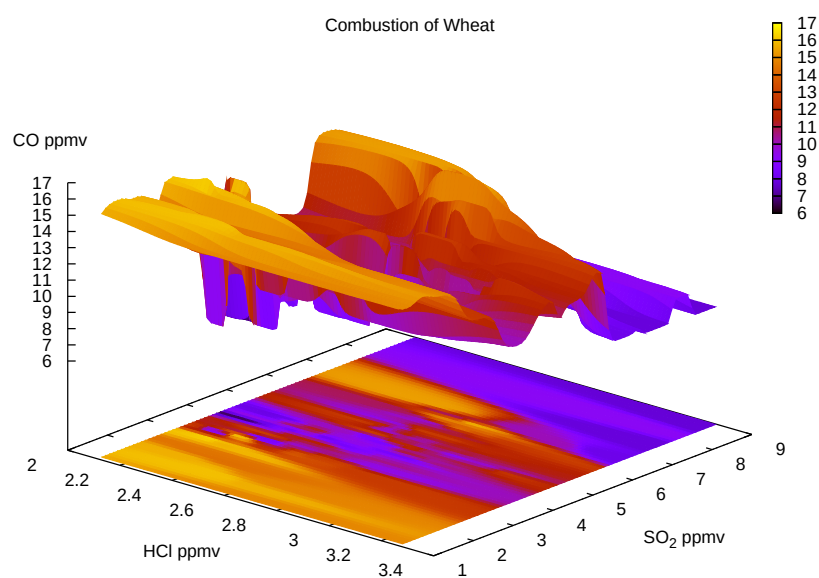


Figure 4.62: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of wheat.

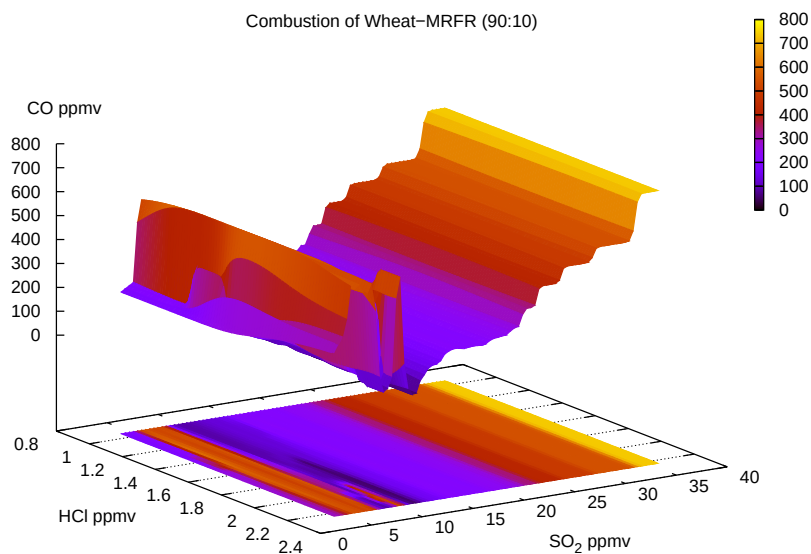


Figure 4.63: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of wheat-MRFR (90:10).

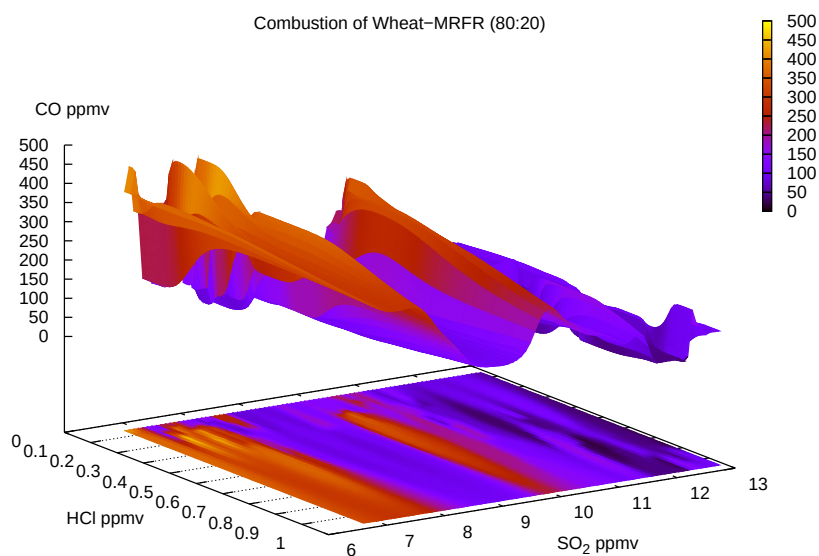


Figure 4.64: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of wheat-MRFR (80:20).

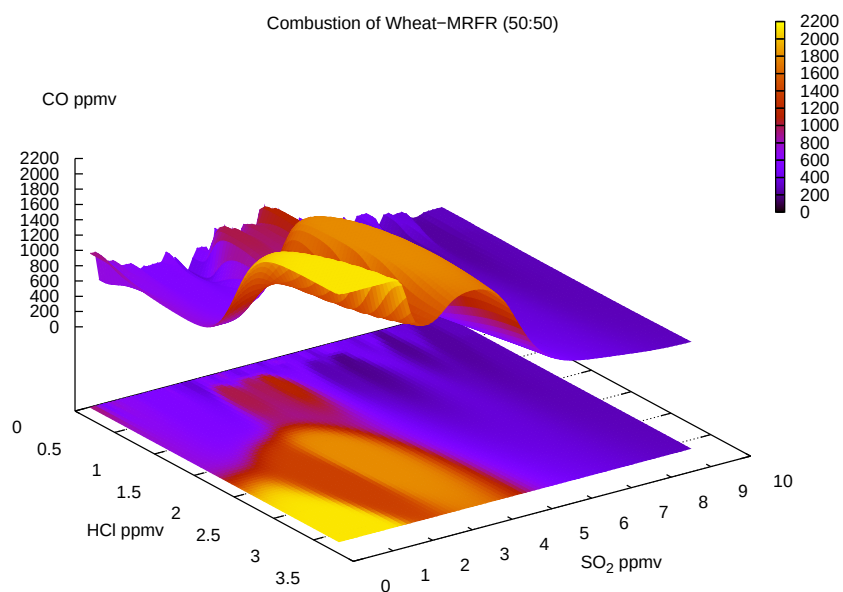


Figure 4.65: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of wheat-MRFR (50:50).

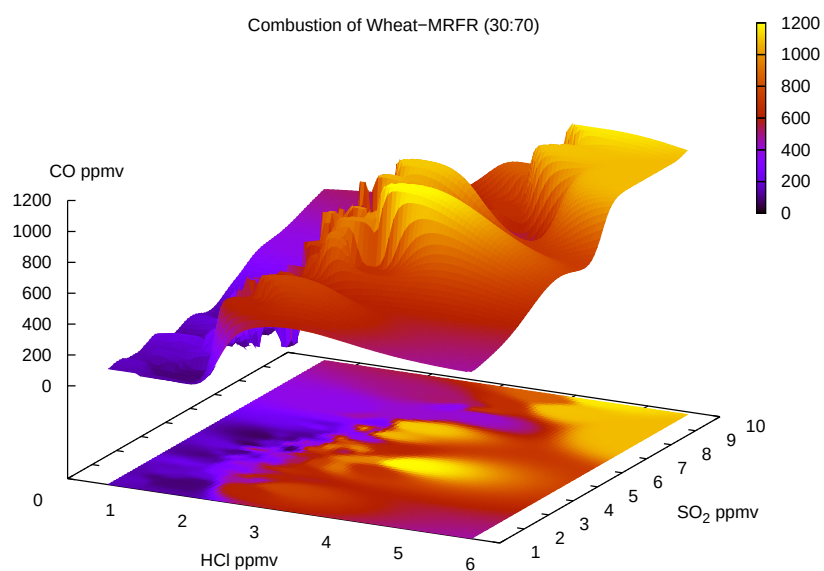


Figure 4.66: Relationship between simultaneous emissions of HCl, SO₂ and CO; combustion of wheat-MRFR (30:70).

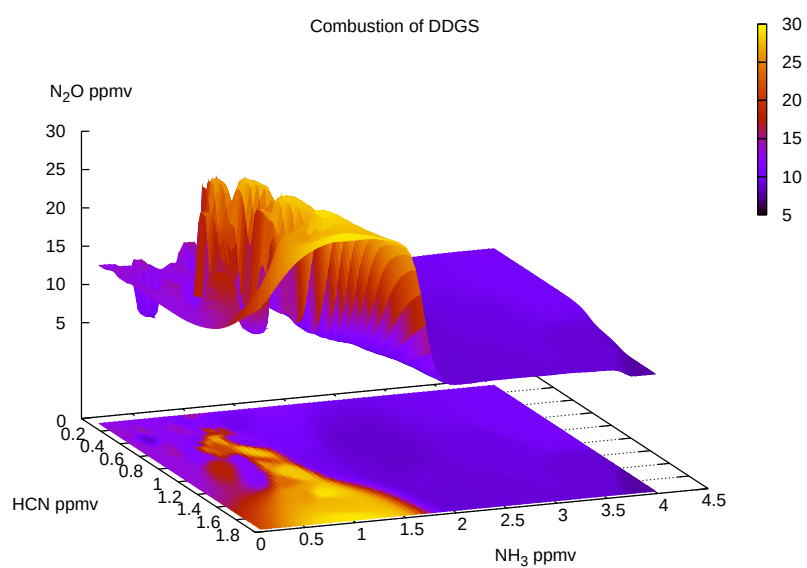


Figure 4.67: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of DDGS.

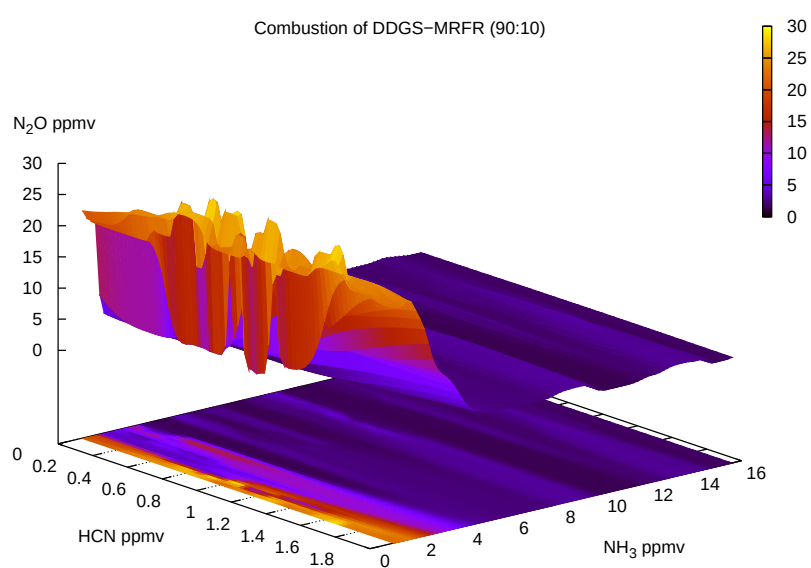


Figure 4.68: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

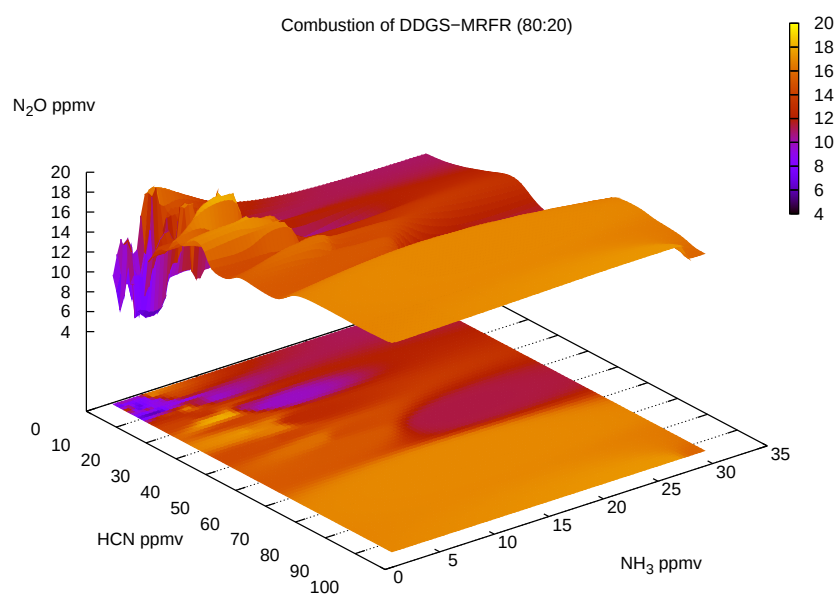


Figure 4.69: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

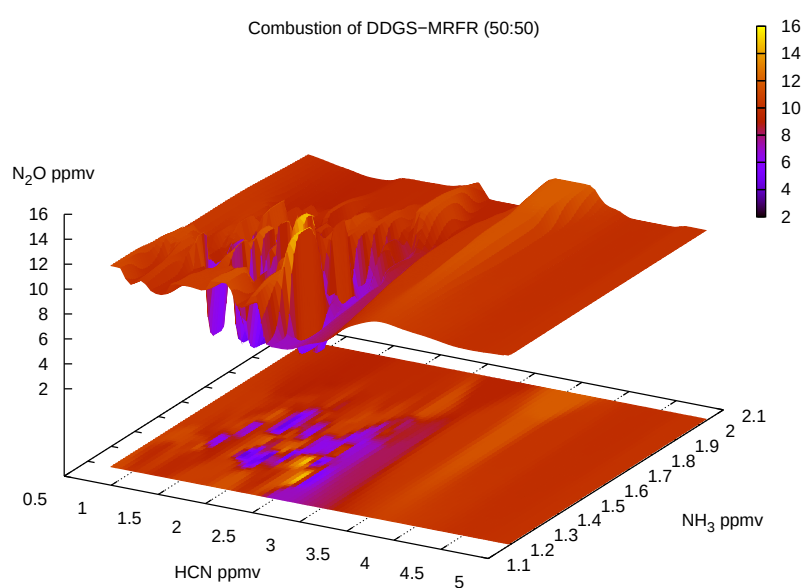


Figure 4.70: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

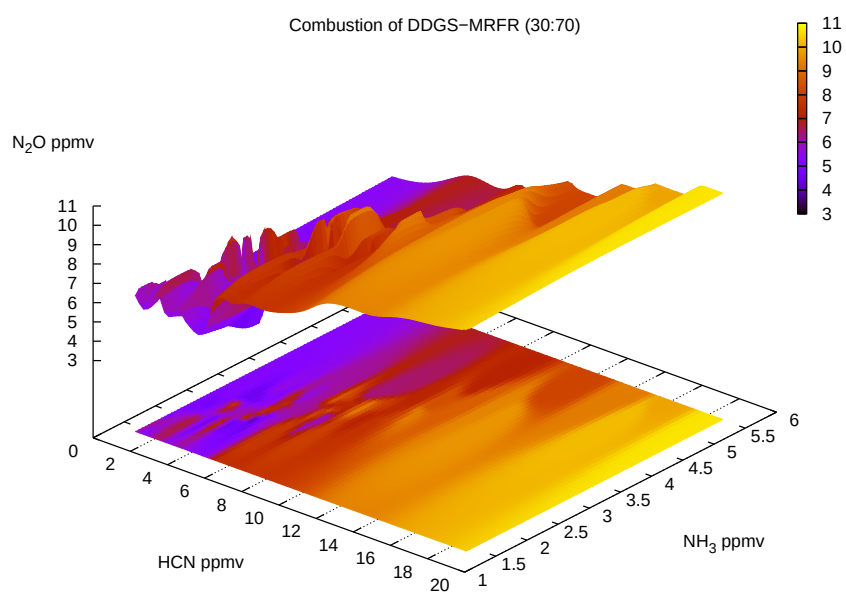


Figure 4.71: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

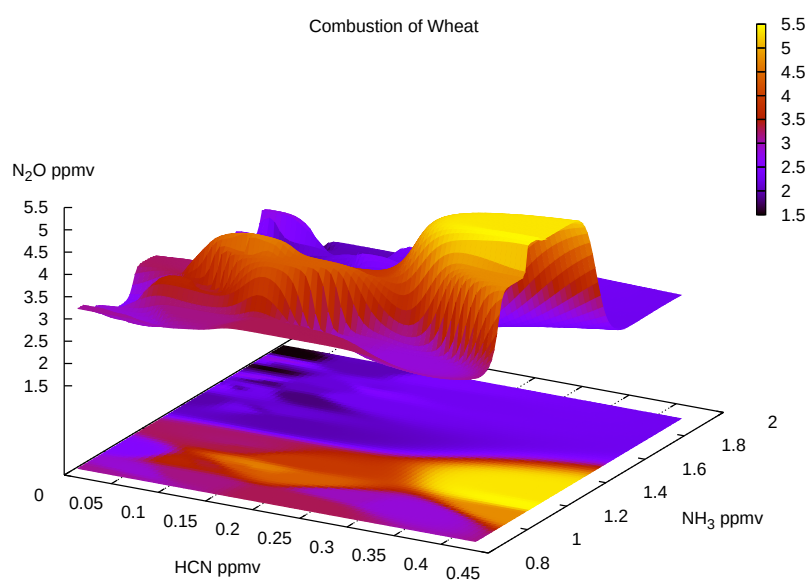


Figure 4.72: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of wheat.

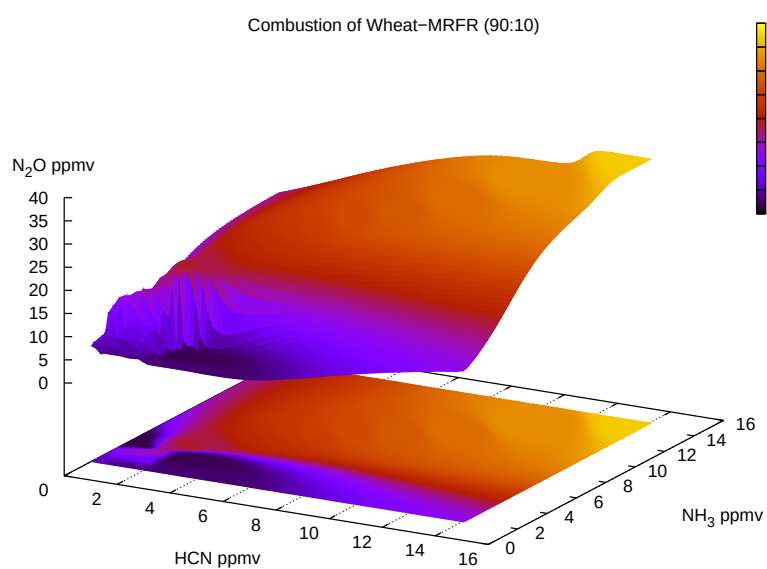


Figure 4.73: Relationship between simultaneous emissions of HCN, NH_3 and N_2O for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

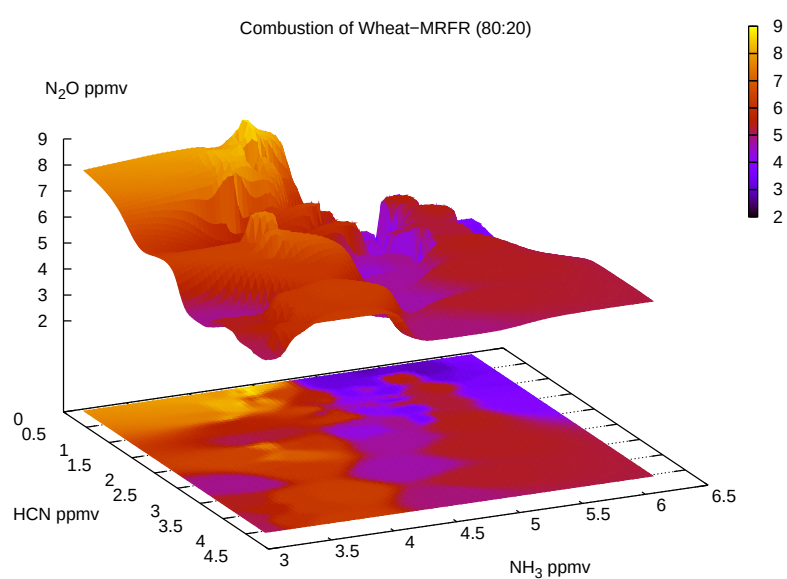


Figure 4.74: Relationship between simultaneous emissions of HCN, NH_3 and N_2O for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

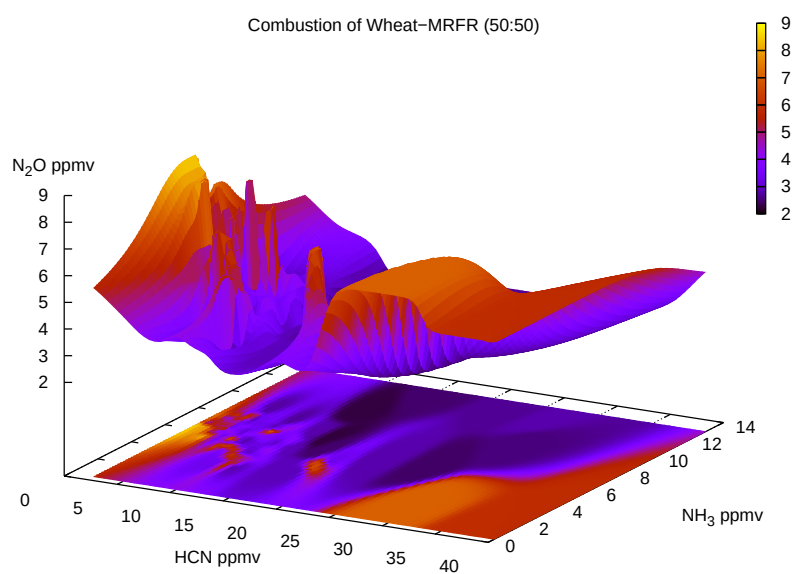


Figure 4.75: Relationship between simultaneous emissions of HCN, NH₃ and N₂O for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

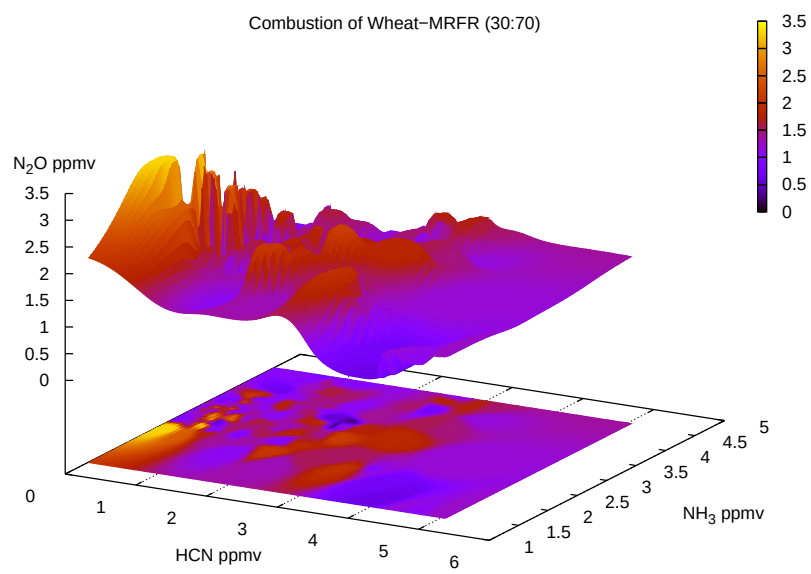


Figure 4.76: Relationship between simultaneous emissions of HCN, NH_3 and N_2O for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

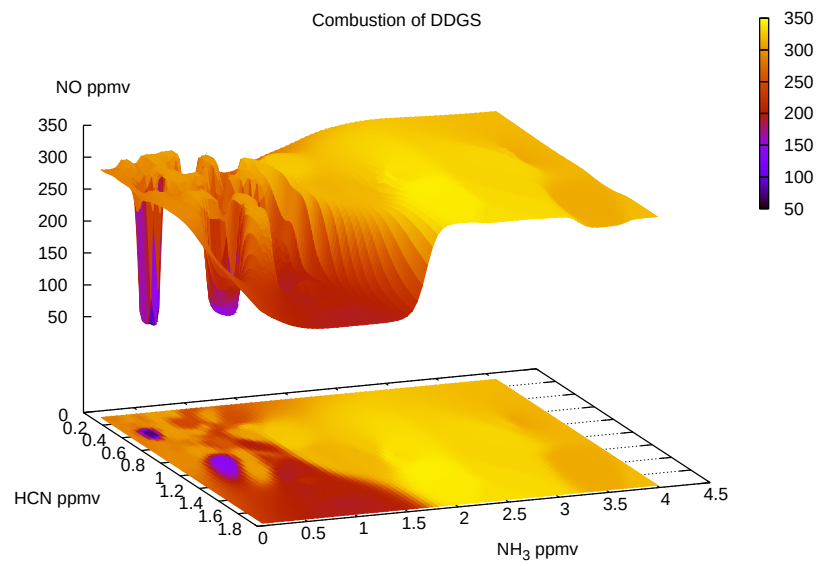


Figure 4.77: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of DDGS.

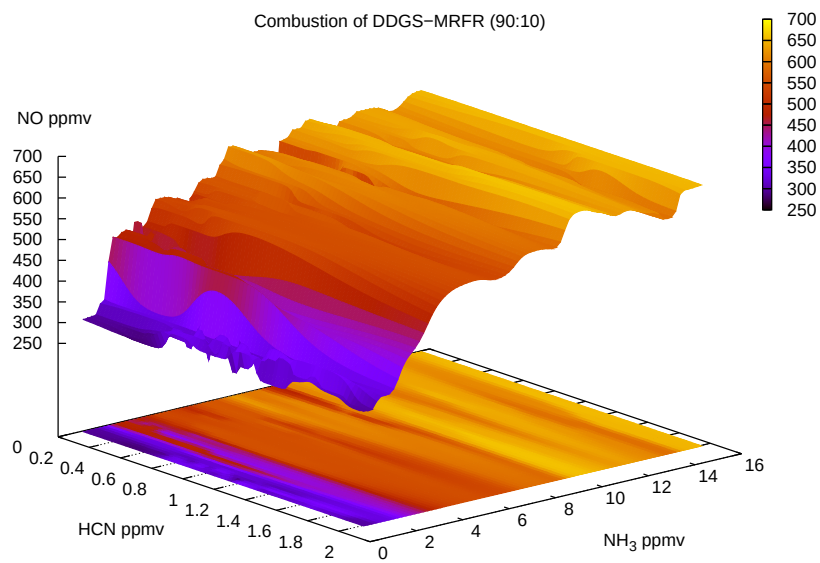


Figure 4.78: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

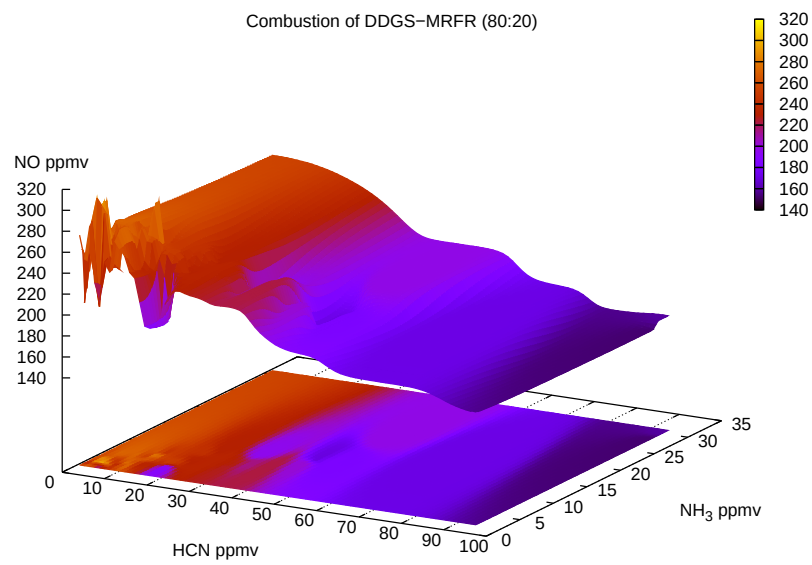


Figure 4.79: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

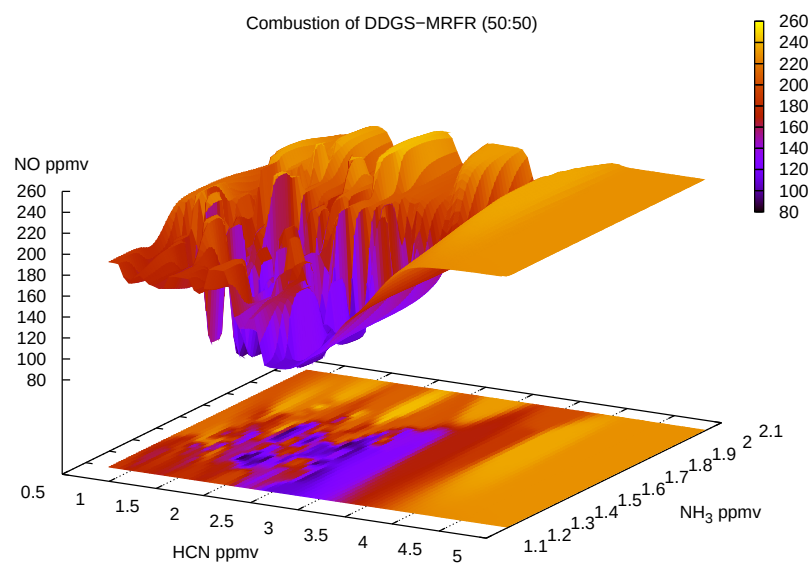


Figure 4.80: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

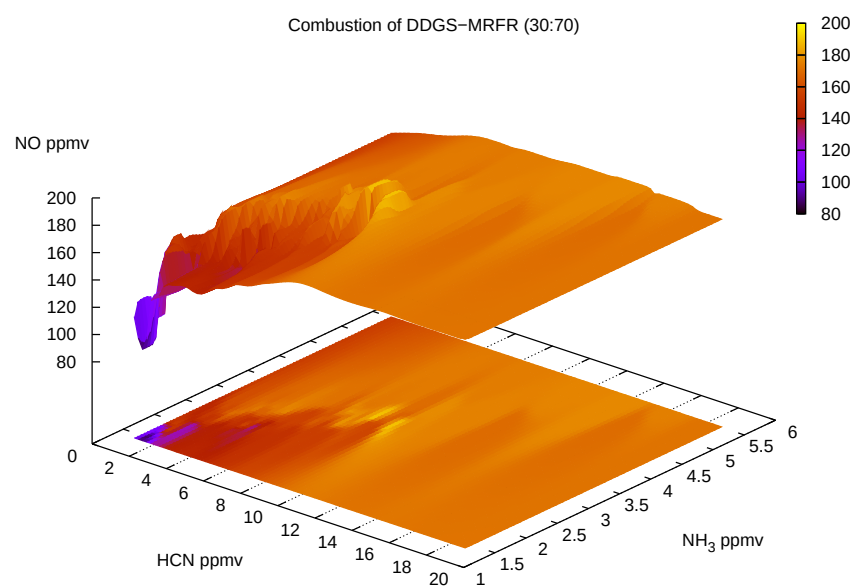


Figure 4.81: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

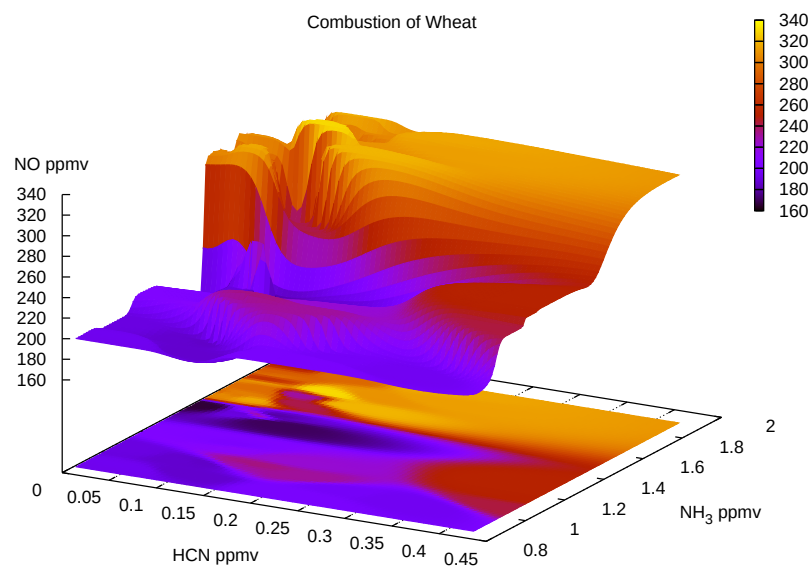


Figure 4.82: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of wheat.

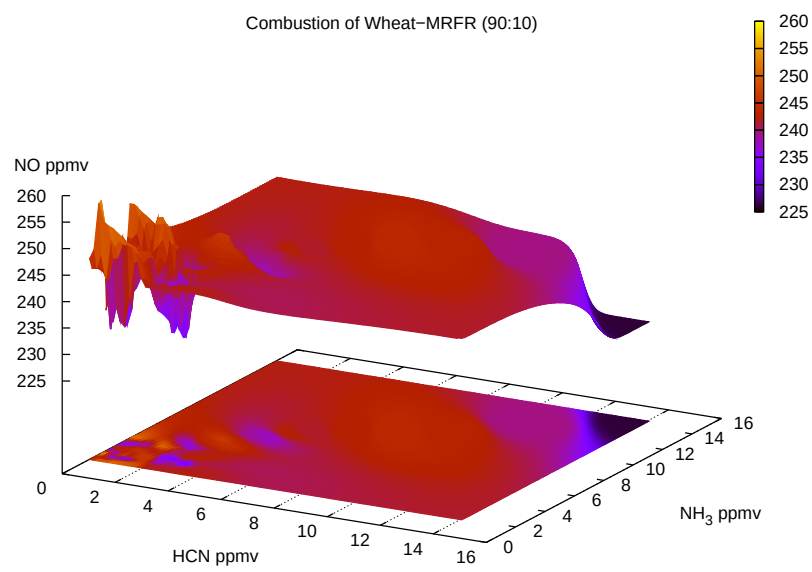


Figure 4.83: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

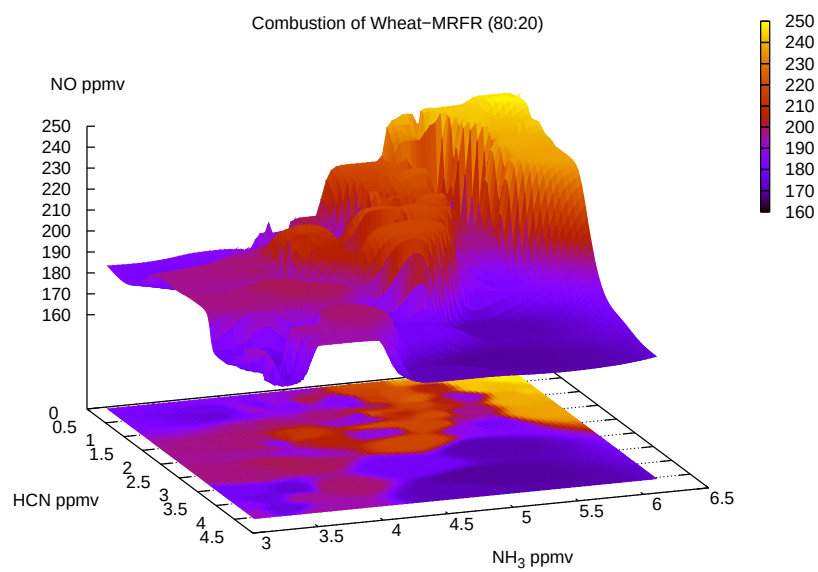


Figure 4.84: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

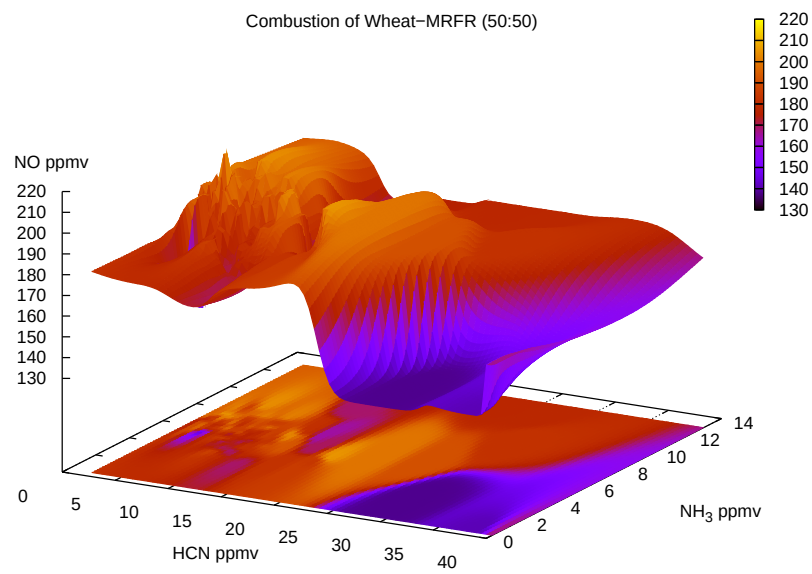


Figure 4.85: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

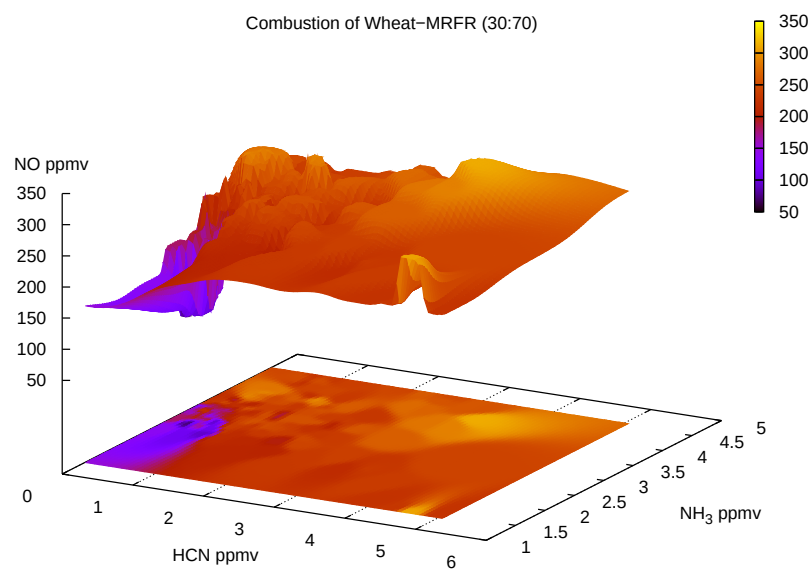


Figure 4.86: Relationship between simultaneous emissions of HCN, NH₃ and NO for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

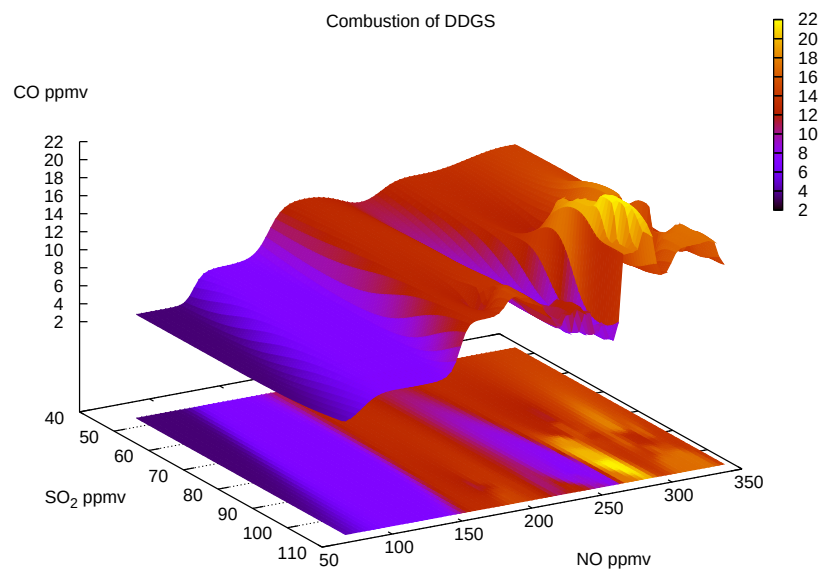


Figure 4.87: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of DDGS.

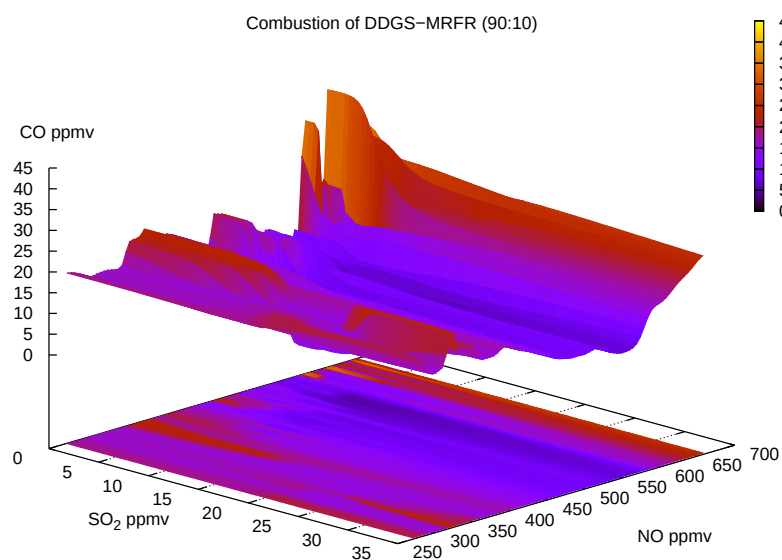


Figure 4.88: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of DDGS-MRFR (90:10).

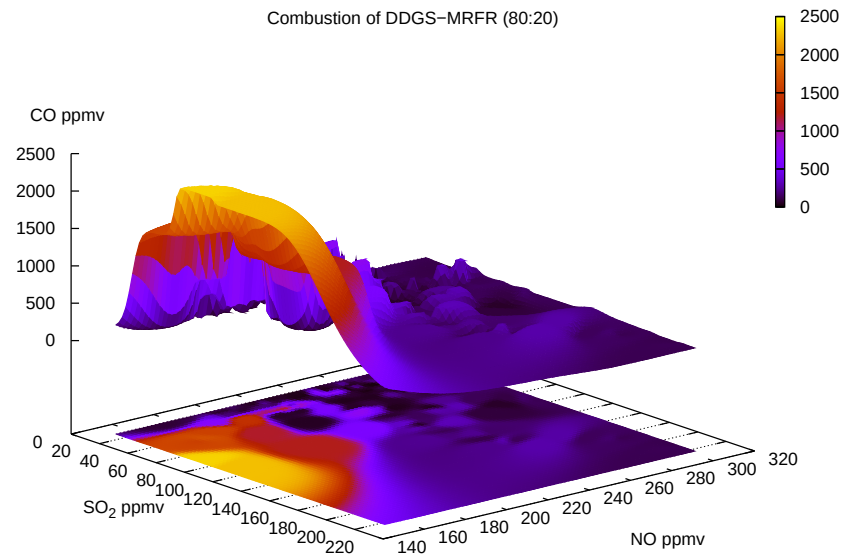


Figure 4.89: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of DDGS-MRFR (80:20).

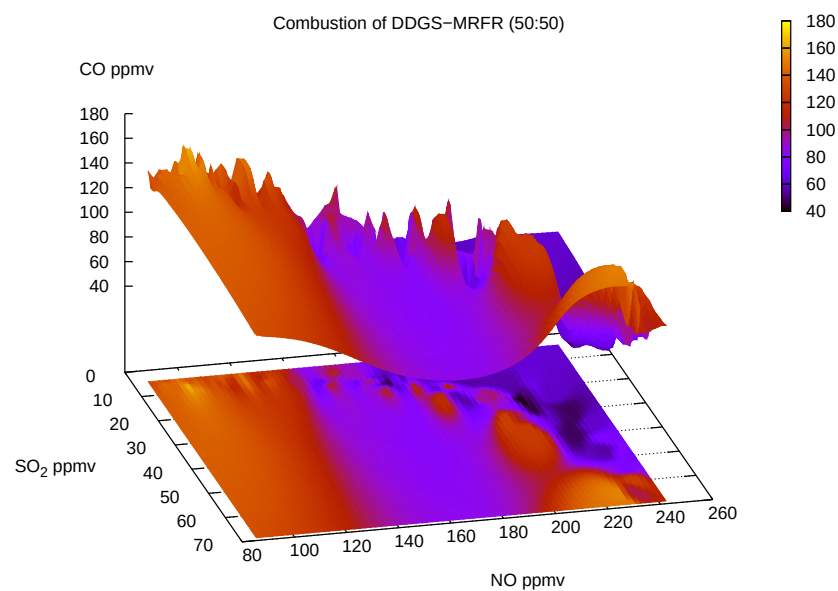


Figure 4.90: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of DDGS-MRFR (50:50).

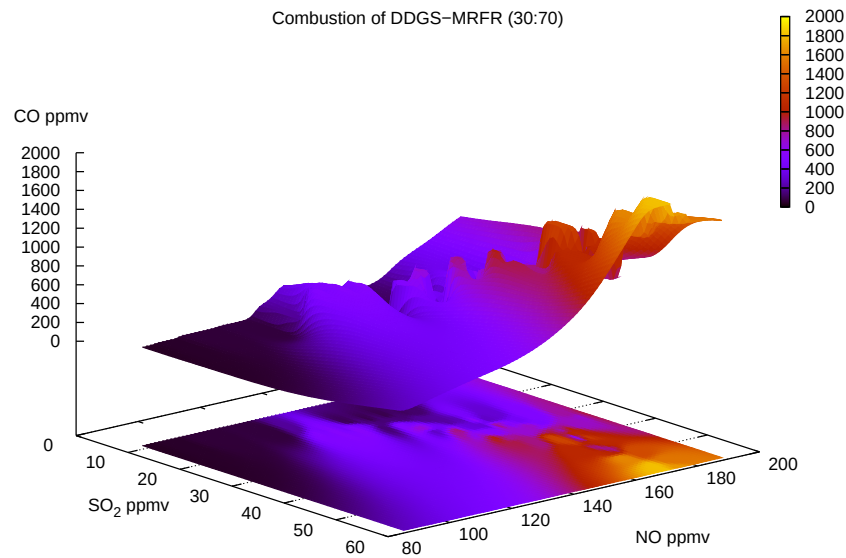


Figure 4.91: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of DDGS-MRFR (30:70).

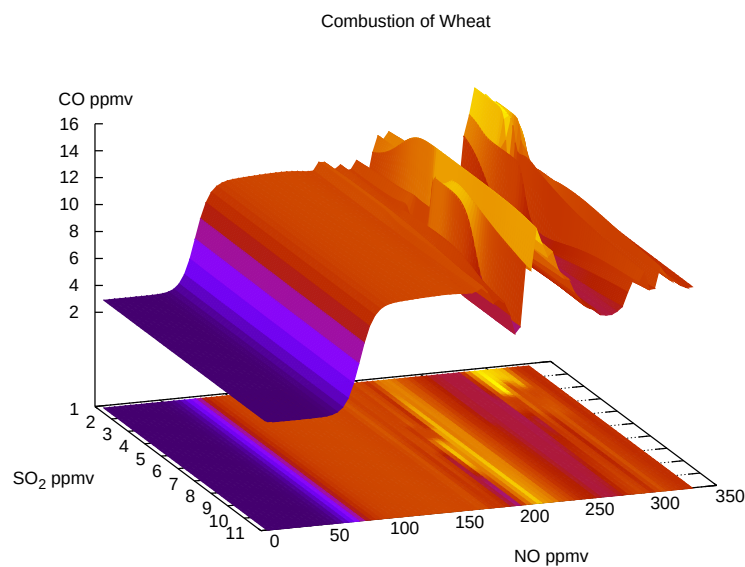


Figure 4.92: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of wheat.

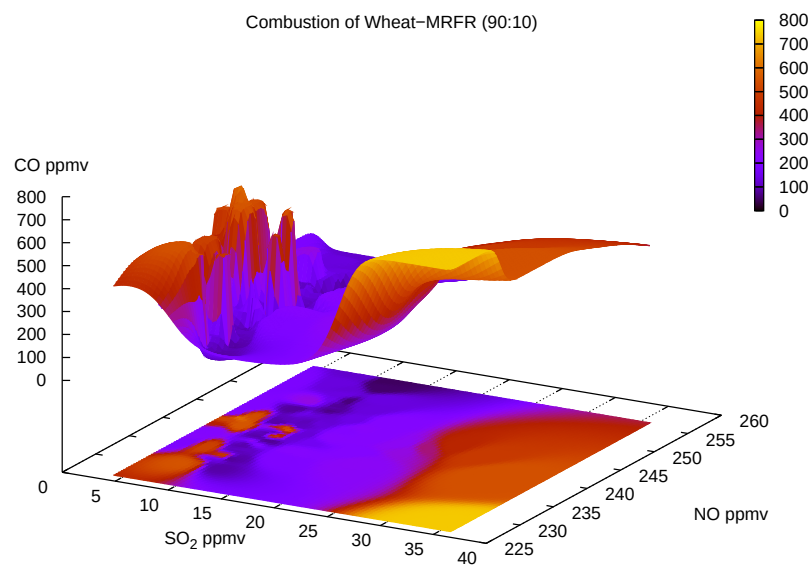


Figure 4.93: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of wheat-MRFR (90:10).

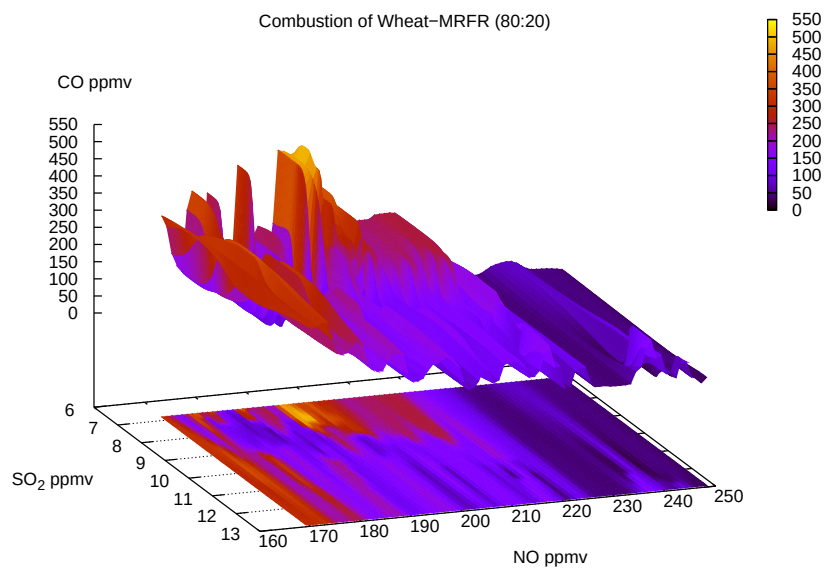


Figure 4.94: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of wheat-MRFR (80:20).

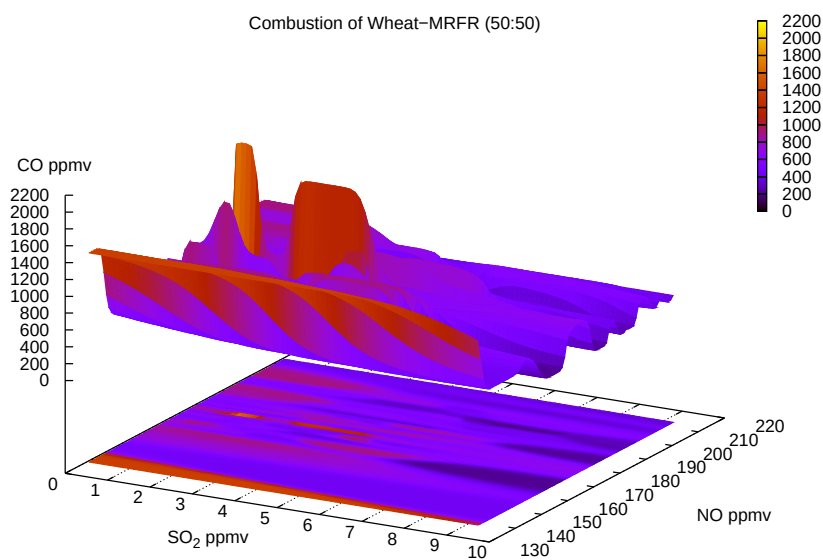


Figure 4.95: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of wheat-MRFR (50:50).

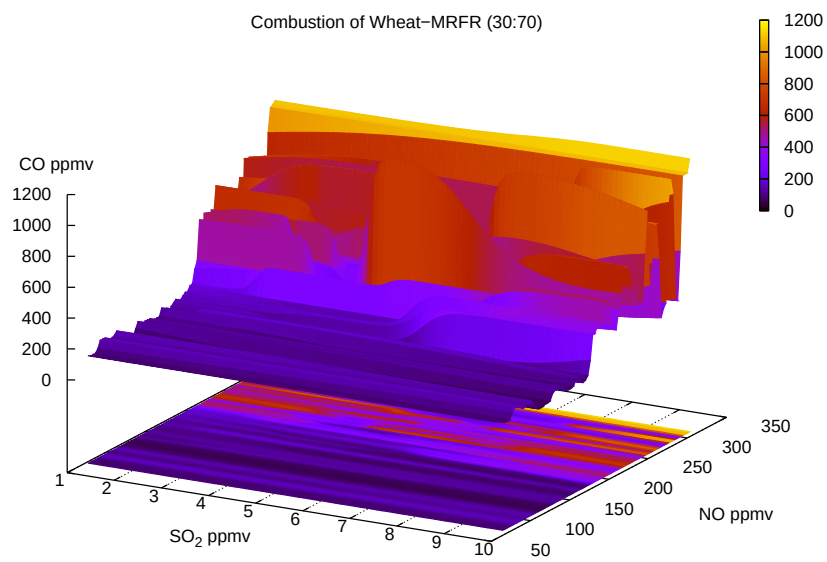


Figure 4.96: Relationship between simultaneous emissions of SO₂, NO and CO for a range of combustion temperatures; combustion of wheat-MRFR (30:70).

4.4 Trace level pollutants flue gas analysis

4.4.1 Trace metal determination

Analysis of trace metals content in the test samples was performed by technical personnel at Queen Mary, University of London using ICP-OES instrumentation. The following table (Table 4.5) shows the results obtained. Values denoted with an asterisk (*) represent measurements recorded below the limit of detection for the corresponding radiation wavelength of the metal.

Table 4.5: Trace metal content in combustion tests' flue gases' samples ($\mu\text{g l}^{-1}$).

	Na	Mg	Al	P	K	Ca
DDGS	2614.25	174.631	44907.4	240.964	1718.73	800.277
DDGS-MRFR (90:10)	2030.23	106.26	53293.2	50.602*	1101.11	963.048
DDGS-MRFR (80:20)	6115.5	416.626	184768.0	798.882	4776.14	6979.42
DDGS-MRFR (50:50)	2173.12	115.501	42229.2	98.265*	1147.09	793.205
DDGS-MRFR (30:70)	6435.86	356.4	425550.0	361.217	5501.3	1738.6
Wheat	3539.98	222.418	140059.0	256.402	2392.85	2772.75
Wheat-MRFR (90:10)	17730.2	1989.1	85134.2	1542.3	5687.12	168465.0
Wheat-MRFR (80:20)	5687.97	267.806	107107.0	80.045*	2348.36	2273.05
Wheat-MRFR (50:50)	5214.24	309.694	93195.2	226.464	4130.91	2569.17
Wheat-MRFR (30:70)	6455.19	513.492	144567.0	364.109	4867.54	5398.1
sample blank	35942.3	111.739	159692.0	55.952*	1298.81	1139.25
Wheat-MRFR (90:10, repeat 1)	11966.1	609.629	225783.0	517.306	7868.93	33744.4
Wheat-MRFR (90:10, repeat 2)	4558.54	243.443	33925.5	50.862*	1376.88	2476.48

Table 4.5: Trace metal content in combustion tests' flue gases' samples ($\mu\text{g l}^{-1}$).

	Ti	V	Cr	Mn	Fe	Co
DDGS	316.636	2.262*	4.331	17.536	353.102	5.085*
DDGS-MRFR (90:10)	223.723	2.935*	3.573*	10.473	423.149	0*
DDGS-MRFR (80:20)	340.075	8.239	15.569	61.195	1052.54	2.689*
DDGS-MRFR (50:50)	290.89	4.514	7.692	13.152	393.435	5.794*
DDGS-MRFR (30:70)	234.771	11.15	8.549	58.996	1054.38	5.716*
Wheat	426.354	9.724	30.644	28.885	1039.72	3.855*
Wheat-MRFR (90:10)	502.201	7.105	45.462	109.199	1499.41	6.91*
Wheat-MRFR (80:20)	515.785	6.142	10.152	14.674	858.581	0.149*
Wheat-MRFR (50:50)	305.89	4.504	8.249	38.762	636.962	2.761*
Wheat-MRFR (30:70)	364.815	6.142	27.616	78.048	867.205	1.14*
sample blank	184.869	7.18	6.015	14.991	707.34	2.196*
Wheat-MRFR (90:10, repeat 1)	440.107	18.136	29.04	67.08	2947.87	1.11*
Wheat-MRFR (90:10, repeat 2)	646.696	2.428*	8.614	9.873	674.02	1.976*

Table 4.5: Trace metal content in combustion tests’ flue gases’ samples ($\mu\text{g l}^{-1}$).

	Ni	Cu	Zn	Sr	Rh
DDGS	12.779*	10.173	1294.02	5.602	0*
DDGS-MRFR (90:10)	6.389*	9.973	307.684	5.489	0*
DDGS-MRFR (80:20)	13.508*	28.932	1341.01	17.922	0*
DDGS-MRFR (50:50)	11.393*	13.578	211.589	8.738	1.63*
DDGS-MRFR (30:70)	9.13*	43.904	664.281	13.817	2.174*
Wheat	15.998*	47.8	432.037	11.936	1.817*
Wheat-MRFR (90:10)	28.916*	55.031	849.488	82.319	0*
Wheat-MRFR (80:20)	187.131	17.036	263.438	13.683	0.849*
Wheat-MRFR (50:50)	10.316*	15.165	758.737	12.304	0.19*
Wheat-MRFR (30:70)	15.032*	44.785	2336.94	18.918	0.448*
sample blank	15.739*	12.006	499.004	5.051	0.406*
Wheat-MRFR (90:10, repeat 1)	19.625*	25.1	790.38	30.78	0*
Wheat-MRFR (90:10, repeat 2)	18.044*	14.567	429.697	14.353	0*

Table 4.5: Trace metal content in combustion tests' flue gases' samples ($\mu\text{g l}^{-1}$).

	Ag	Cd	Sn	Hg	Pb
DDGS	6.944	0*	0*	70.815*	10.785*
DDGS-MRFR (90:10)	9.554	1.446*	0*	226.291	15.221*
DDGS-MRFR (80:20)	5.026	4.593*	0*	73.094*	22.801*
DDGS-MRFR (50:50)	13.452	0*	1.887*	160.042	7.284*
DDGS-MRFR (30:70)	3.471	0*	0*	527.644	0.071*
Wheat	1.769*	0*	4.364*	96.052	37.03*
Wheat-MRFR (90:10)	221.952	27.436*	10.254*	65.255*	60.524*
Wheat-MRFR (80:20)	11.71	2.755*	1.101*	416.849	11.23*
Wheat-MRFR (50:50)	29.751	0*	0*	425.334	29.596*
Wheat-MRFR (30:70)	0.967*	1.307*	6.354*	185.982	84.89*
sample blank	17.915	0*	0*	81.806	0*
Wheat-MRFR (90:10, repeat 1)	5.762	27.478*	1.083*	289.207	19.9*
Wheat-MRFR (90:10, repeat 2)	41.763	3.762*	0*	112.539	35.017*

Normalisation of trace metal analyses data

In order to compare gaseous emissions during the various combustion tests, a process of normalisation is required to allow measurements to be reviewed in the context of standard conditions. An example of the use of normalisation is the requirement to report gaseous pollutants data for incineration of waste (European Parliament, 2000), where emissions values must be expressed relative to a specific oxygen content in the flue gas. The following procedure describes the tasks performed to convert the data of analyses of trace metals in the fly ash samples, which were reported in Table 4.5.

1. A sample of flue gas fly ash was collected, dissolved in acid solution and then ultra-pure water (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was added to create a solution of volume 100 ml.
2. The result of metal content in an example ICP-OES analysis was reported as $88 \mu\text{g l}^{-1}$; therefore in the original sample there was $8.8 \mu\text{g}$ of the metal analyte.
3. After combustion of a fuel, the total volume of flue gas analysed was 1.3 m^3 (measured using the flue gas extraction apparatus as depicted in Figure 3.8).
4. Average combustion temperature was 750°C , 1023 K .
5. Atmospheric pressure estimated at 10^5 Pa , Standard temperature 0°C , 273 K
6. Pressure in combustor 99824 Pa (this was obtained from operation of combustor at slight vacuum of -18 mm water gauge pressure, conversion $1 \text{ mm} = 9.8 \text{ Pa}$ and “gauge pressure” defined as the *difference* from atmospheric pressure, i.e. $10^5 \text{ Pa} - 176$).
7. Using the ideal gas equation, $\frac{p_1 v_1}{t_1} = \frac{p_2 v_2}{t_2}$, ‘ v_2 ’ would be the gas volume of the flue gas at standard temperature (0°C) and pressure (100 kPa). Re-arranging the equation, a flue gas volume is obtained: $3.5 \times 10^{-1} \text{ m}^3$. Thus:

$$\frac{8.8 \times 10^{-6}}{3.5 \times 10^{-1}} = \text{quantity metal, g Nm}^{-3} = 2.5 \times 10^{-5} \text{mg Nm}^{-3}$$

8. The fuel burnt was 11.9 kg, so metal content could be expressed as $0.7 \mu\text{g kg}^{-1}$ fuel (i.e. mass per unit normalised volume $\times$ flue gas volume $\div$ fuel consumption).

An additional convention to express metal content relates trace metal values to the mass of fuel (i.e. expression of content in terms of as a proportion of unit mass of fuel). Data in Table 4.5 is adjusted accordingly (Table 4.6; values denoted with an asterisk (*) represent measurements recorded below the limit of detection for the corresponding radiation wavelength of the metal.).

Table 4.6: Trace metal content in combustion tests' flue gases' samples expressed as (g kg^{-1} of fuel).

	Na	Mg	Al	P	K	Ca
DDGS	3.46×10^{-5}	2.31×10^{-6}	5.94×10^{-4}	3.19×10^{-6}	2.27×10^{-5}	1.06×10^{-5}
DDGS-MRFR (90:10)	1.09×10^{-5}	5.71×10^{-7}	2.86×10^{-4}	$2.72 \times 10^{-7*}$	5.91×10^{-6}	5.17×10^{-6}
DDGS-MRFR (80:20)	5.20×10^{-5}	3.54×10^{-6}	1.57×10^{-3}	6.79×10^{-6}	4.06×10^{-5}	5.94×10^{-5}
DDGS-MRFR (50:50)	2.49×10^{-5}	1.32×10^{-6}	4.84×10^{-4}	$1.13 \times 10^{-6*}$	1.31×10^{-5}	9.09×10^{-6}
DDGS-MRFR (30:70)	4.11×10^{-5}	2.28×10^{-6}	2.72×10^{-3}	2.31×10^{-6}	3.51×10^{-5}	1.11×10^{-5}
Wheat	2.46×10^{-5}	1.55×10^{-6}	9.75×10^{-4}	1.78×10^{-6}	1.67×10^{-5}	1.93×10^{-5}
Wheat-MRFR (90:10)	5.55×10^{-4}	6.22×10^{-5}	2.66×10^{-3}	4.83×10^{-5}	1.78×10^{-4}	5.27×10^{-3}
Wheat-MRFR (80:20)	1.43×10^{-4}	6.72×10^{-6}	2.69×10^{-3}	$2.01 \times 10^{-6*}$	5.89×10^{-5}	5.70×10^{-5}
Wheat-MRFR (50:50)	1.37×10^{-4}	8.14×10^{-6}	2.45×10^{-3}	5.95×10^{-6}	1.09×10^{-4}	6.75×10^{-5}
Wheat-MRFR (30:70)	5.42×10^{-5}	4.31×10^{-6}	1.21×10^{-3}	3.06×10^{-6}	4.09×10^{-5}	4.54×10^{-5}
Wheat-MRFR (90:10 repeat 1)	2.52×10^{-4}	1.28×10^{-5}	4.76×10^{-3}	1.09×10^{-5}	1.66×10^{-4}	7.11×10^{-4}
Wheat-MRFR (90:10 repeat 2)	1.13×10^{-4}	6.02×10^{-6}	8.39×10^{-4}	$1.26 \times 10^{-6*}$	3.40×10^{-5}	6.12×10^{-5}

Table 4.6: Trace metal content in combustion tests' flue gases' samples expressed as (g kg⁻¹ of fuel).

	Ti	V	Cr	Mn	Fe	Co
DDGS	4.19×10^{-6}	$2.99 \times 10^{-8*}$	5.73×10^{-8}	2.32×10^{-7}	4.67×10^{-6}	$6.73 \times 10^{-8*}$
DDGS-MRFR (90:10)	1.20×10^{-6}	$1.58 \times 10^{-8*}$	$1.92 \times 10^{-8*}$	5.62×10^{-8}	2.27×10^{-6}	0*
DDGS-MRFR (80:20)	2.89×10^{-6}	7.01×10^{-8}	1.32×10^{-7}	5.20×10^{-7}	8.95×10^{-6}	$2.29 \times 10^{-8*}$
DDGS-MRFR (50:50)	3.33×10^{-6}	5.17×10^{-8}	8.81×10^{-8}	1.51×10^{-7}	4.51×10^{-6}	$6.64 \times 10^{-8*}$
DDGS-MRFR (30:70)	1.50×10^{-6}	7.12×10^{-8}	5.46×10^{-8}	3.77×10^{-7}	6.74×10^{-6}	$3.65 \times 10^{-8*}$
Wheat	2.97×10^{-6}	6.77×10^{-8}	2.13×10^{-7}	2.01×10^{-7}	7.23×10^{-6}	$2.68 \times 10^{-8*}$
Wheat-MRFR (90:10)	1.57×10^{-5}	2.22×10^{-7}	1.42×10^{-6}	3.42×10^{-6}	4.69×10^{-5}	$2.16 \times 10^{-7*}$
Wheat-MRFR (80:20)	1.29×10^{-5}	1.54×10^{-7}	2.55×10^{-7}	3.68×10^{-7}	2.15×10^{-5}	$3.74 \times 10^{-9*}$
Wheat-MRFR (50:50)	8.04×10^{-6}	1.18×10^{-7}	2.17×10^{-7}	1.02×10^{-6}	1.67×10^{-5}	$7.26 \times 10^{-8*}$
Wheat-MRFR (30:70)	3.06×10^{-6}	5.16×10^{-8}	2.32×10^{-7}	6.56×10^{-7}	7.29×10^{-6}	$9.58 \times 10^{-9*}$
Wheat-MRFR (90:10 repeat 1)	9.27×10^{-6}	3.82×10^{-7}	6.12×10^{-7}	1.41×10^{-6}	6.21×10^{-5}	$2.34 \times 10^{-8*}$
Wheat-MRFR (90:10 repeat 2)	1.60×10^{-5}	6.00×10^{-8}	2.13×10^{-7}	2.44×10^{-7}	1.67×10^{-5}	$4.88 \times 10^{-8*}$

Table 4.6: Trace metal content in combustion tests' flue gases' samples expressed as (g kg^{-1} of fuel).

	Ni	Cu	Zn	Sr	Rh
DDGS	$1.69 \times 10^{-7*}$	1.35×10^{-7}	1.71×10^{-5}	7.41×10^{-8}	0^*
DDGS-MRFR (90:10)	$3.43 \times 10^{-8*}$	5.36×10^{-8}	1.65×10^{-6}	2.95×10^{-8}	0^*
DDGS-MRFR (80:20)	$1.15 \times 10^{-7*}$	2.46×10^{-7}	1.14×10^{-5}	1.52×10^{-7}	0^*
DDGS-MRFR (50:50)	$1.31 \times 10^{-7*}$	1.56×10^{-7}	2.42×10^{-6}	1.00×10^{-7}	$1.87 \times 10^{-8*}$
DDGS-MRFR (30:70)	$5.83 \times 10^{-8*}$	2.80×10^{-7}	4.24×10^{-6}	8.83×10^{-8}	$1.39 \times 10^{-8*}$
Wheat	$1.11 \times 10^{-7*}$	3.33×10^{-7}	3.01×10^{-6}	8.31×10^{-8}	$1.26 \times 10^{-8*}$
Wheat-MRFR (90:10)	$9.05 \times 10^{-7*}$	1.72×10^{-6}	2.66×10^{-5}	2.58×10^{-6}	0^*
Wheat-MRFR (80:20)	4.70×10^{-6}	4.28×10^{-7}	6.61×10^{-6}	3.43×10^{-7}	$2.13 \times 10^{-8*}$
Wheat-MRFR (50:50)	$2.71 \times 10^{-7*}$	3.99×10^{-7}	1.99×10^{-5}	3.23×10^{-7}	$4.99 \times 10^{-9*}$
Wheat-MRFR (30:70)	$1.26 \times 10^{-7*}$	3.76×10^{-7}	1.96×10^{-5}	1.59×10^{-7}	$3.76 \times 10^{-9*}$
Wheat-MRFR (90:10 repeat 1)	$2.34 \times 10^{-4*}$	3.00×10^{-4}	9.44×10^{-3}	3.68×10^{-4}	0^*
Wheat-MRFR (90:10 repeat 2)	$2.53 \times 10^{-4*}$	2.04×10^{-4}	6.02×10^{-3}	2.01×10^{-4}	0^*

Table 4.6: Trace metal content in combustion tests' flue gases' samples expressed as (g kg⁻¹ of fuel).

	Ag	Cd	Sn	Hg	Pb
DDGS	5.21×10^{-5}	0*	0*	$5.32 \times 10^{-4*}$	$8.10 \times 10^{-5*}$
DDGS-MRFR (90:10)	2.91×10^{-5}	$4.40 \times 10^{-6*}$	0*	6.89×10^{-4}	4.64×10^{-5}
DDGS-MRFR (80:20)	2.42×10^{-5}	$2.22 \times 10^{-5*}$	0*	$3.53 \times 10^{-4*}$	$1.10 \times 10^{-4*}$
DDGS-MRFR (50:50)	8.74×10^{-5}	0*	$1.23 \times 10^{-5*}$	1.04×10^{-3}	4.73×10^{-5}
DDGS-MRFR (30:70)	1.26×10^{-5}	0*	0*	1.91×10^{-3}	2.57×10^{-7}
Wheat	$6.98 \times 10^{-6*}$	0*	$1.72 \times 10^{-5*}$	3.79×10^{-4}	$1.46 \times 10^{-4*}$
Wheat-MRFR (90:10)	3.94×10^{-3}	$4.87 \times 10^{-4*}$	$1.82 \times 10^{-4*}$	$1.16 \times 10^{-3*}$	$1.07 \times 10^{-3*}$
Wheat-MRFR (80:20)	1.67×10^{-4}	$3.92 \times 10^{-5*}$	$1.57 \times 10^{-5*}$	5.93×10^{-3}	1.60×10^{-4}
Wheat-MRFR (50:50)	4.44×10^{-4}	0*	0*	6.34×10^{-3}	4.41×10^{-4}
Wheat-MRFR (30:70)	$4.61 \times 10^{-6*}$	$6.23 \times 10^{-6*}$	$3.03 \times 10^{-5*}$	8.86×10^{-4}	$4.05 \times 10^{-4*}$
Wheat-MRFR (90:10 repeat 1)	6.88×10^{-5}	$3.28 \times 10^{-4*}$	$1.29 \times 10^{-5*}$	3.45×10^{-3}	2.38×10^{-4}
Wheat-MRFR (90:10 repeat 2)	5.85×10^{-4}	$5.27 \times 10^{-5*}$	0*	1.58×10^{-3}	4.91×10^{-4}

4.4.2 PCDD and PCDF determination

A sample comprising standard fly ash material was analysed using the GC-MS, to test the capability of the gas sampling method used in this PhD project. Resultant gas chromatograms and mass spectra are shown in Figure 4.97–Figure 4.101. Subsequent chromatograms and spectra correspond to analyses of combustion tests samples (Figure 4.102–Figure 4.110); interpretation of these results is described in § 3.5.3.

The TIC in Figure 4.97 may be considered an ‘initial’ gas chromatogram, in that it represents the eluants from all compounds that can be detected by the GC-MS instrument. The chromatogram is characteristic of the known compounds in the reference standard used to produce the chromatogram and therefore may be used for comparison with unknown samples; where the unknown sample resembles the chromatogram of known compounds in the reference standard, it may be inferred that the unknown samples contains constituents equivalent to the reference standard. However, further confirmation of the identity of the eluants is required, which is made possible by the mass detector of the GC-MS. The chromatogram in Figure 4.98 is produced by configuration of the GC-MS to measure elution based upon a specific ionic mass within the mass scan range; an ionic mass of mass-charge (m/z) ratio 252 corresponds to the molecular weight of a PCDD congener, dichloro-*p*-dioxin ($C_{12}O_2Cl_2$; molecular weights of other congeners are shown in Table 3.7). The appearance of eluants in Figure 4.98 is indicative that the mass of the aforementioned congener is detected; comparison of the resultant mass spectrum of the eluants for the compound of m/z 252 with a reference (Figure 3.10) concludes that the congener dichloro-*p*-dioxin exists in the standard fly ash analysed. Similarly for Figure 4.100 and Figure 4.101, which are indicative of the detection of the congener tetrachlorofuran ($C_{12}OCl_4$). The chromatograms for all of the combustion tests samples subjected to GC-MS analysis are characterised by the appearance of early eluent peaks at the start of each chromatogram, with an increase of the ‘baseline’ at the end of the chromatogram. The absence of any chromatographic peaks at times similar to those described in the TIC for

the standard fly ash chromatogram suggest that no target compounds were produced during the combustion tests.

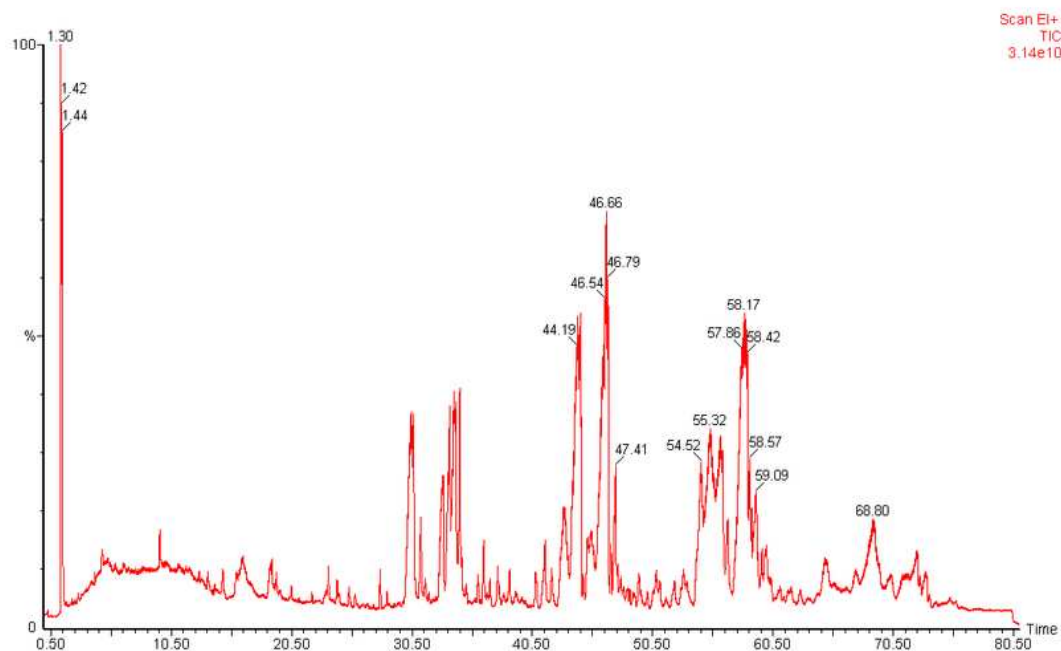


Figure 4.97: Total-ion current (TIC) gas chromatogram of standard fly ash.

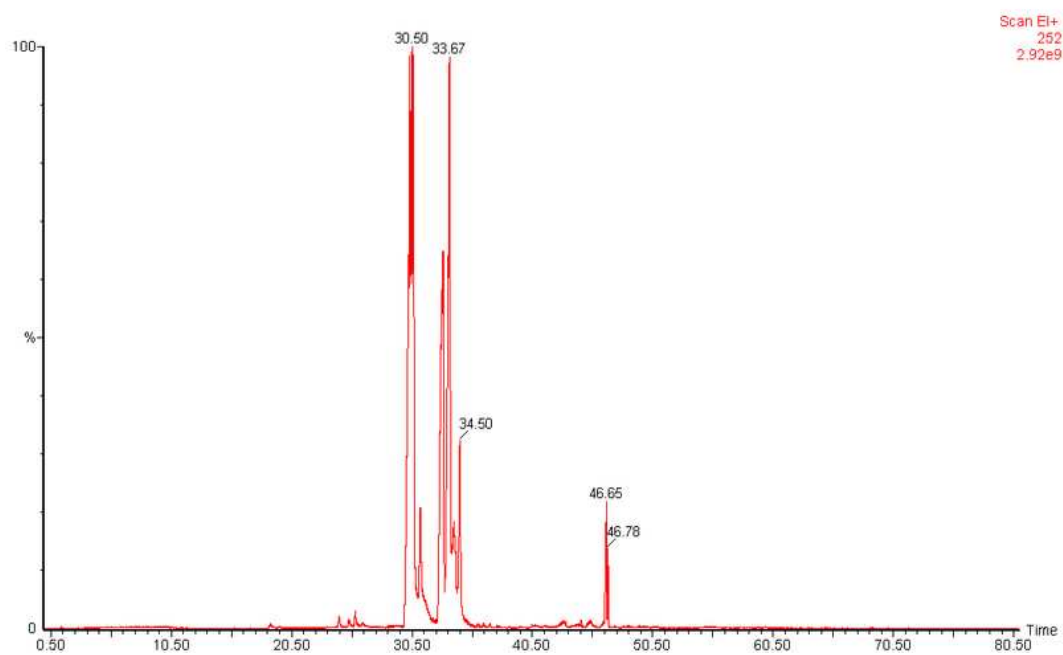


Figure 4.98: Mass (selected-ion) chromatogram of standard fly ash, m/z 252.

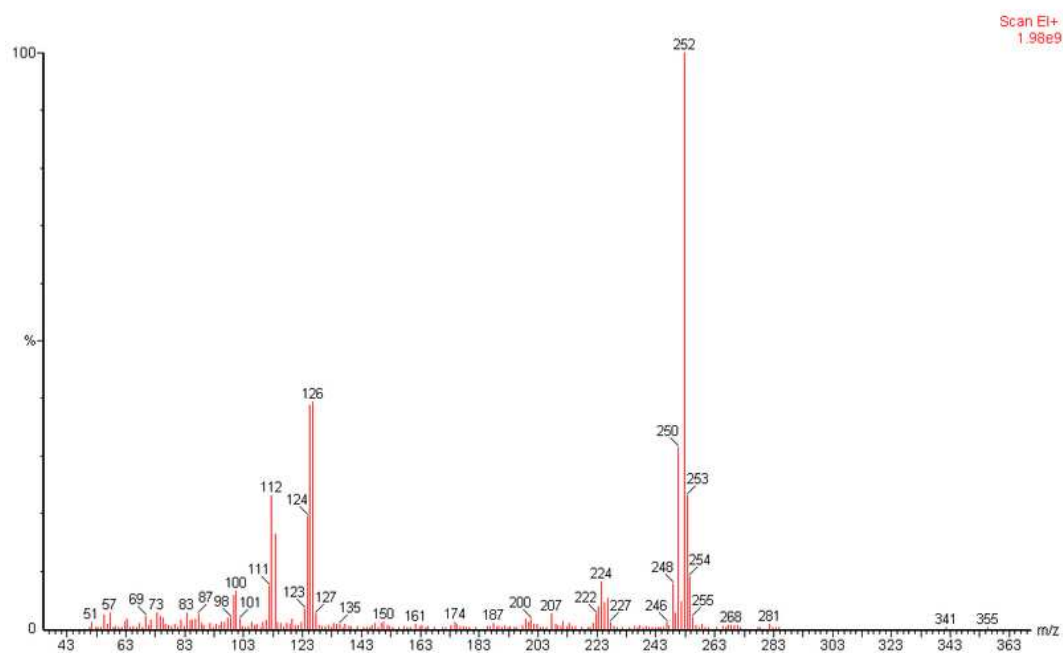


Figure 4.99: Mass spectrum for precedent mass chromatogram (Figure 4.98) of standard fly ash, m/z 252.

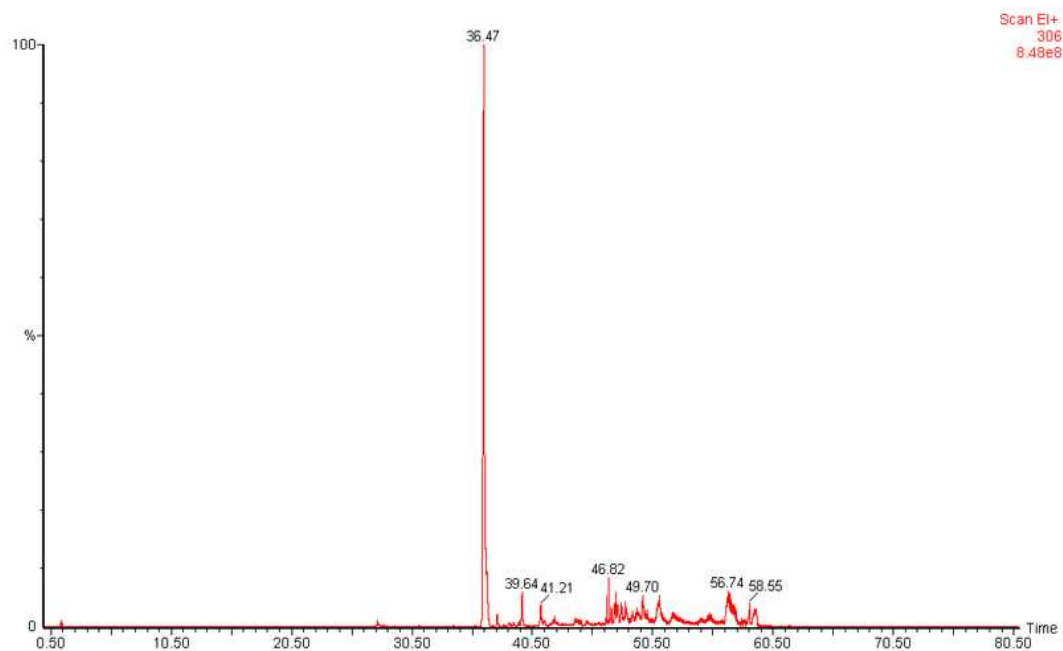


Figure 4.100: Mass chromatogram of standard fly ash, m/z 306.

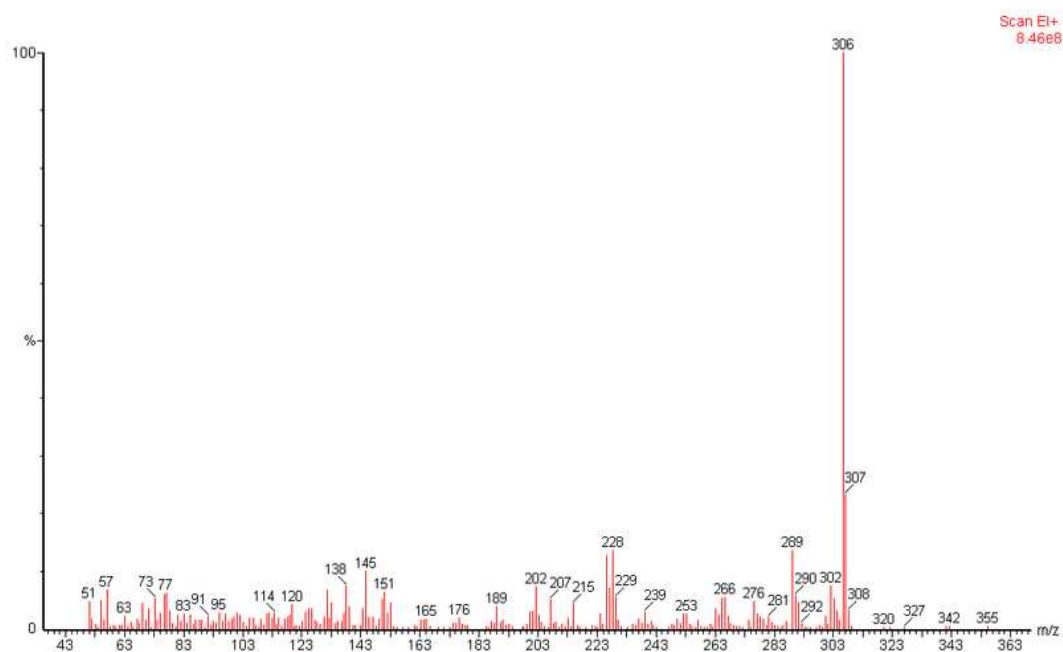


Figure 4.101: Mass spectrum for precedent mass chromatogram (Figure 4.100) of standard fly ash, m/z 306.

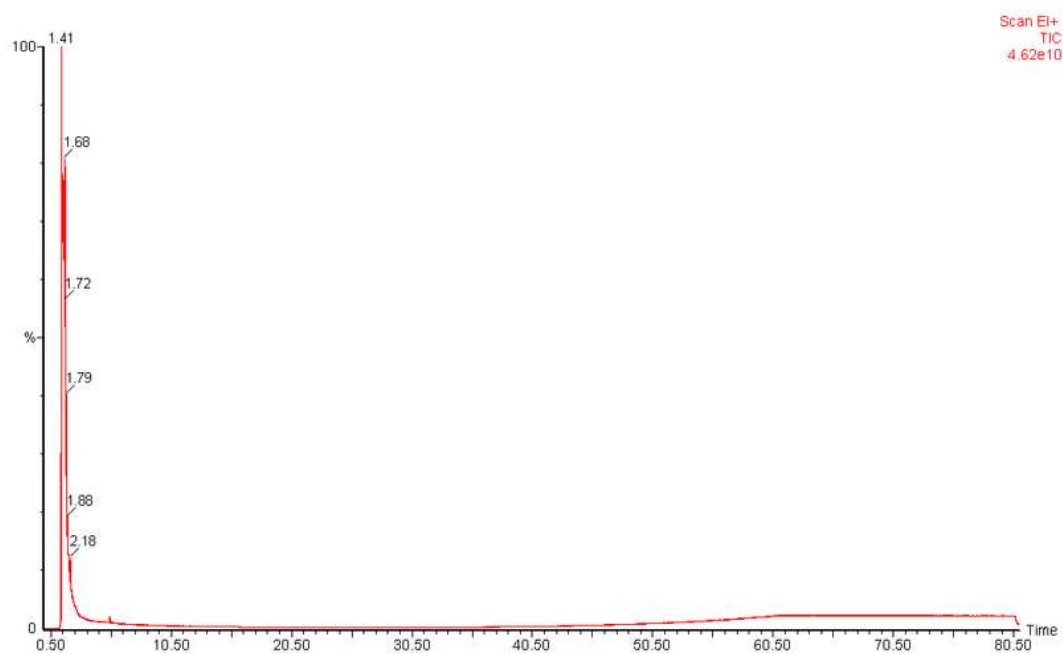


Figure 4.102: TIC gas chromatogram, DDGS-MRFR (90:10).

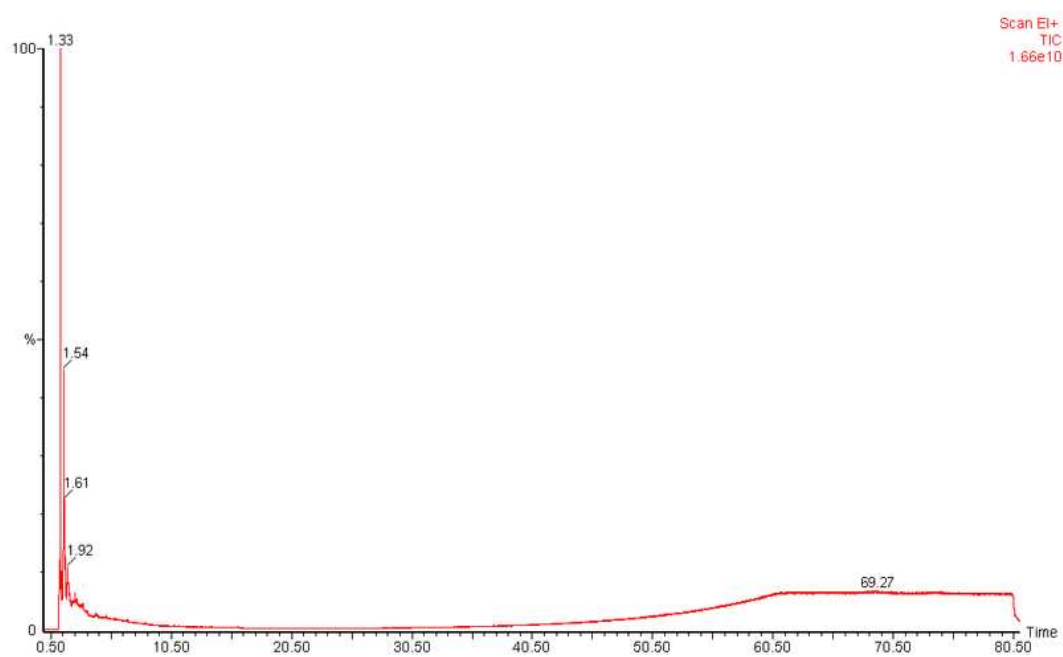


Figure 4.103: TIC gas chromatogram, DDGS-MRFR (80:20).

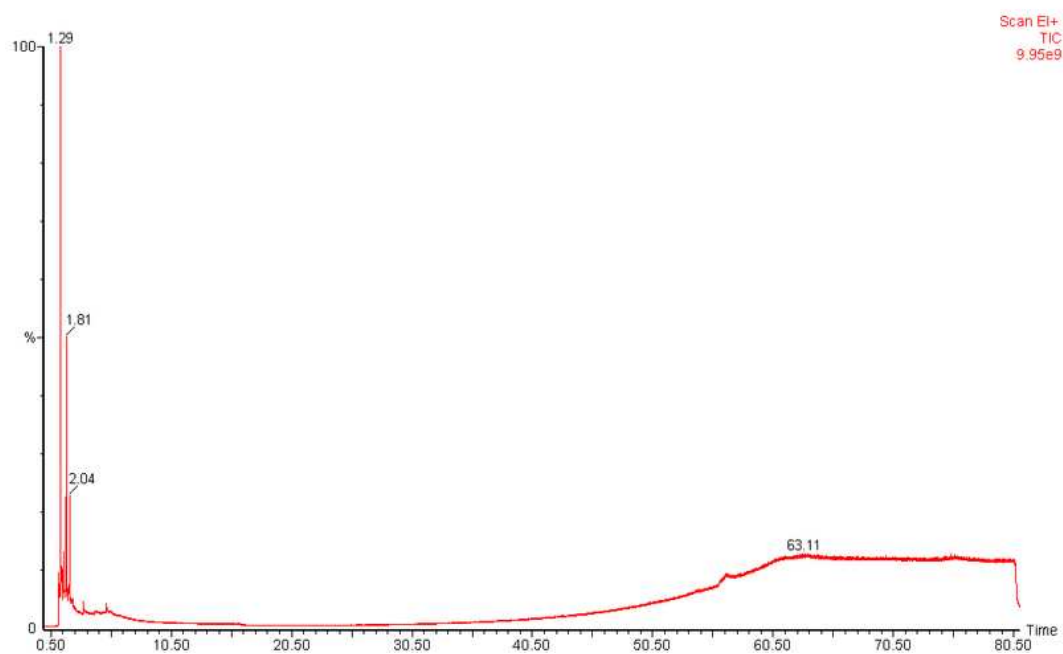


Figure 4.104: TIC gas chromatogram, DDGS-MRFR (50:50).

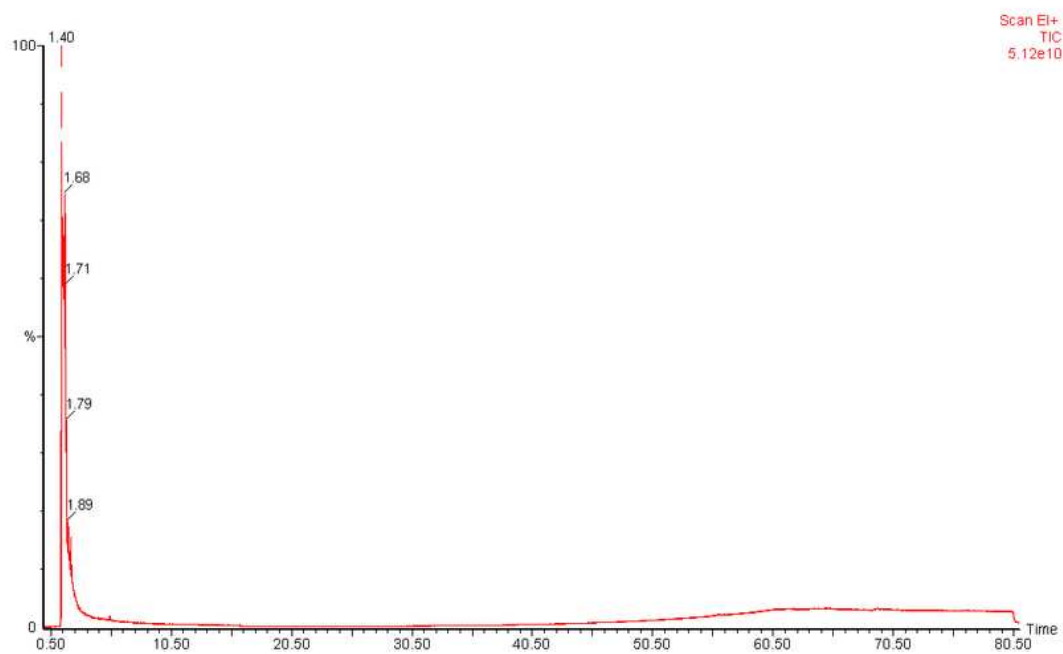


Figure 4.105: TIC gas chromatogram, DDGS-MRFR (30:70).

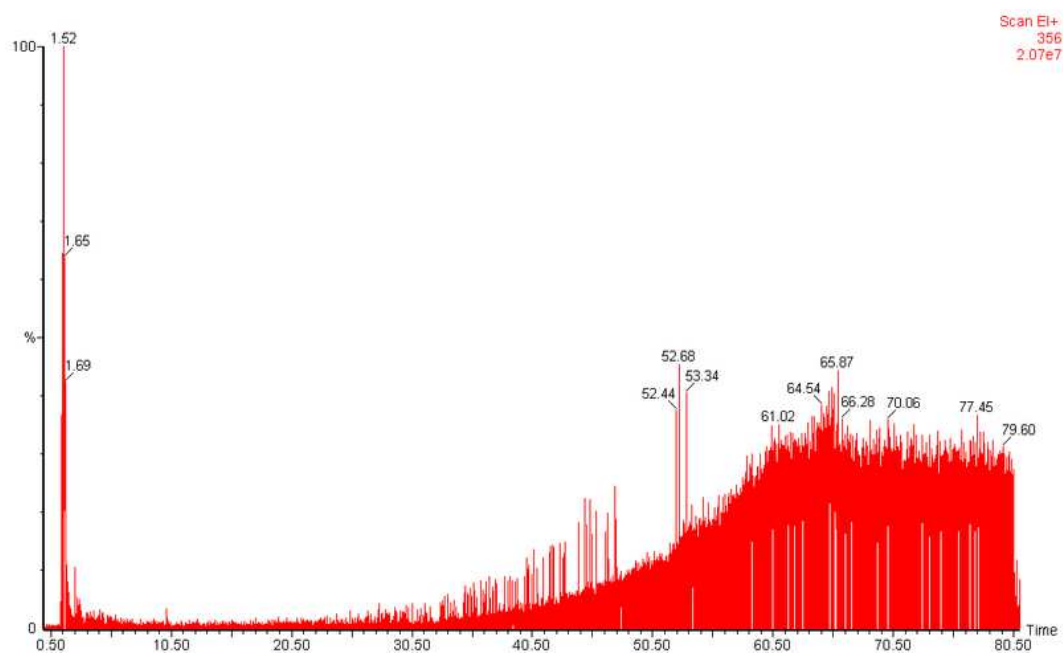
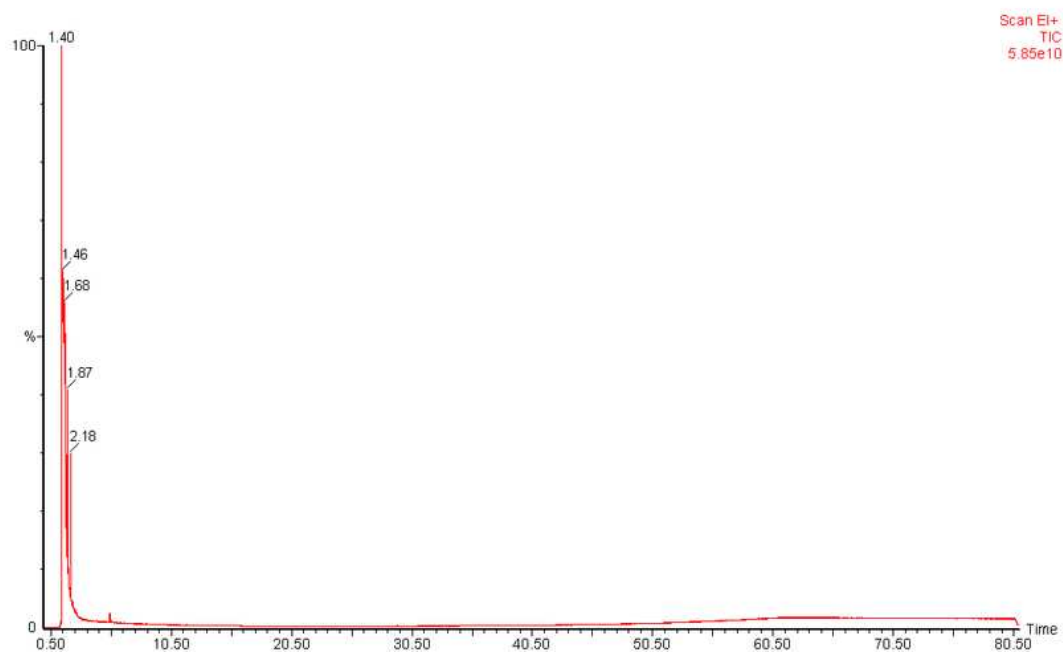
Figure 4.106: Mass chromatogram, m/z 356, DDGS-MRFR (30:70).

Figure 4.107: TIC gas chromatogram, wheat-MRFR (90:10).

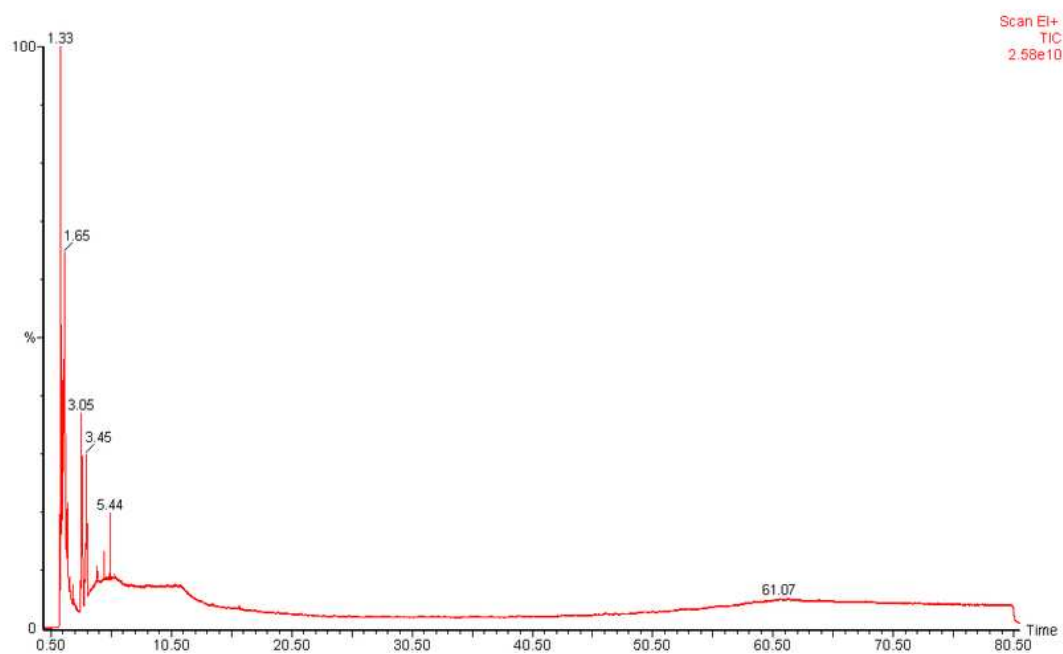


Figure 4.108: TIC gas chromatogram, wheat-MRFR (80:20).

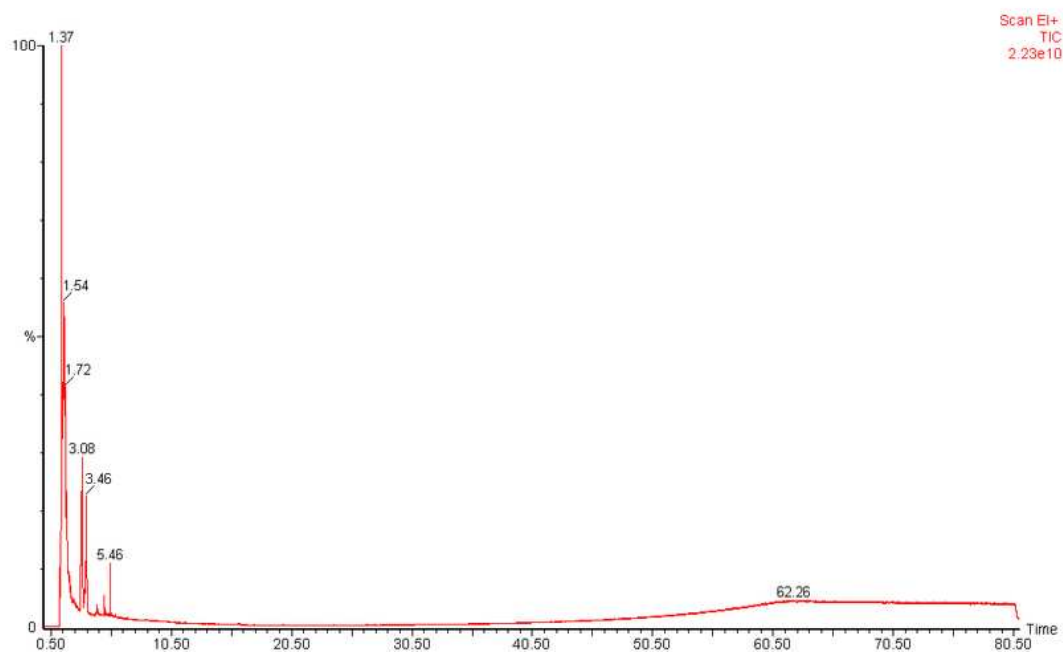


Figure 4.109: TIC gas chromatogram, wheat-MRFR (50:50).

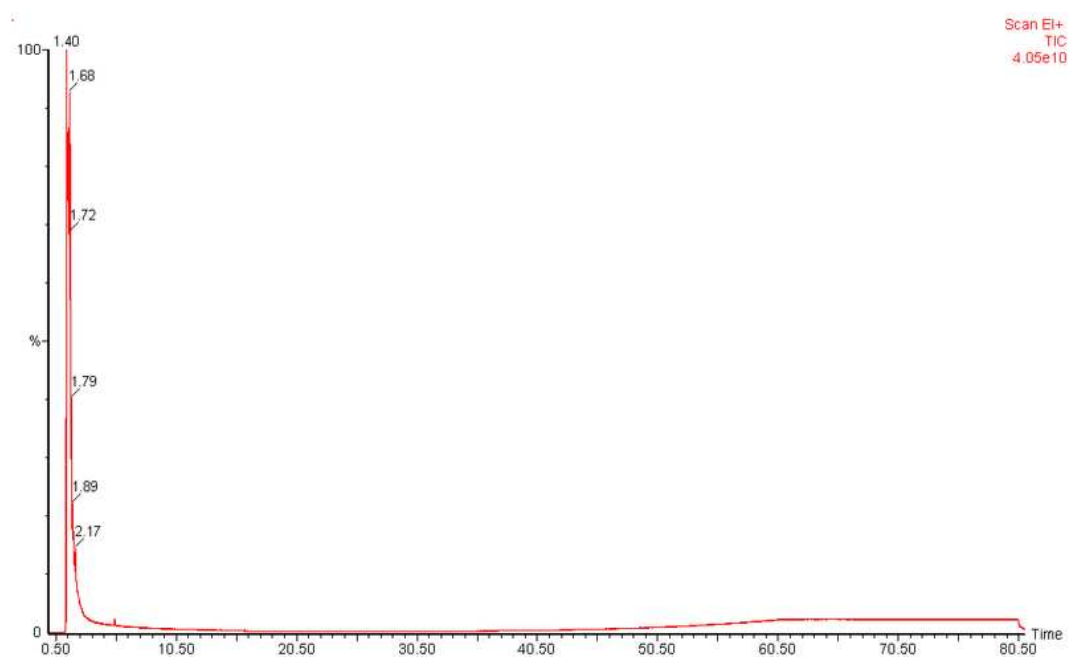


Figure 4.110: TIC gas chromatogram, wheat-MRFR (30:70)

Chapter 5

Discussion

To assess the performance of the combustion system, various analyses were conducted. The following measurements concerning the flue gases are required in order to quantify pollutant emissions (EPA, 2002), although it was not possible to measure all of these parameters (e.g. pitot tubes of a suitable size to measure flue gas flow velocity were not available):

- composition;
- density;
- moisture;
- pressure;
- temperature;
- velocity;
- volumetric flow rate.

5.1 Material & Energy balance of system

A comparison was made between the projections of flue gas composition using the energy and material balances spreadsheet (Table 5.1 and Table 5.2) and measurements recorded by the FTIR gas analyser. The excess air value was

calculated on the basis of complete combustion (equation 5.1 and equation 5.2), i.e. calculating the (unknown) molar quantity of oxygen as equivalent to the (known) molar quantities of carbon and hydrogen in the ultimate analysis. In general, excess air conditions were prevalent during all combustion tests which was to be expected since air was used to create sufficient fluidisation of the fluidised bed material, in addition to facilitating combustion of the fuels. Although excess air conditions did occur, levels of carbon dioxide detected by the FTIR gas analyser were consistently higher than theoretical predictions, to suggest that the air flow into the fluidised bed combustor was less than shown on the air flowmeters. This apparent discrepancy may be explained by a potential mis-calibration of the flowmeters with air flow pumps.



The spreadsheet described in § 3.2 was used to indicate the transport of species such as compounds of chloride and sulphur, to aid interpretation of the gaseous emissions data. This spreadsheet was revised further to assess the discrepancy between values detected by the gas analyser instrument and theoretical values based upon calculations in the aforementioned spreadsheet and comparisons of these values are summarised in Table 5.1 and Table 5.2. Mean values are shown, which correspond to entire duration of combustion tests when biomass and waste fuels were consumed. Excess air values are calculated on the basis of air flow rates as shown in Table 4.3, which were found to be most suitable to avoidance of agglomeration of the fluidised bed material. Ideal air flow rates calculated from chemical reactions of complete combustion of fuel to yield carbon dioxide and water. Emissions of both hydrogen chloride and sulphur dioxide (Table 5.2) detected by the gas analyser are lower than theoretical calculations because the spreadsheet does not consider the extent of absorption of these compounds by the limestone within the fluidised bed. The level of potential absorption of both of these compounds is shown in Table 5.2. High levels of absorption may be attributed to the use of excess quantities of limestone within the fluidised bed material (Table 5.3); for exam-

ple during combustion of DDGS-MRFR (90:10), the calcium:sulphur ratio was estimated at more than 400:1 because of the large quantity of limestone within the fluidised bed material composition (50 % by weight) at the start of each combustion test. There is also the possibility that hydrogen chloride levels are lower than to be expected due to conversion to calcium chloride because of the presence of lime (see equation 2.29 in § 2.7.4). Similarly with respect to sulphur dioxide emission levels, where detection may be lower than to be expected due to potential conversion to sulphur trioxide to give the impression of higher absorption efficiencies, as suggested elsewhere (Anthony, 1995). An alternative possible explanation for the discrepancy between expected levels of gases and detected levels, is that the FTIR gas analyser is inaccurate in determination of these compounds. For example, due to similarities in characteristic absorption of infrared radiation by cyanide and nitric oxide chemical bonds (Table 3.6), infrared spectra may be unable to distinguish the presence of compounds containing these structural functional groups, although proprietary computer modelling software is said to predict this behaviour (as well as hydrogen bonding of water) and adjust the results accordingly (Toy, 2010). With reference to calorific values, the value of 19.5 MJ kg^{-1} in Table 5.2 for DDGS-MRFR (90:10) is calculated from the sum of 90 % of calorific value DDGS (i.e. 90 % of 19.3 MJ kg^{-1} and 10 % of calorific value MRFR (i.e. 10 % of 21.8 MJ kg^{-1}). Mean values shown correspond to entire duration of combustion tests when biomass and waste fuels were consumed. Calorific values calculated using the spreadsheet were based upon the ‘total enthalpy form’ method (Reklaitis, 1983) as described in § 3.3. Calorific values denoted with the asterisk (*) symbol indicate that values for these mixtures were calculated from percentage proportions of the calorific value of pure biomass fuels measured from laboratory analysis as shown in Table 4.1. Values in parentheses correspond to normalisation at 10 % O_2 .

Table 5.1: Comparison of gaseous emissions data between values for CO₂ and O₂ calculated by spreadsheets and empirical data.

	CO ₂ (%)		O ₂ (%)		Excess air (%)	Ideal air flow
	calculated	detected	calculated	detected	calculated	(lmin ⁻¹) calculated
DDGS	5.7	9.3	13.4	10.6	159	542
DDGS-MRFR (90:10)	5.1	8.1	14.2	11.9	191	482
DDGS-MRFR (80:20)	5.0	9.3	14.4	11	198	470
DDGS-MRFR (50:50)	3.4 [†]	7.4	16.5	12.5	350	311
DDGS-MRFR (30:70)	5.7	9	13.5	11	162	535
Wheat	5.8	8.9	13.7	11.2	178	468
Wheat-MRFR (90:10)	4.1	11.4	15.7	10	293	356
Wheat-MRFR (80:20)	4.2	7.4	15.7	13.1	288	360
Wheat-MRFR (50:50)	4.2	8.2	15.6	11	274	374
Wheat-MRFR (30:70)	4.1	10.2	15.5	10.7	271	351

[†] relatively low value attributed to lower fuel feed rate

Table 5.2: Comparison of gaseous emissions data between calculated and empirical values for HCl and SO₂.

	HCl			SO ₂		
	calculated	detected	absorbed	calculated	detected	absorbed
	(ppmv)		(%)	(ppmv)		(%)
DDGS	85.6	19.4 (20.5)	77.3	284	96.6 (102.2)	66.0
DDGS-MRFR (90:10)	82.5	0.5 (0.6)	99.4	236	9.9 (12.0)	95.8
DDGS-MRFR (80:20)	86.5	6.9 (7.6)	92.0	213	44.8 (49.3)	79.0
DDGS-MRFR (50:50)	53.7	11.8 (15.3)	78.0	76.2	20.6 (26.7)	73.0
DDGS-MRFR (30:70)	134	17.4 (19.1)	87.0	135	28.7 (31.6)	78.7
Wheat	101	2.5 (2.8)	97.5	56.0	5.3 (6.0)	90.5
Wheat-MRFR (90:10)	76.5	1.4 (1.4)	98.2	40.5	9.8 (9.8)	75.8
Wheat-MRFR (80:20)	81.2	0.4 (0.6)	99.5	41.3	10.8 (15.0)	73.8
Wheat-MRFR (50:50)	95.4	2.2 (2.4)	97.7	43.8	2.9 (3.2)	93.4
Wheat-MRFR (30:70)	103	1.9 (2.0)	98.2	44.8	5.8 (6.2)	87.1

Table 5.3: Calcium:sulphur ratios for combustion tests, calculated from ultimate analysis data (Table 4.1) and fluidised bed composition (Table 4.2).

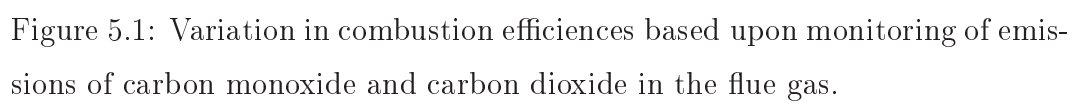
Ca:S ratio (% weight)	
DDGS	347
DDGS-MRFR (90:10)	419
DDGS-MRFR (80:20)	465
DDGS-MRFR (50:50)	946
DDGS-MRFR (30:70)	732
Wheat	1649
Wheat-MRFR (90:10)	2157
Wheat-MRFR (80:20)	2115
Wheat-MRFR (50:50)	2000
Wheat-MRFR (30:70)	2111

5.2 Combustion gas monitoring

As discussed briefly in the preceding section, instantaneous data were collected for the emission of major combustion gases such as carbon dioxide and sulphur dioxide. Carbon oxide emissions are useful to indicate combustion efficiency in terms of concentrations of carbon monoxide and dioxide (Lee & Huffman, 1989), such that the ratios of emissions of these oxides were calculated for each fuel mixture composition (equation 5.3):

$$\text{combustion efficiency} = \frac{\text{CO}_2}{(\text{CO}_2 + \text{CO})} \times 100 \quad (5.3)$$

A general trend is evident from Figure 5.1, namely that as the MRFR fraction in the fuel mixture increases, the combustion efficiency declines. Combustion efficiencies were calculated using equation 5.3 in conjunction with gas analyser data. A likely explanation for this observation is that for certain operating



conditions (see Table 4.3), components of the MRFR fraction are not able to be oxidised completely. Incomplete oxidation may be due to numerous factors as described earlier in § 2.7.1. Insufficient residence time of the fuel (specifically some components of the MRFR fraction) in the combustor prevented complete combustion, although the only operating parameter that could be adjusted to improve residence time would be to reduce the fluidisation air velocity. This option is not possible due to the need to maintain agitated fluidisation of the fluidised bed material using a minimum fluidisation flow rate of gas. However from perspective of future design, residence time could be extended by use of a larger freeboard area. Localised reducing conditions may occur within the fluidised bed material, yet there is an excess quantity of oxygen overall (from the excess air injected to create fluidisation conditions) and therefore lack of oxygen is not considered a cause for a decline in combustion efficiency. At industrial scale with a grate-fired type combustor, staged combustion would be applied by addition of secondary over-fire air to promote complete combustion of fuel (Yin *et al.*, 2008). This action is preceded by restriction of primary air at the fuel-rich zone where the ignition flame is situated, in order to reduce nitrogen oxides emissions. Thus, carbon monoxide emissions in an industrial plant would be potentially indicative of non-optimal control of primary and secondary air supplies, to control effectively emissions of nitrogen oxides. Combustion temperatures are known to promote oxidation of carbon monoxide which is indicated in Figure 4.13, where the increase in combustion temperature causes the emission of carbon monoxide to decline. As examined in the literature review performed for this research project (§ 2.7.1), the availability of free radicals is another factor affecting carbon monoxide emissions. During the combustion of DDGS (100 %, Figure 4.17) it is shown that above a certain temperature (*circa* 860 °C) the ability of hydrogen chloride to inhibit carbon monoxide oxidation is reduced. The increase in combustion temperature appears to *increase* carbon monoxide emissions during some tests (Figure 4.17, Figure 4.21) and the presence of hydrogen chloride for a given temperature results in higher carbon monoxide emissions. This observation of the effect of both hydrogen chloride and temperature upon carbon monox-

ide emissions is consistent with other studies (e.g. Becker *et al.* (1990)), such as the relationships between these parameters shown in Figure 5.2; although the temperatures are higher than those obtained during this PhD project, the strongest effect shown at the lower temperature of 950 °C would suggest an increasing effect of hydrogen chloride as combustion temperatures are reduced. The effects of various chemical intermediates upon carbon monoxide emissions were examined in § 2.7.1. Results in this research project indicated how carbon monoxide emissions are affected by factors such as temperature and relative concentrations of other gaseous pollutants, specifically nitrogen and sulphur oxides, hydrogen chloride. In the majority of combustion tests, there was no correlation between carbon oxides emissions although the following table (Table 5.4) summarises the few tests where good correlation was found (also indicated graphically in Figure 4.6 and Figure 4.7). This scarcity of correlation between carbon oxides emissions would suggest that the single action to increase combustion temperature is insufficient to minimise carbon monoxide emissions.

Temperature was shown to have a clear effect in emissions of NO_x and N_2O . It was possible to initiate combustion of pure biomass fuels (i.e. combustion tests 100 % DDGS, 100 % wheat straw) at a lower fluidised bed sand temperature compared to other tests where the waste fraction was part of the the fuel mix. Consequently with these tests measurement of gaseous emissions during lower combustion temperatures was achieved; graphs in Figure 4.15 and Figure 4.16 shows how relatively higher temperatures minimise N_2O emissions and yet enhance NO emissions. The initial increase in emission of N_2O during the temperature range 650–750 °C is probably due to burning of fuel char (equation 2.18) and subsequent reduction of NO, before the higher temperatures begin to favour nitrous oxide decomposition. The suggestion that HCN is the primary source of nitrous oxide (Boavida *et al.*, 1996) may be inferred from the various visualisations presented in this research project, where ammonia occasionally has an additional impact: Figure 4.67; Figure 4.69; Figure 4.73. The term ‘ NO_x ’ encompasses both nitrogen compounds NO and NO_2 ; during fluidised bed combustion of coal, NO_x is said to consist of approximately

95 % as NO (Oka, 2004o). The combustion of DDGS and wheat straw showed a higher composition of NO_x as NO (Table 5.5; the value for Wheat-MRFR (50:50) was omitted due to a random error with measurement of NO_x that occurred with the gas analyser during the combustion test).

Emissions of nitric oxide do not appear to be affected by hydrogen chloride in a consistent way. Hydrogen chloride appears to inhibit nitric oxide emissions during combustion of DDGS (Figure 4.27, DDGS-MRFR (90:10, Figure 4.28), and DDGS-MRFR (50:50, Figure 4.30), in that for a given temperature, nitric oxide emissions decrease as hydrogen chloride increases. This effect ceases to occur beyond a minimal temperature limit (850–890 °C) after which nitric oxide emissions are high irrespective of hydrogen chloride. However, during other combustion tests (e.g. Figure 4.31, Figure 4.34) NO emissions appeared to increase with temperature independent of the hydrogen chloride content; overall these observations are summarised in Figure 5.3. As indicated in the literature review (§ 2.7.25.1), this inconsistent effect of hydrogen chloride is attributed to different combustion conditions of involving both heterogeneous oxidation of fuel char and homogeneous gas-phase reactions with free radicals. It has also been suggested that the observation of decreased NO emissions is due to insufficient lime within the fluidised bed, when limestone is supplied with the fuel to the combustor (Becker *et al.*, 1990). However, this hypothesis is not applicable to the test conditions of this research project, because limestone exists in excess as part of the fluidised bed material composition.

In a fluidised bed combustor, nitric oxides emissions originate from *fuel-bound* nitrogen (see § 2.7.2). Formation of nitric oxide is possible from the fuel-bound nitrogen, initially via thermal decomposition of amines (in proteins within the biomass matter). Studies have indicated that this decomposition is rapid and occurs during approximately simultaneous energy release (Glassman & Yetter, 2008); this is consistent with the observation in this PhD research project, of a rapid increase in temperature at the start of combustion of DDGS (Figure 5.4). The rapid increase in temperature at the start of combustion corresponded to initial addition of DDGS to the combustor and subsequent rapid devolatilisation of the fuel, to yield heat release and associated thermal

decomposition of volatile components of the biomass fraction of the fuel.

Interactions between nitrogen oxides and pre-cursor compounds such as ammonia and (hydrogen) cyanide were investigated to view any patterns that may be evident. Other studies have demonstrated that, in general, HCN is the main source for N_2O formation and NH_3 for NO (Winter *et al.*, 1999). In addition, ammonia is produced more favourably from fuels containing amino groups (Hämäläinen & Aho, 1995) which is more prevalent in biomass type fuels than fossil fuels such as coal. Combustion of 100 % DDGS was an example combustion test to show how N_2O are highest at low levels of NH_3 and high levels of HCN (Figure 4.67). Similarly with combustion of 90 % DDGS-10 % MRFR (Figure 4.68) and 30 % DDGS-70 % MRFR (Figure 4.71), low emissions of NH_3 correspond to high N_2O emissions, supporting the general observation in previous studies of a positive correlation between HCN and N_2O .

With the intentional use of limestone as a component of the fluidised bed material, it was to be expected that sulphur dioxide emissions were suppressed. This is generally evident in the summary of emissions for all combustion tests (Figure 4.12), with comparison between sulphur dioxide and nitric oxide emissions worthy of comment. In particular, the combustion tests with 90 % biomass (i.e. DDGS and wheat straw) indicate that emissions of these gases are inversely proportional to each other. If limestone and its derivative lime catalyse production of nitric oxide, as indicated from previous studies such as those mentioned in § 2.7.2, this mechanism would have the effect of promoting nitric oxide emissions. Consequently, the availability of free radicals would be reduced with the effect of minimising sulphur dioxide formation, in addition to the limestone sulphation mechanism (equation 2.28). In contrast to preceding work (Julien *et al.* (1996), Ferrer *et al.* (2005)), in this research project there seemed to be a positive correlation between sulphur dioxide and hydrogen chloride, for example as shown in Figure 4.41. In consideration of equation 2.30, it may be more likely in the fluidised bed combustor that deposition of calcium chloride may be occurring within general fouling of the combustor walls, to result in reduction of lime by hydrogen chloride being more favourable. The presence of calcium chloride would also be expected to have an effect upon

the ability of limestone to absorb sulphur (see § 2.7.4) and this behaviour may explain the apparent failure to achieve full absorption of sulphur by limestone, indicated by the low levels of absorption of SO_2 as shown in Table 5.2. Due to the excess quantities of limestone in the fluidised bed material at the beginning of each combustion test, complete conversion to calcium sulphate (i.e. 100 % absorption of SO_2 by limestone) was to be expected. Furthermore, despite the excess quantities of limestone, the difference in sulphur content of the fuels (see chemical composition in Table 4.1) appears to be the cause of higher levels of sulphur dioxide emissions for DDGS fuel mixtures compared to wheat straw fuel mixtures (Figure 4.12). These observations of absorption of hydrogen chloride by limestone are consistent with a previous study (Partanen *et al.*, 2005a), where hydrogen chloride absorption was affected *inter alia* by the presence of water and temperature. With reference to the impact of water, the reversible reaction of lime and hydrogen chloride (equation 2.29 and equation 2.30) is said to tolerate moisture content of up to 14 % for the formation of calcium chloride; this would seem plausible for experiments in this PhD project where the water content was less (Table 4.4). At temperatures of approximately 650 °C, calcium chloride absorption was enhanced by carbon dioxide where simultaneous reaction of recarbonation of lime occurs also. Again, this would seem possible during combustion tests in this PhD project where temperatures of the fluidised bed combustor were typically within the temperature range of approximately 650 °C at the outlet and 850 °C within the freeboard zone (Figure 4.3).

The general trend in emissions of hydrogen chloride with increase in MRFR fraction of the fuel mixture is shown in Figure 4.9, is mostly in agreement with predictions calculated using the mass balance spreadsheet (Table 5.2). Of interest to note is the predicted reduction in hydrogen chloride from 80 % DDGS to 50 % DDGS, when actual results showed *both* an increase in hydrogen chloride detection and absorption (by limestone, Table 5.2). This observation is also evident from corresponding data for the transition from wheat straw-MRFR (80:20) to wheat straw-MRFR (50:50). One possible explanation could be that at this quantity of chloride from the fuel mixture, the effect of a

limited quantity of free radicals could start to diminish and the total quantity of chloride is sufficient for both increased net emissions of hydrogen chloride and absorption of hydrogen chloride by limestone to occur.

Measurement and publication of gaseous emissions data may be expressed to standard, or normalised, conditions in accordance with numerous European Union legislations, such as the waste incineration directive (European Parliament, 2000). As stated in Table A.3, emission limits for certain pollutants are specified and the method of normalisation is applied as shown in Figure 5.5–Figure 5.8 for emissions data of this PhD research project. After normalisation, it is apparent that emissions of some compounds are below mandatory limits (e.g. hydrogen chloride during combustion of wheat straw fuel mixtures, Figure 5.10) even *before* the compulsory installation of air pollution control devices such as baghouse filters (to remove particulates) and scrubbers (water based deposition to remove sulphur oxides). Levels of carbon monoxide emissions (Figure 5.5 and Figure 5.9) increases with the proportion of MRFR and are above the emission limit in all cases. With reference to other pollutants, hydrogen chloride emissions were lower than the emission limit for all combustion tests with wheat straw (Figure 5.10), but only with one combustion test of DDGS (Figure 5.6). Whilst the general trend in nitric oxide emissions is a decrease as the biomass (i.e. DDGS) content also decreases (Figure 5.7), analogous emissions with wheat straw (Figure 5.11) are more erratic although more combustion tests experienced emissions below the emissions limit compared to combustion tests of DDGS fuel mixtures. Sulphur levels are below emission limits for all combustion tests (Figure 5.8 and Figure 5.12) as is expected due to the use of limestone as absorbent additive to the fluidised bed material. Such low gaseous emissions would have implications for reducing the operating costs of air pollution control devices. However, due to the absence of replicate tests, these observed variations may be attributed in part to experimental error and/or change in composition of the fuels.

Table 5.4: Correlation (Pearson's method) between carbon monoxide and carbon dioxide emissions

Fuel mixture	Correlation factor
DDGS-MRFR (80:20)	0.81
DDGS-MRFR (30:70)	0.87
Wheat-MRFR (50:50)	0.79
Wheat-MRFR (30:70)	0.81

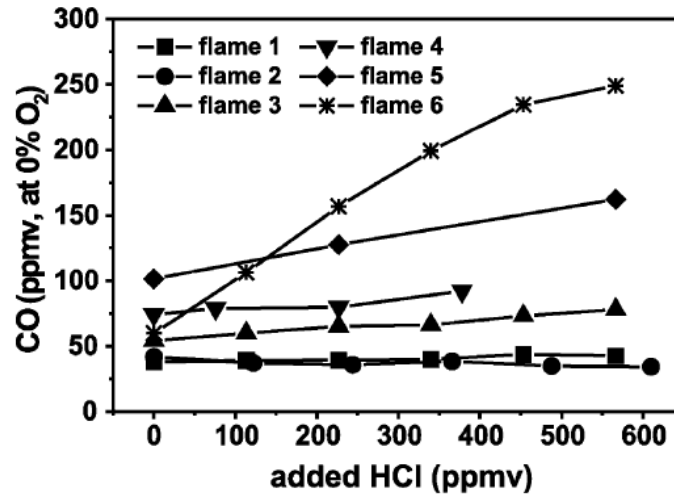


Figure 5.2: Interactions between CO, HCl and temperature during combustion of coal (Wei *et al.*, 2004). Flame temperatures range from 1250 °C (flame 1) to 950 °C (flame 6).

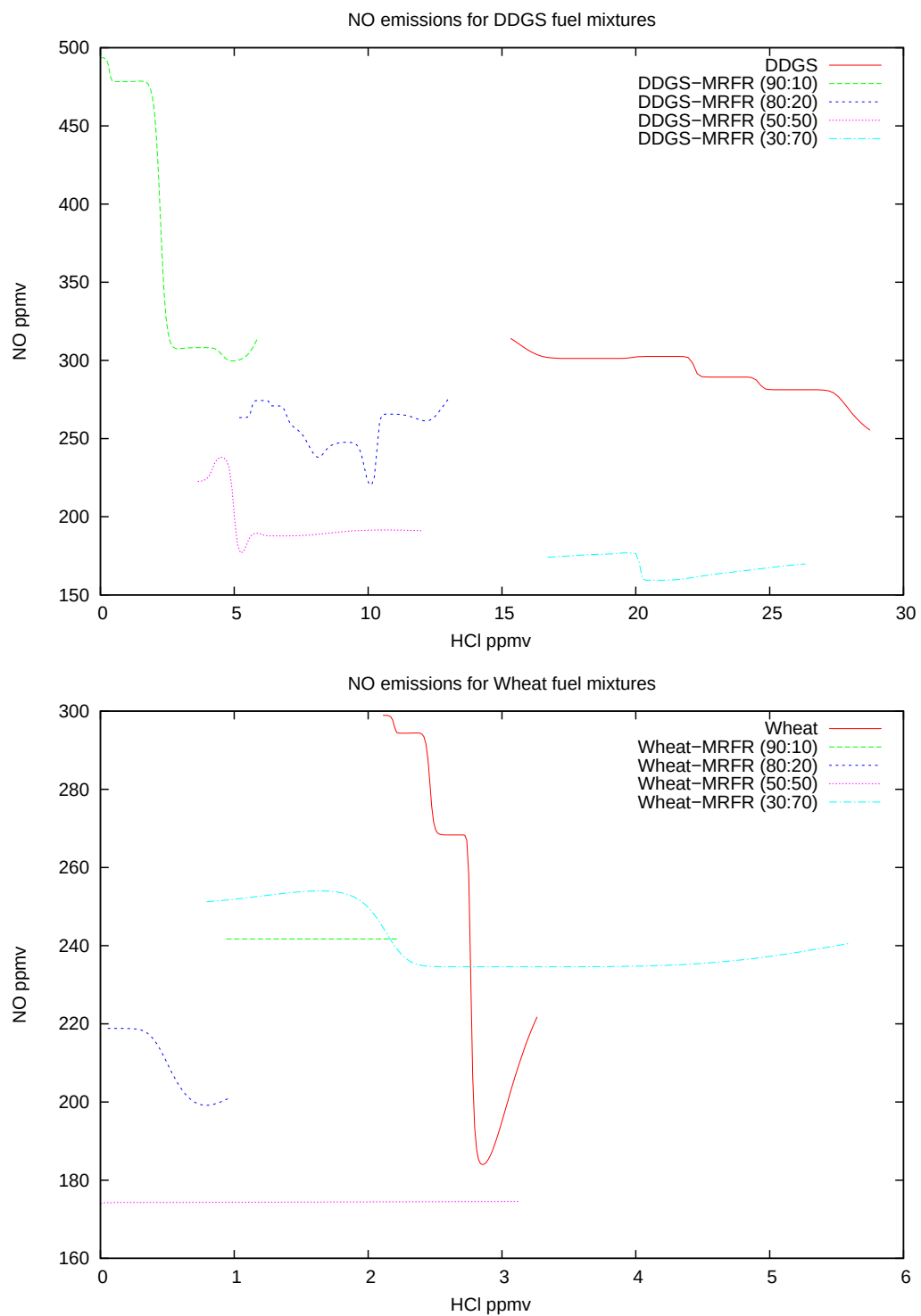


Figure 5.3: Summary of HCl, NO emissions; DDGS and wheat, for a temperature approximately 850 °C

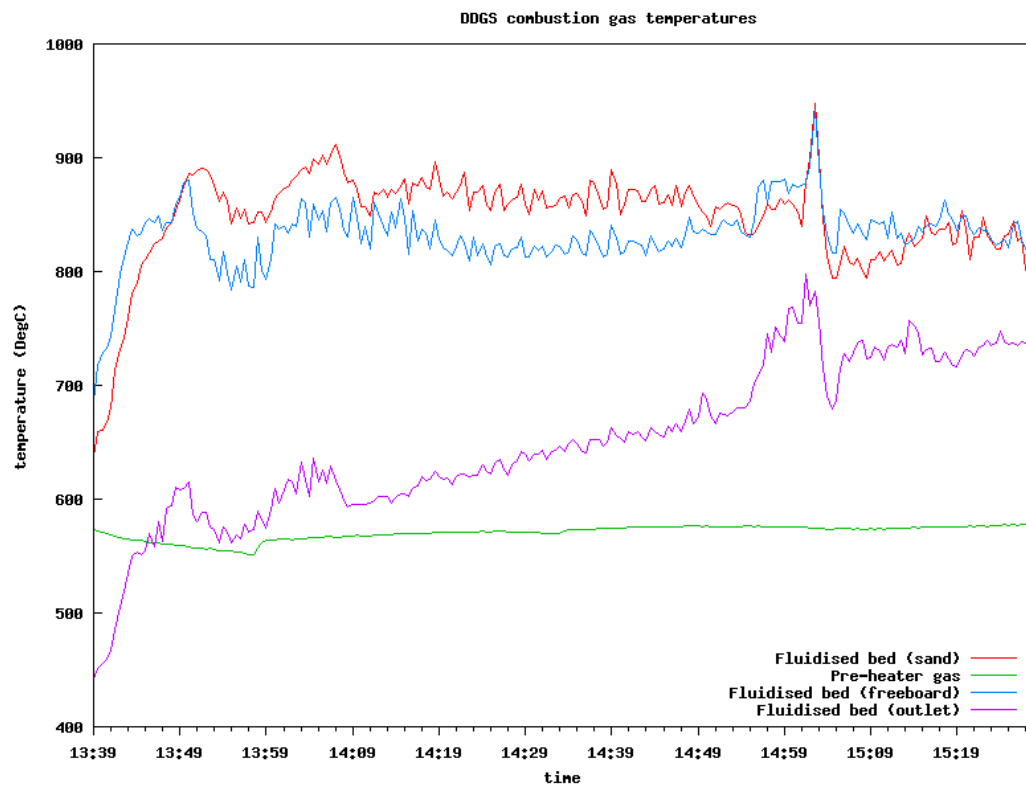


Figure 5.4: Time series profile of temperatures during combustion of DDGS.

Table 5.5: Median NO emissions as a proportion of NO_x.

Fuel mixture	NO/NO _x (%)
DDGS	98.9
DDGS-MRFR (90:10)	98.8
DDGS-MRFR (80:20)	98.8
DDGS-MRFR (50:50)	99.0
DDGS-MRFR (30:70)	99.4
Wheat	99.3
Wheat-MRFR (90:10)	99.8
Wheat-MRFR (80:20)	99.7
Wheat-MRFR (50:50)	-
Wheat-MRFR (30:70)	99.9

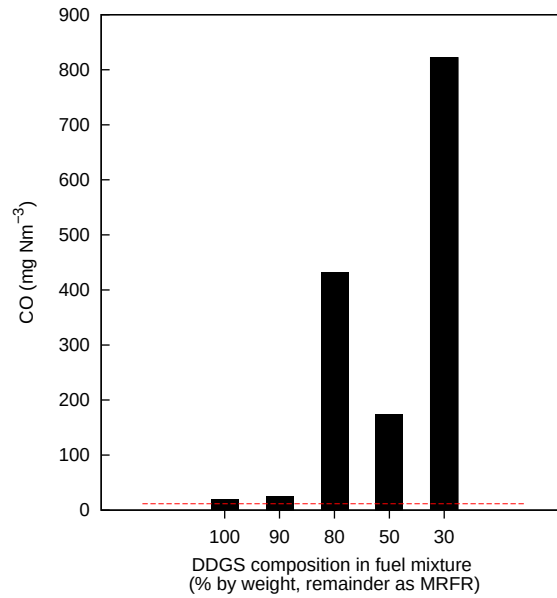


Figure 5.5: Variation in flue gas carbon monoxide for DDGS fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Horizontal line (dash style, red) indicates the emission limit.

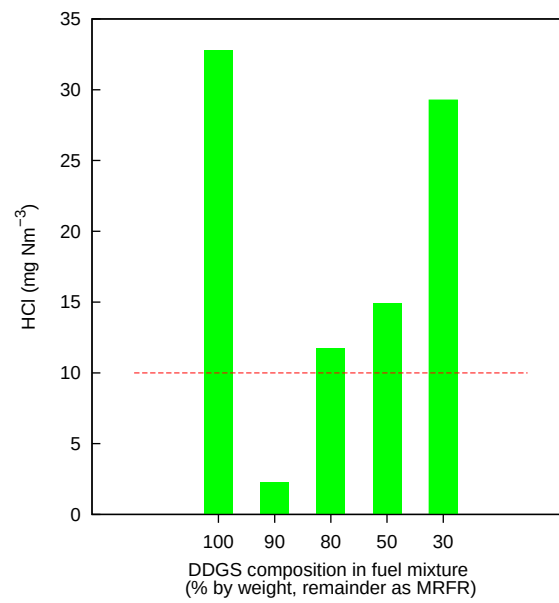


Figure 5.6: Variation in flue gas HCl for DDGS fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Horizontal line (dash style, red) indicates the emission limit.

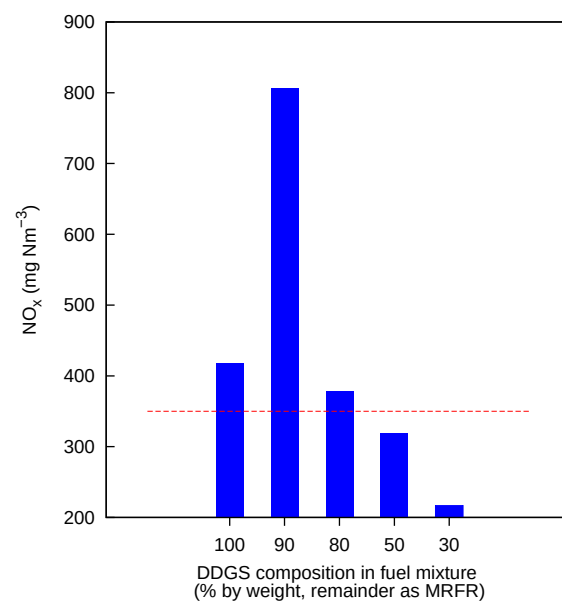


Figure 5.7: Variation in flue gas nitrogen oxides for DDGS fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Horizontal line (dash style, red) indicates the emission limit.

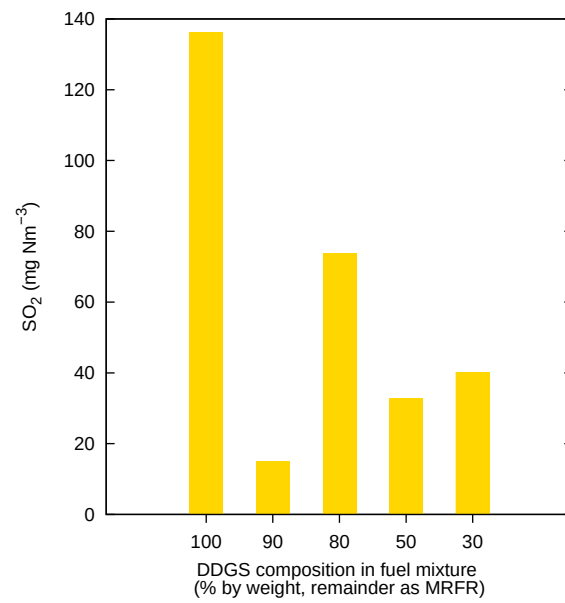


Figure 5.8: Variation in flue gas sulphur dioxide for DDGS fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Emissions below limit of 200 mg m⁻³

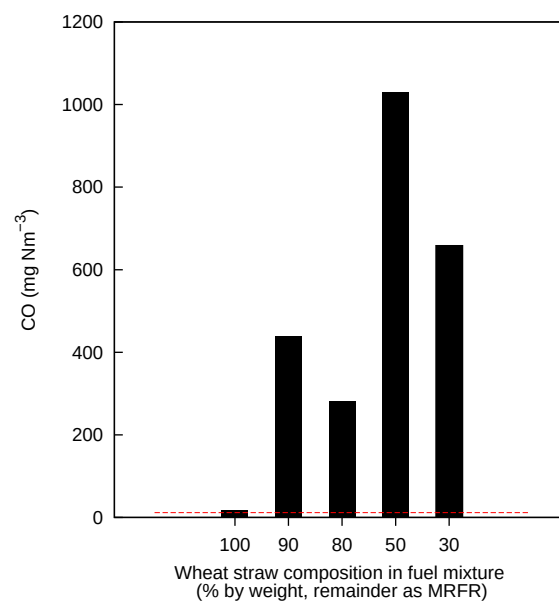


Figure 5.9: Variation in flue gas carbon monoxide for wheat straw fuel mixtures, derived from mean values and normalised to O_2 content 6 %. Horizontal line (dash style, red) indicates the emission limit.

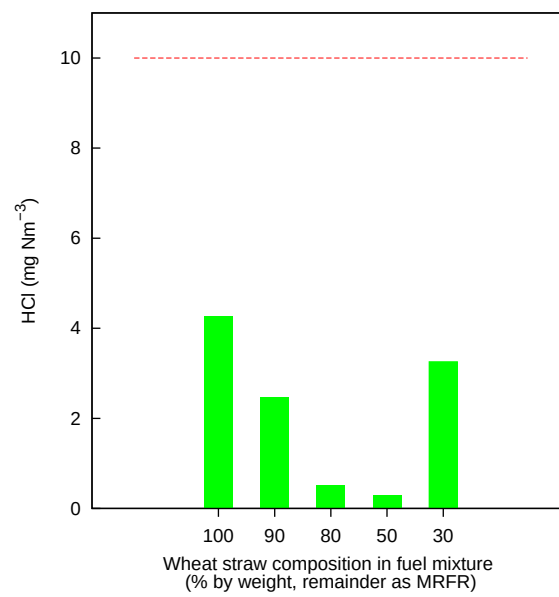


Figure 5.10: Variation in flue gas HCl for wheat straw fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Horizontal line (dash style, red) indicates the emission limit.

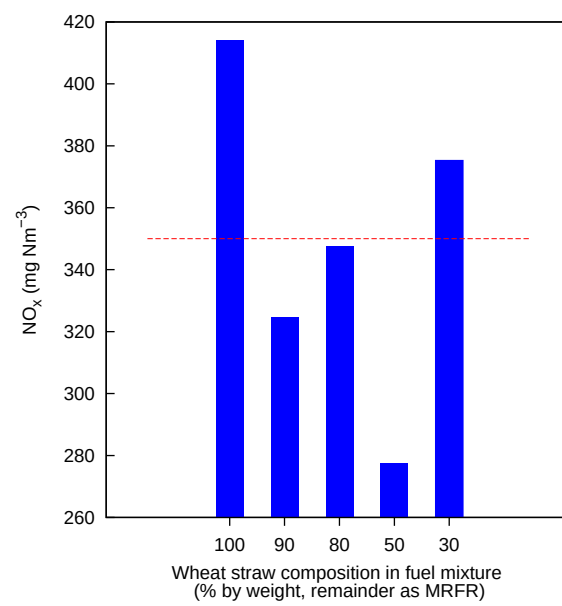


Figure 5.11: Variation in flue gas nitrogen oxides for wheat straw fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Horizontal line (dash style, red) indicates the emission limit.

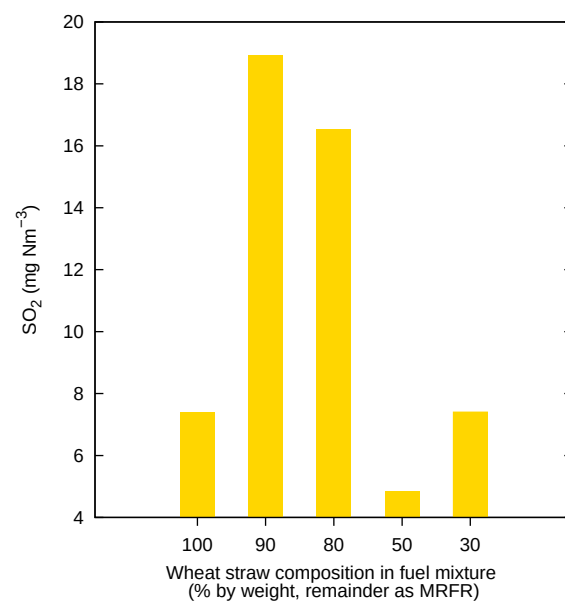


Figure 5.12: Variation in flue gas sulphur dioxide for wheat straw fuel mixtures, derived from mean values and normalised to O₂ content 6 %. Emissions below limit of 200 mg m⁻³

5.3 Measurement of transport of trace metals

An initial observation of the data presented in Table 4.5 is that the wide variation in metals contents for wheat-MRFR (90:10) is indicative of low precision. This is to be expected considering the heterogeneous characteristic of MSW and suggests that without significant quantities of repeated tests (perhaps 10–20 repeats of each combustion test composition mixture), reasonable conclusions from the metals content data presented here cannot be made. As an alternative to a large number of repeat tests, the use of additional flue gas sample collection apparatus configured in series would be another method of obtaining an increased population of samples. However, from the results obtained it is evident that: aluminium was the most prevalent metal detected; the toxic metals mercury, cadmium and lead were not emitted at levels above the limit of detection for the analytical equipment used; concentration of metals did not increase with concentration of MRFR in the fuel mixture as would be reasonably expected.

The sample blank was prepared in the laboratory but not fitted to the flue gas sample collection apparatus and exposed to operation of the fluidised bed combustor. Values of metals contents in the sample blank are potentially indicative of loss of adsorption and filtration media during flue gas sample collection for each combustion test, which would explain the observation of higher metal content values in the sample blank where there was no exposure to the sample collection pump (see Figure 3.8) and therefore potential loss of adsorption & filtration media materials.

5.4 Trace organic compounds

Analysis of a certified standard fly ash sample using thermal desorption GC-MS (Figure 4.97) demonstrated the capability the technique for detection of PCDD/F congeners. Results for analysis of the combustion tests samples were all negative, characterised generally by a solvent peak at the start of the chromatogram (e.g. farthest left of chromatogram in Figure 4.102) and slight

‘column bleed’ at the end of the chromatogram (farthest right area) where the baseline appears relatively elevated and this gradual increase is usually indicative of the stationary phase leaking from the GC column. This observation of column bleed was evident further in the mass chromatogram shown in Figure 4.106, where peaks of individual mass fragments are obscured by the increasing baseline noise, to prevent identification.

The lack of any chromatographic peaks suggests that significant, detectable quantities of PCDD/F congeners were not produced during the combustion tests. Alternatively, the apparatus used to collect the sample was not effective in collecting sufficient concentration of analytes, or the duration of the combustion test was similarly insufficient. However, chromatographic results obtained for combustion of willow (see § Appendix D) suggests that the apparatus was successful in collecting sufficient flue gas sample. This inference is made on the basis of comparison of chromatograms of the reference standard (Figure 4.98) and willow-MRFR (Figure D.5) as well as the consequent associated mass spectra (Figure 4.99 and Figure D.6).

Detection of PCDD/F congeners is complicated by the fact that these compounds may be subject to destruction within the combustion zone, yet formation may occur beyond the combustion zone farther downstream from the combustor via two reaction pathways: precursor reactions with compounds such as chlorophenol; *de novo* synthesis where metal catalysts (such as copper) are involved in formation of PCDD/F congeners using fly ash and unburned carbon (Kobyashi *et al.*, 2005). Laboratory-scale studies have demonstrated that PCDD/F congeners are susceptible to thermal desorption from fly-ash particles at temperatures of 200–300 °C (Cunliffe & Williams, 2007), analogous to conditions within post-combustion zones of MSW incinerators. Similarly, at industrial scale it has been shown that emissions of PCDD/F congeners were higher after the furnace when the incineration system featured a waste heat boiler as a cooling system prior to emissions to the flue outlet (Kim *et al.*, 2007). Thus, the results obtained in this PhD research project should be considered in the context of previous research on the formation of PCDD/F compounds, in terms of the flue gas sampling conditions.

Chapter 6

Conclusions & Recommendations

6.1 Conclusions

There are a range of biomass and municipal solid waste materials that are available for exploitation to provide renewable energy in the form of heat and electrical power generation. Certain forms of biomass such as surplus wheat straw can be used as an energy resource without impact upon food supply since such biomass forms are agricultural by-products of the food supply chain. Similarly, non-recyclable municipal solid waste (e.g. MRFR) is available for energy conversion without impact upon materials recycling activities, as part of an integrated waste management programme. Previous studies into the thermal conversion of MSW have not made an explicit consideration of whether such fuel should be exploited at the expense of materials recycling and consequently, this research project sought to investigate if a residual waste source could be identified for detailed assessment of combustion characteristics. A pilot-scale fluidised bed combustor was used to demonstrate that various mixtures of biomass and MRFR can be burned successfully, during which gaseous emissions from combustion tests were measured for the presence of certain flue gas components (such as hydrogen chloride) and other pollutants such as volatile trace metals. With reference to flue gas composition, the mechanism of “limited free radical pool” was suggested as a likely explanation for the trend in gas emissions as the proportion of MRFR fraction within the fuel mixture was

increased. If the concentration of free radical intermediates is insufficient, elevated formation of specific compounds (e.g. carbon monoxide) occurs due to competition of free radicals for preferential formation of other pollutants such as nitric oxide.

An extensive review of the literature revealed that the concept of concurrent combustion of biomass and municipal solid waste materials had not been investigated to any significant extent. Whilst sufficient volumes of these resources are available for exploitation as energy supply (2.1) and fractions of MSW may be produced to high specification in the form of SRF, concerns about gaseous emissions during combustion have prevented use of MSW within the energy sector (Supergen, 2007). The historic scarcity of research into combustion of biomass with MSW was highlighted in 2.1. Combustion tests performed during this PhD research project have demonstrated that it is practical to utilise both of these renewable energy resources without the requirement of coal as the predominant fuel component, i.e. biomass is capable of replacing coal as a main fuel with municipal solid waste materials added as an auxilliary fuel component. It was shown that stable combustion conditions can be sustained using biomass and waste materials, due to the more reactive (relative to coal) characteristics of biomass facilitating combustion of less reactive (yet higher energy content) components of the MRFR fraction such as dense plastics.

As the proportion of MRFR was increased in the fuel mixture, combustion efficiency declined, an observation attributed to insufficient residence time of this fuel fraction within the freeboard zone of the fluidised bed combustor. The addition of MRFR to the fuel mixture had the effect of *reducing* emissions of some pollutants. Compared to combustion of pure biomass (i.e. 100 % DDGS and 100 % wheat straw), emissions of: hydrogen chloride; nitric oxide and sulphur dioxide were lower for the majority of combustion tests where MRFR constituted part of the fuel mixture. Data collected from the measurement of gaseous emissions showed that emissions of some pollutants (notably hydrogen chloride as an example), are inhibited by the addition of MRFR to the fuel mixture of biomass and waste materials. A mechanism to explain this observation was proposed, based upon previous studies, that inhibition of pollutants

is due to the competition for a limited quantity of free radical intermediates that are necessary for formation of pollutant compounds. Comparison of concomitant nitrogen oxide emissions suggested that the nitric oxide emissions in particular were inversely proportional to sulphur dioxide emissions and it was suggested that this was due to the “limited free radical pool” mechanism. Emissions of sulphur dioxide were primarily controlled and minimised by the use of limestone as part of the fluidised bed material composition, where the presence of a significantly *excessive* quantity of limestone was a treatment contrary to the practice performed in previous studies elsewhere to use a defined calcium:sulphur ratio concomitant with the dynamic fuel feed rate. With respect to hydrogen chloride, the reversible reaction of lime and calcium chloride with hydrogen chloride and water was suggested as a plausible mechanism to account for seemingly high rates of absorption of hydrogen chloride.

Interactions between selections of gaseous pollutants were investigated. It was found that simultaneous emissions of hydrogen chloride and carbon monoxide were such that increases in the combustion temperature is not necessarily an effective action to improve combustion efficiency by reducing carbon monoxide emissions; the presence of hydrogen chloride has the effect of inhibition of complete oxidation of carbon in biomass and MRFR fuels. A contrasting effect was evident from analysis of emissions of hydrogen chloride and nitric oxide, with respect to combustion temperature; for some fuel mixtures the normal positive correlation between nitric oxide emissions and combustion temperature was inhibited by the presence of hydrogen chloride but the effect of hydrogen chloride was strongest at relatively low concentrations with the effect decreasing as the concentration of hydrogen chloride increased.

Detection of the emissions of PCDD/F congeners using a novel simplified apparatus was devised for this PhD project. Results indicated that these compounds were not detected to a significant level, to suggest that these pollutants may not be produced. Similarly, emissions of metals were also not significant. However, the possibility that the flue gas sample collection apparatus was not wholly successful cannot be disregarded and therefore interpretation of the results with reference to trace metals and PCDD/F congeners is inconclusive.

Due to limitations of the PhD project scope and time constraints, it was not possible to perform complete method validation for comparison with existing validated standard methods of determination of PCDD/F congeners and metals in flue gas.

Detailed investigation of the gaseous emissions data for combustion of biomass and MRFR materials was performed to provide new knowledge of the behaviour for the concurrent combustion of these fuels, in the absence of coal as the main component solid fuel. From the range of fuel mixtures tested, the data obtained during this PhD research project indicates that some gaseous pollutant emissions may be minimised using fuel mixtures where waste materials are added to biomass fuel at a range of between 90 and 50 % (by weight) of biomass in the fuel mixture. This is a thermal conversion scenario that has not been previously researched to major significance within the academic research community. New knowledge has been provided within the field of pilot-scale combustion of biomass and MSW. A practical application of this contribution to knowledge should be the development of new, smaller industrial scale power systems capable of utilising biomass and MSW for the provision of combined heat and electrical power. A novel apparatus was designed to enable relatively rapid qualitative detection of PCDD/F congeners. Further development of such apparatus — including method validation — offers the prospect of increased monitoring of MSW combustors that should assuage public concern about the safe operation of EfW systems. It is envisaged that the gaseous emissions data obtained during this PhD research project will be used for validation of theoretical models developed previously elsewhere. Consequently, the aims and objectives of the PhD research project were achieved.

6.2 Recommendations for further research

6.2.1 Fuels

A wider range of biomass fuels could be investigated, to represent both a wider potential range within UK geography and also fuels available internationally,

e.g. agricultural waste by-products from oil palm, sugar cane and rice cultivation. Other waste materials may also be of interest for concurrent combustion with biomass such as clinical waste, SRF from MBT facilities and hazardous waste (e.g. chemically treated wood waste).

6.2.2 Experimental design improvements

Due to the laboratory scale limitations of the equipment used, the MRFR burnt in the fluidised bed chamber could not be fully represented. Some waste components such as beverage bottles were too large to be comminuted by the cutting mill. Moreover, materials such as tinned food cans or broken glass, were not selected due to both anticipated failure of the cutting mill and also that such materials do not contain any calorific value. Consequently, the combustion efficiency observations in this study are biased positively in that combustion is greater than would be expected had these materials been included.

Pitot tubes suited to the fluidised bed combustor flue gas exit should be made available to allow isokinetic flue gas sampling conditions to be monitored for greater accuracy of analysis of trace pollutants such as PCDD/F congeners and metals. The apparatus devised in this PhD project should be considered for a future project to validate the procedures used to achieve flue gas sampling and analysis. Additional experimental improvements for flue gas sample analysis to consider are: *a)* production of more than one laboratory sample blank; *b)* production of “combustion test” blank, where a number of sample blanks are connected to the flue gas sample collection apparatus and flue gas is extracted during operation of the combustor without any fuel mixture added; *c)* repetition of combustion tests to enable statistical analysis.

6.2.3 Ash characterisation

Some combustion tests conducted during the early phase of this PhD research project resulted in the formation of agglomerated fluidised bed ash (see § Appendix E). Analysis of both agglomerated and granular fluidised bed ash showed that agglomeration can be avoided by selection of a suitable mix-

ture of fluidised bed materials that contain calcium, to facilitate formation of granular ash particle which enables operation of the fluidised bed combustor for longer duration.

The fluidised bed bottom ash should be investigated for potential to be used as an aggregate for cement mortar as existing studies have been made, for example concerning leaching of metals (Saikia *et al.*, 2008). Other similar studies for investigation in the future should include characterisation of slag (e.g. the presence of metals in compounds such as calcium chloride) and fouling deposits.

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Appendix A

Legislation

A consequence of the multi-disciplinary aspect of this research project is that commercial application would require a wide range of regulations to be considered. In general, the use of biomass would offer various incentives to act as an encouragement whilst combustion of MRFR would demand the satisfactory adherence to compulsory regulations on environmental pollution control and also disposal of waste.

For the European Union, it has been agreed to generate electricity from renewable energy sources at a target of 22.1% of total electricity consumption by 2010 (European Parliament, 2001), which is achieved by a range of individual national scale targets (the UK target is 10%). These targets are indicated in Table A.2, where percentages values shown represent the national proportion of gross national electricity consumption to be generated from renewable energy sources by 2010. The range of national limits is indicated by Austria and Luxembourg which show largest and smallest national targets respectively. British implementation of this target is achieved via the Renewables Obligation, a “green certification” scheme that specifies minimum quantities of electricity generated from renewable energy sources that are supplied to the market (as shown in Figure A.1). It is a market-orientated method of introducing renewable energy to the supply chain, beneficial in minimising demand for government subsidies in comparison to a ‘feed-in tariff’ (Menanteau *et al.*, 2003), where renewable energy is supplied at a guaranteed price. The Renew-

ables Obligation determines a level of renewable energy derived electricity that must be supplied and this level increases at an annual rate (Table A.1). After public consultation, the British government published the Renewables Obligation Order 2009 with a new revision to allow for renewable energy technologies to qualify for various renewable energy certificates' values. Combustion of biomass (exclusively) with or without CHP provision is assigned a renewables obligation certificate value of 1.8 GJ (0.5 MWh) and energy from waste (with mandatory provision of CHP), 3.6 GJ (1 MWh). This example demonstrates that according to the mechanism of the scheme an electricity supplier can redeem twice as many renewables obligation certificates from a biomass combustor compared to an energy from waste with CHP. It should be noted that this legislation does not seem to differentiate between MSW being sorted (i.e. using MRFR or SRF) or not. In addition, energy from waste without provision of CHP does not qualify for any renewables obligation certificates. For the scenario of concurrent combustion of biomass and MRFR it would seem that renewables obligation certificates may be received only for a system configured to provide CHP and certified to be "good quality". Definitions of good quality CHP are defined in documentation published within 'Combined Heat and Power Quality Assurance', a government initiative to: "monitor, assess and improve the quality of UK Combined Heat and Power" (CHPQA, 2009). The qualifying terms for receipt of renewables obligation certificates are described separately, dependent upon power output of the CHP system and the quantity of renewable (biodegradable) material content in the waste fraction (CHPQA, 2008).

The concept of the waste hierarchy was introduced at the early part of this document (Figure 1.2). Combustion of MRFR would be classified for control via the Environmental Permitting (England and Wales) Regulations 2007, in accordance with the European Directive on waste incineration and administered by the Environment Agency in Great Britain. Of relevant to this research project, the Directive specifies limits on gaseous pollutant emissions (Table A.3). As a result of the European Directive on landfill of waste and implementation of secondary legislation in England of the Landfill Tax Regu-

Table A.1: Schedule of minimum quantities of renewable energy that must be used to generate electricity (Great Britain, 2009).

Period	Minimum quantity of renewable energy required (%)
01-04-09/31-03-10	9.7
01-04-10/31-03-11	10.4
01-04-11/31-03-12	11.4
01-04-12/31-03-13	12.4
01-04-13/31-03-14	13.4
01-04-14/31-03-15	14.4
01-04-15/31-03-16	15.4
and subsequent periods to 31-03-27	

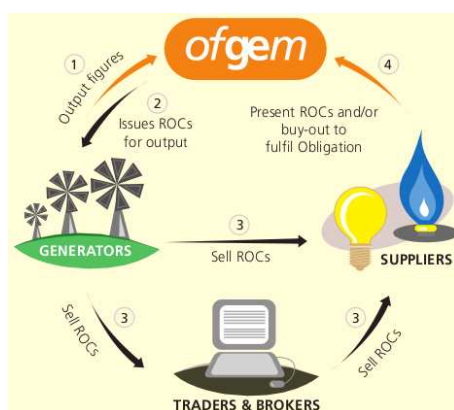


Figure A.1: Graphical representation of the Renewables Obligation Order administered by the government regulatory agency *Office of gas and electricity markets* (OFGEM).

lations (1996), the disposal of waste imposes financial costs, based upon the market value of land used for landfill disposal and an additional landfill tax imposition. These financial costs are represented by a ‘landfill gate fee’ and typical current values of the gate fee are £8–42 per tonne in addition to the landfill tax of £40 per tonne (WRAP, 2009). As a consequence, operators of waste combustion facilities are able to charge a fee to the supplier of waste prior to combustion of waste materials; typical waste combustion gate fees are £68–141 per tonne. Full technical-economic analysis of biomass-MRFR power systems was outside the scope of this PhD research project, although it has been demonstrated elsewhere (Yassin *et al.*, 2009) that use of waste materials in conjunction with fluidised bed combustion technology to be economically viable, although fluidised bed gasification was found to be more viable in consideration of the various legislative financial support mechanisms.

The Renewable Heat Incentive (RHI) is a new UK government scheme currently in preparation, intended to provide financial support for heat provision from renewable energy sources (DECC, 2010). The proposal of the RHI is to subsidise the supply of heat generated from renewable energy resources, using a tariff rate for each qualifying type of renewable energy. In the case of using biomass and MSW for supply of CHP the tariff rates are proposed on the basis of providing a rate of return of 12%. Tariff rates will vary, depending on the

Table A.2: Targets for generation of electricity from renewable energy sources for a selection of European Union member countries (European Parliament, 2001).

Austria	78.1
France	21
Germany	12.5
Italy	25
Luxembourg	5.7
United Kingdom	10

power output of the system; a large installation is classified by a power output of more than 500 kW, where the tariff rate would be 1.6–2.5 pence kWh⁻¹ for a duration of 15 years. When MSW is also utilised, the tariff rate for the fuel mixture containing the MSW component would be 50 % of the biomass tariff rate. This qualification of MSW for subsidy is applicable only to medium (45–500 kW) and large scale installations.

Emissions limits for various gaseous pollutants are shown in Table A.3, with respect to two thermal power outputs of power stations using fluidised bed technology and solid fuels including co-firing of waste (European Parliament, 2000). The carbon monoxide limit is set by national authorities (Environment Agency, 2008) in accordance with EU legislation. Nitrogen and sulphur oxides limits correspond to daily average values; metals, sample duration between 30 minutes and 8 hours; dioxins & furans, 6–8 hours. The unit of measurement is mg m⁻³ (normalised to O₂ content 6 %), except for dioxins and furans (ng m⁻³). An emissions limit of 50 ng m⁻³ for dust is also applicable when MSW forms part of the fuel.

Table A.3: Emissions limits for gaseous pollutants when fluidised bed combustion technology is employed for thermal conversion of fuel containing MSW.

Pollutant	Total emission limit	
	< 50 MW _{th}	50–100 MW _{th}
SO ₂	-	200
NO _x	-	350
CO		11.6
HCl		10
Cd, Tl		0.05
Sb+As+Pb+Cr+Co		0.5
+Cu+Mn+Ni+V		
Dioxins & Furans		0.1

Appendix B

Fuel composition data conversion

In general, fuel composition is often expressed in terms of dry material whilst for practical purposes such as calculating the quantity of air required for complete combustion, the fuel composition on the basis of *as received* is more useful. Thus, “as received” is calculated as:

$$\text{ar} = \text{elements} + \text{ash} + \text{water} = 100$$

Similiarly for dry and DAF:

$$\text{dry} = \text{elements} + \text{ash} = 100$$

$$\text{daf} = \text{elements} = 100$$

where “elements” corresponds to a sum of all elements relevant in the fuel (carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, etc.) and ash (silica, potassium oxide, sodium oxide, aluminium oxide, etc.). Using values for *ar*:

Total elements = 100 - ash - water. Therefore,

$$\text{element } x \text{ (ar)} = \frac{x(\text{daf}) * (100 - \text{ash} - \text{water})}{100}$$

Ash (ar) is obtained from:

$$\text{ash (\% weight dry)} = \text{ash (\% weight ar)} * \frac{100}{100 - \text{water (\% weight)}}$$

It may be necessary to convert calorific values of fuels between gross and net expressions, the former being defined as the heat content during combus-

tion when the water formed is in liquid phase with fuel, water and flue gas temperatures are identical before combustion. Similarly, net calorific value is defined in the context of water formed in the *gaseous* phase and conversion between these two definitions is described below (van Loo & Koppejan, 2008).

$$\text{NCV} = \text{GCV} \left(1 - \frac{w}{100}\right) - 2.444 \times \frac{w}{100} - 2.444 \times \frac{h}{100} \times 8.936 \left(1 - \frac{w}{100}\right)$$

- NCV net calorific value (MJ kg^{-1} fuel)
- GCV gross calorific value (MJ kg^{-1} fuel)
- w moisture content of fuel (weight % ar)
- h concentration of hydrogen in fuel (weight % ar)
- 2.444 enthalphy difference of water in gaseous and liquid forms at 25°C
- 8.936 molecular mass ratio of water and hydrogen

Appendix C

Fuel quality standards

Specifications for the standard of solid biofuels and solid recovery fuels were introduced in § 2.4. For the fuels tested in this PhD research project, standard specifications have been deduced using the technical guidance documents. Relevant standards documentation is listed as follows:

- DD CEN/TS 14961:2005. Solid biofuels — fuel specifications and classes;
- PD CEN/TR 14745:2003. Solid Recovered Fuels;
- PD CEN/TR 15508:2006 Key properties on solid recovered fuels to be used for establishing a classification system.

C.1 Biomass solid fuel quality

C.1.1 DDGS

The by-product from manufacture of ethanol by fermentation of cereal crops such as wheat straw is classified as a herbaceous industrial process residue. DDGS was supplied in the form of pellets and as a consequence a specification for the properties of this fuel may be summarised in Table C.1.

Values for each parameter, e.g. pellet dimensions D06 correspond to the definition stated in the draft document technical specification 14961 (Standards, 2005).

Where values are greater than the upper limit, the value is shown in parentheses (e.g. S0.20+(0.59) indicates an upper limit for sulphur of 0.2 % weight on dry basis and an actual value detected of 0.59 %).

Table C.1: Specification of DDGS in accordance with fuel quality guidance documentation (Standards, 2005)

Specification of DDGS	
Origin	2.2.1.1 — herbaceous biomass, cereal crops and grasses
Traded form	pellets
Dimensions	D06
Moisture	M10
Ash	A6.0
(% weight dry basis)	
Sulphur	S0.20+(0.59)
(% weight dry basis)	
Mechanical durability	-
Amount of fines	-
Additives	none
Nitrogen	N3.0+(5.2)
(% weight dry basis)	
Net calorific value	18
(MJ kg ⁻¹ as received basis)	
Chlorine	Cl 0.10+(0.21)
(% weight dry basis)	

C.1.2 Wheat straw

The standard specification of the wheat pellets used in this PhD project is described in Table C.2.

Table C.2: Specification of wheat straw in accordance with fuel quality guidance documentation (Standards, 2005)

Specification of wheat straw	
Origin	2.1.1.2 — herbaceous biomass, agriculture and horticulture herb, cereal crops, straw parts
Traded form	pellets
Dimensions	D08
Moisture	M15
Ash (% weight dry basis)	A6.0+ (7)
Sulphur (% weight dry basis)	S0.10
Mechanical durability	-
Amount of fines	-
Additives	none
Nitrogen (% weight dry basis)	N3.0
Net calorific value (MJ kg ⁻¹ as received basis)	14
Chlorine (% weight dry basis)	Cl 0.10+(0.2)

C.2 Solid recovery fuel quality

A technical report has been published to establish a system of classification for SRF in general (British Standards, 2006a), based upon measurement of a number of parameters (Table C.3). On this basis it would suggest that the composition of MRFR (see Table 4.1) constitutes an SRF quality fuel.

Table C.3: Classification system for SRF

Classification of SRF	
Calorific value	13.5 MJ kg ⁻¹ , ar (range 9–18)
Chlorine	0.4 % ar, mean 1.4 % maximum
Mercury	0.028 mg MJ ⁻¹ ar, maximum

Appendix D

Supplementary biomass combustion

D.1 Trial of experimental parameters

During the development of the experimental test plan for this PhD project, other biomass fuels were investigated in conjunction with various fluidised bed combustor operating conditions; these supplementary fuels are shown in Table D.2 and Table D.3, with chemical compositions shown in Table D.1. The physical characteristics of these biomass fuels tested: miscanthus (with sodium hydroxide as binder); dimensions 6–8 mm diameter, 30 mm length; willow chips (particle size estimated at < 50 mm). All values shown on “as received” weight percentages basis. Composition of MRFR is shown in Table 4.1.

Table D.1: Compositions of miscanthus and willow biomass fuels.

	Miscanthus	Willow
Carbon	39.9	42
Hydrogen	4.64	4.8
Oxygen	35.5	36.2
Nitrogen	0.6	0.6
Chlorine	0.1	0
Sulphur	0.1	0
Ash	6.3	1.3
Moisture	13	15.1
Calorific value (gross, MJ kg ⁻¹)	16	17

Table D.2: Summary of operation of fluidised bed combustor. Median values shown for temperature and flue gas data.

Fuel mixture	Fuel feed (kg h ⁻¹)	Inlet air (l min ⁻¹)	Combustion temperature (fluidised bed sand, °C)	Flue gas content CO ₂ (% vol.)	Flue gas content O ₂ (% vol.)	Duration (hours)
Miscanthus	4	1400	818	8.0	12.2	4
Miscanthus-MRFR (90:10)	6	1150	746	-	-	1
Miscanthus-MRFR (80:20)	2	1050	605	-	-	3
Miscanthus-MRFR (50:50)	2	1400	715	7	12.5	2
Miscanthus-MRFR (30:70)	4	1300	827	8.4	11.8	3
Willow	4	1400	814	8.5	11.7	2
Willow-MRFR (90:10)	4	1400	709	7.1	12.7	3
Willow-MRFR (80:20)	6	1400	638	6.7	14.0	2
Willow-MRFR (50:50)	3	1400	719	6.8	13.4	3
Willow-MRFR (30:70)	4	1400	701	7.4	13.2	4

Table D.3: Operational characteristics of fluidised bed material

Fuel mixture	Fluidised bed total mass (kg)	Fluidised bed composition (SiO ₂ :CaCO ₃)	Fluidisation rate (mm H ₂ O)
Miscanthus	22	50:50	25
Miscanthus-MRFR (90:10)	22	100:0	15
Miscanthus-MRFR (80:20)	22	50:50	15
Miscanthus-MRFR (50:50)	22	20:80	20
Miscanthus-MRFR (30:70)	25	50:50	75
Willow	25	80:20	15
Willow-MRFR (90:10)	22	100:0	15
Willow-MRFR (80:20)	22	50:50	15
Willow-MRFR (50:50)	22	50:50	10
Willow-MRFR (30:70)	25	80:20	40

D.2 Combustion data results

Measurement of the combustion temperatures of the fluidised bed combustor was found to be very erratic for miscanthus and willow fuel mixtures (Figure D.1 and Figure D.2). As a result, periods of stable combustion could not be identified and therefore comparisons of gaseous emissions was not considered justified. Nevertheless, summaries of emissions data for a selection of gaseous pollutants are shown in Figure D.3. Unlike corresponding emissions data for DDGS and wheat straw fuel mixtures (i.e. Figure 4.9), hydrogen chloride emissions increase with the proportion of MRFR in the fuel mixture. Interestingly, whilst sulphur dioxide emissions are suppressed by addition of MRFR similarly to combustion of DDGS fuel mixtures (Figure 4.12), the trend for nitric oxide emissions for willow contrasted with that for DDGS fuel mixtures (Figure 4.11).

The unstable combustion conditions experienced using willow is probably a reason for the positive detection of eluants from the GC-MS analysis, since (the high) carbon monoxide emissions (Table D.4) due to incomplete combustion are associated with favourable conditions for formation of PCDD/F congeners (van Loo & Koppejan, 2008).

Table D.4: Mean carbon monoxide emissions during the combustion of willow fuel mixtures

Fuel mixture	CO emission (ppmv)
Willow chips	509
Willow chips-MRFR (90:10)	400
Willow chips-MRFR (80:20)	447
Willow chips-MRFR (50:50)	311
Willow chips-MRFR (30:70)	688

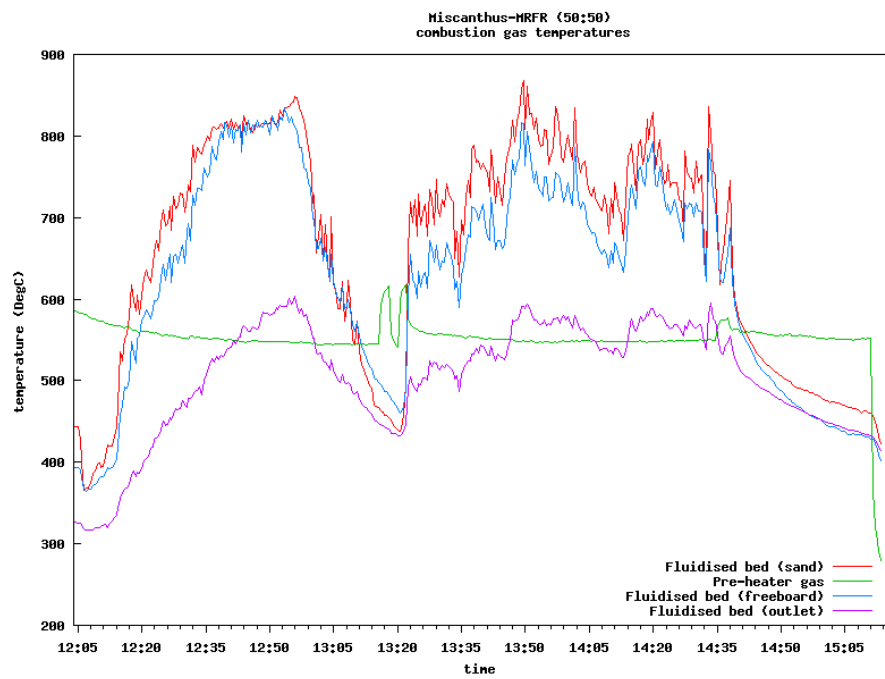


Figure D.1: Time series plot of temperatures during combustion of miscanthus-MRFR (50:50)

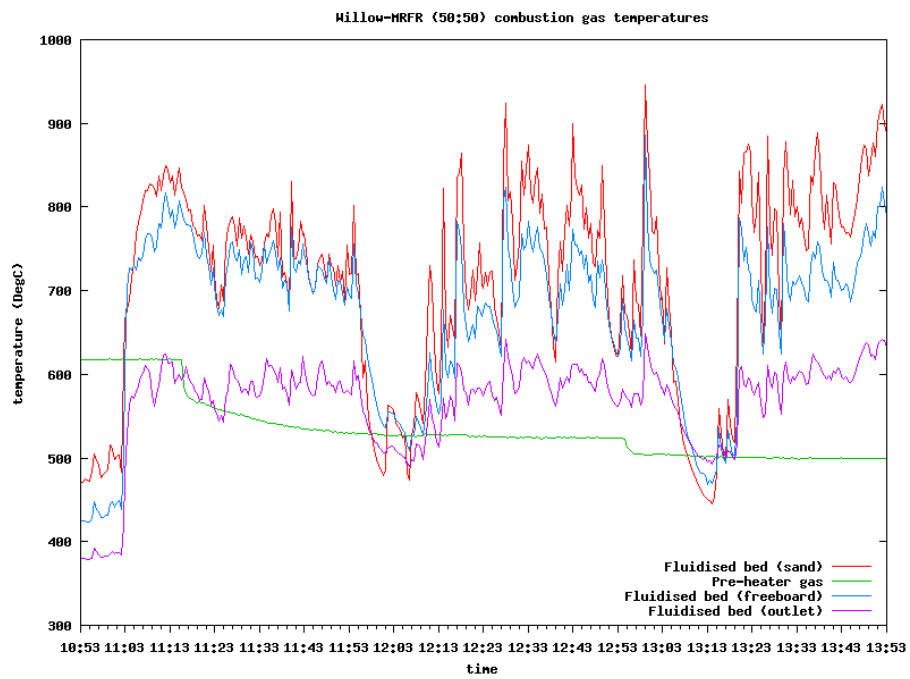


Figure D.2: Time series plot of temperatures during combustion of willow-MRFR (50:50)

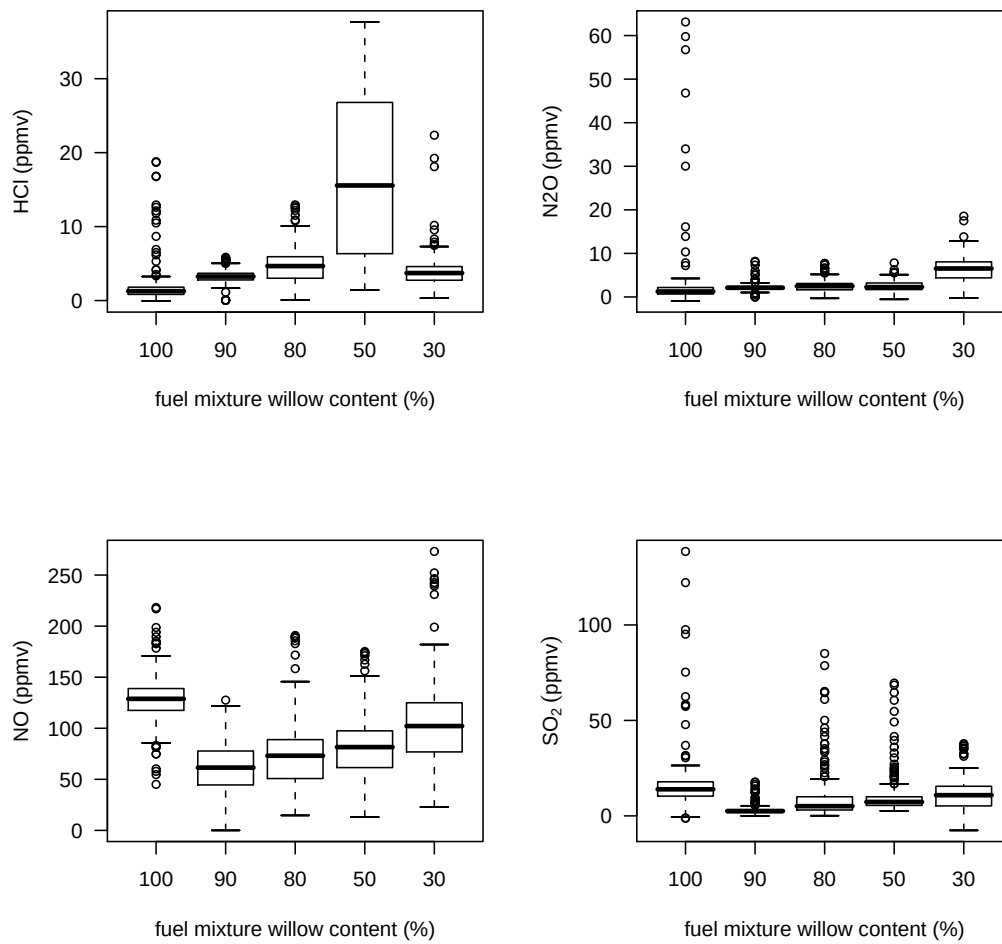


Figure D.3: Variation in a selection of gaseous pollutant emissions for a range of mixtures of willow-MRFR fuels

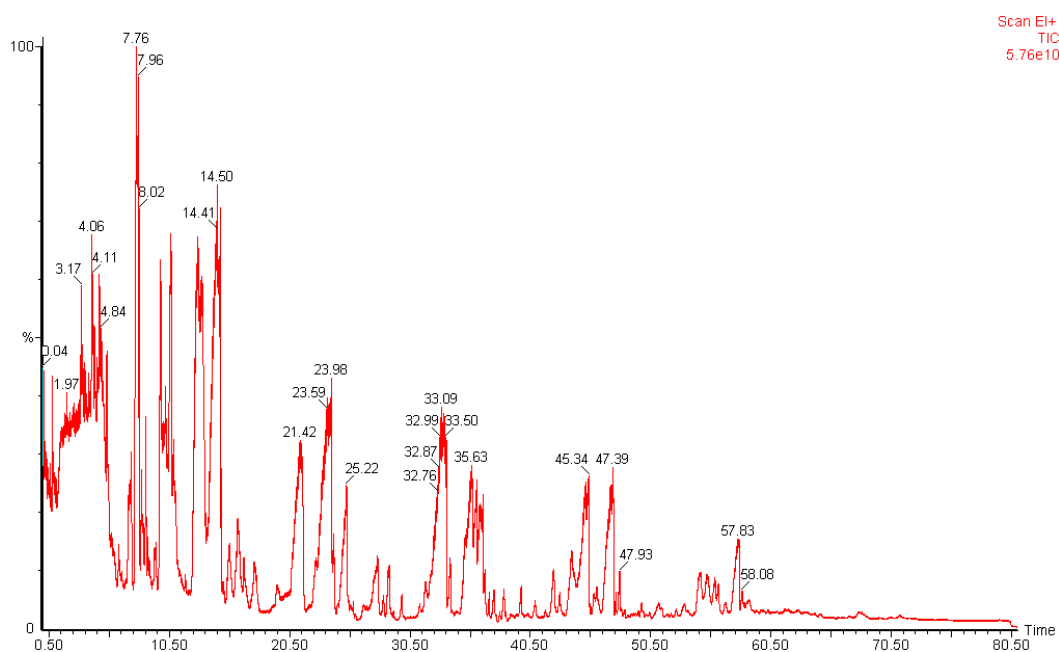
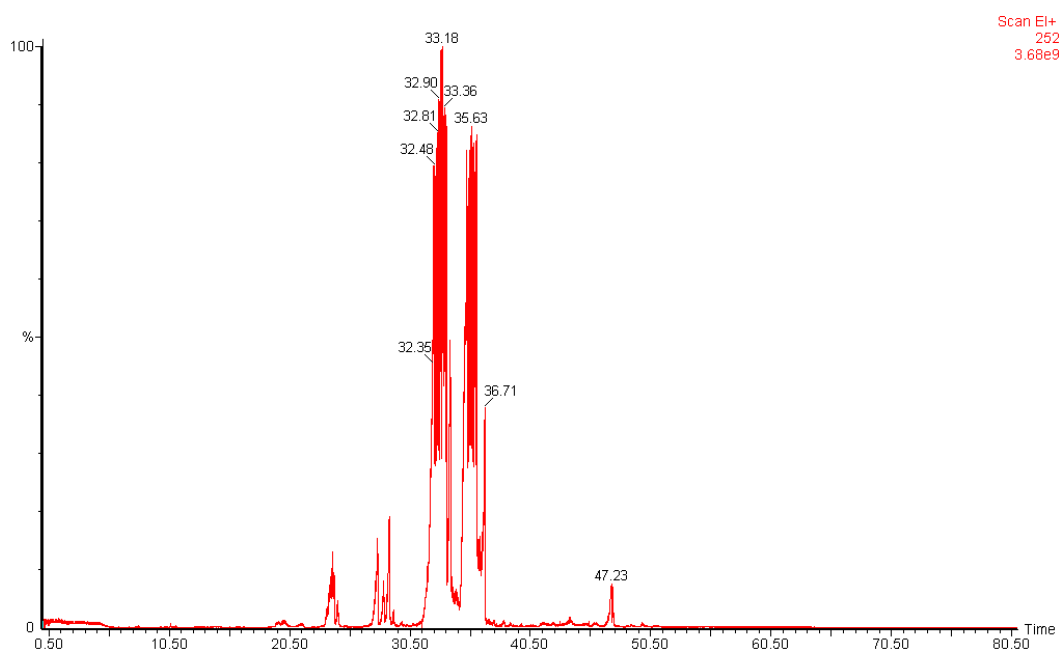


Figure D.4: Total-ion current (TIC) gas chromatogram, willow-MRFR 30:70.

Figure D.5: Mass (selected-ion) chromatogram, willow-MRFR 30:70, m/z 252.

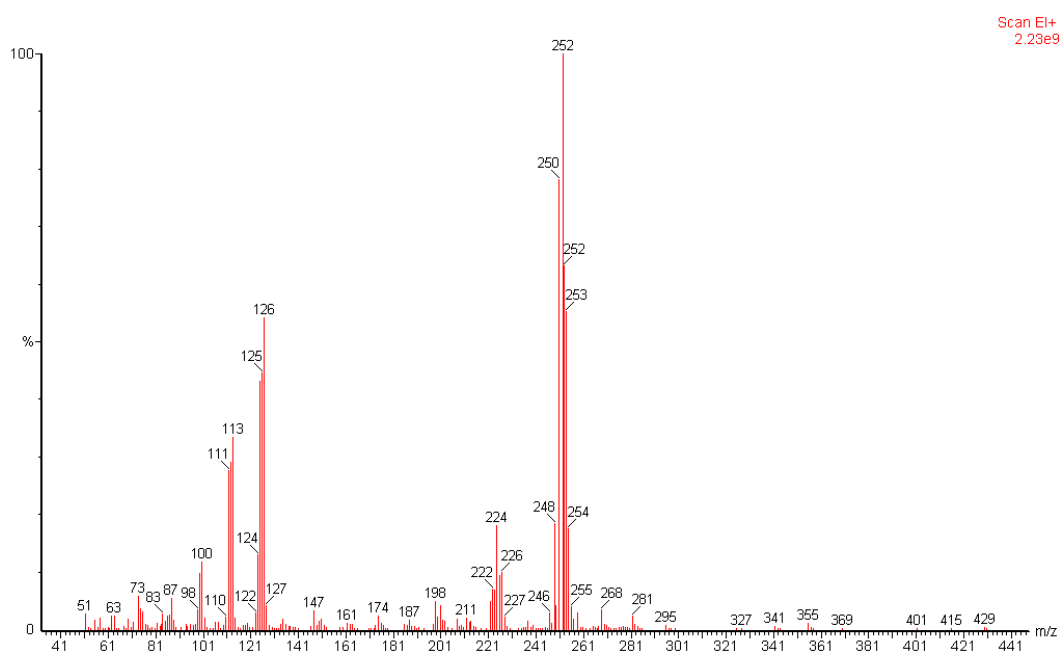


Figure D.6: Mass spectrum for precedent mass chromatogram (Figure D.5), willow-MRFR 30:70, m/z 252.

Appendix E

Structural analysis of combustion ash

E.1 De-fluidisation of combustor bed material

Agglomeration of the fluidised bed was considered a detriment to achieving good quality data by preventing operation of the fluidised bed combustor for significant duration and therefore analysis of the fluidised bed was not an objective of this research project. Nevertheless when agglomeration did occur (Figure E.2–Figure E.3), samples of the fluidised bed were analysed to determine the composition and structure of the fused material.

Agglomeration of fuel ash with the fluidised bed material was investigated using scanning electron microscopy (Philips, Eindhoven), connected to energy dispersive X-ray detection (Oxford Instruments, Abingdon); described together as SEM-EDX where the latter technique was used to make semi-quantitative analysis of elemental composition of the bottom ash. In this context the “semi-quantitative” results are defined as an approximate analyte concentration, “perhaps to within an order of magnitude or sometime better” (Green *et al.*, 2001) which seems appropriate for a technique that features uncertainties in the surface topography and the lack of homogeneity of the sample (Garratt-Reed & Bell, 2003) as well as a limit of detection of 0.1 % for such instrumentation.



Figure E.1: De-fluidisation of fluidised bed material during combustion of DDGS-MRFR (90:10); appearance of the fluidised bed from above (viewing downwards), using the inspection hole at the top of the combustor. Circular areas of fluidised bed material correspond to areas immediately above the gas distribution grid nozzles where air flow was able to agitate the granules, to maintain fluidisation. The areas appearing as lines correspond to static areas of defluidisation where the fluidised bed material was stationary, i.e. where agglomeration had occurred.



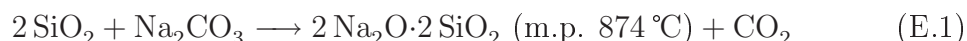
Figure E.2: Formation of fouling deposit (white colour) along internal walls of combustor during combustion of DDGS-MRFR (90:10). Tube located at top right of the photograph is the fuel “drop” tube as shown in Figure 3.5. Thin wires protruding into the freeboard are thermocouples as shown in Figure 3.7



Figure E.3: Agglomeration of fluidised bed material during combustion of DDGS-MRFR (90:10). The hole is the drain as shown in Figure 3.4

E.2 Scanning Electron Microscopy

Ash from biomass fuels are likely to agglomerate during combustion in a fluidised bed combustor and this behaviour is attributed to the formation of eutectic salts of sodium and potassium that change between liquid and solid phases at temperatures commonly found in this type of combustor (Basu, 2006). When a traditional fluidised bed material such as silica sand is used, a eutectic salt may be formed (equation E.1).



The corresponding potassium silicate has a similar melting point of 754°C . When partial melting of the silicates and similar compounds of comparable melting points occurs, this is known as *sintering*. Agglomeration is also said to be caused by additional interactions between ash and fluidised bed material. At the sintering temperature, (alumino-)silicates compounds within the fuel ash may become partially soluble in the liquid phases that forms ‘necks’ between fluidised bed material particles, to enhance inter-particle agglomeration. Furthermore chemical reactions contribute to agglomeration, such as sulphation (by SO_2) of lime on fluidised bed material particles to form calcium sulphate (van Loo & Koppejan, 2008).

Scanning electron microscopy (SEM) is the visual inspection of solids using electrons and X-ray radiation emitted as a result of the sample being subjected to a focussed beam of incident electrons (Figure E.4). Various interactions occur between the incident electron beam and atoms in the sample. Some interactions occur between the incident electron beam and lower weight atoms, to produce atomic excitation with the incident electrons travelling onward (‘secondary electrons’, at slightly lower energy) in a similar direction (Garratt-Reed & Bell, 2003). Other interactions occur between electrons and relatively heavier weight atoms that cause significant resultant changes in the direction in electron velocity; where the angle of diversion is greater than 90° , the diversions of incident electrons is classified as “backscattered”. The backscattered electrons are characterised as being high energy whilst the secondary electrons are low energy, both types being used to create an SEM image using separate

detectors. Electron measurement (both from the sample and also “bounced” electrons from the incident electron beam) is interpreted by computer software to produce an image of the sample surface. The X-ray emissions are detected by the auxillary energy dispersive X-ray detector (EDX), to obtain an estimation of the composition of the sample. An example instrumental configuration is SEM-EDX, where the SEM is connected to energy dispersive X-ray detection and the latter technique was used to make semi-quantitative analysis of elemental composition of the fluidised bed “bottom” ash.

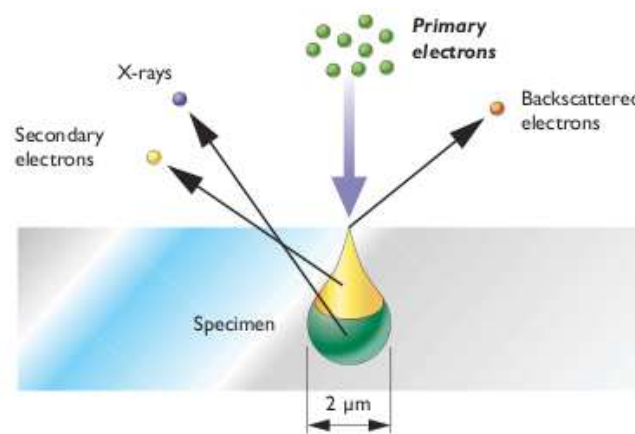


Figure E.4: Schematic diagram of SEM analysis (Vervest, 2005)

E.3 Agglomeration study by SEM-EDX

Low level magnification was performed using standard operating conditions of the instrument, whilst high level magnification involved the creation of a cross-sectional area of the sample (e.g. Figure E.14). At low levels of magnification, fluidised bed material can be seen to be either agglomerated or remaining in finely divided granular form (Figure E.5–Figure E.15).

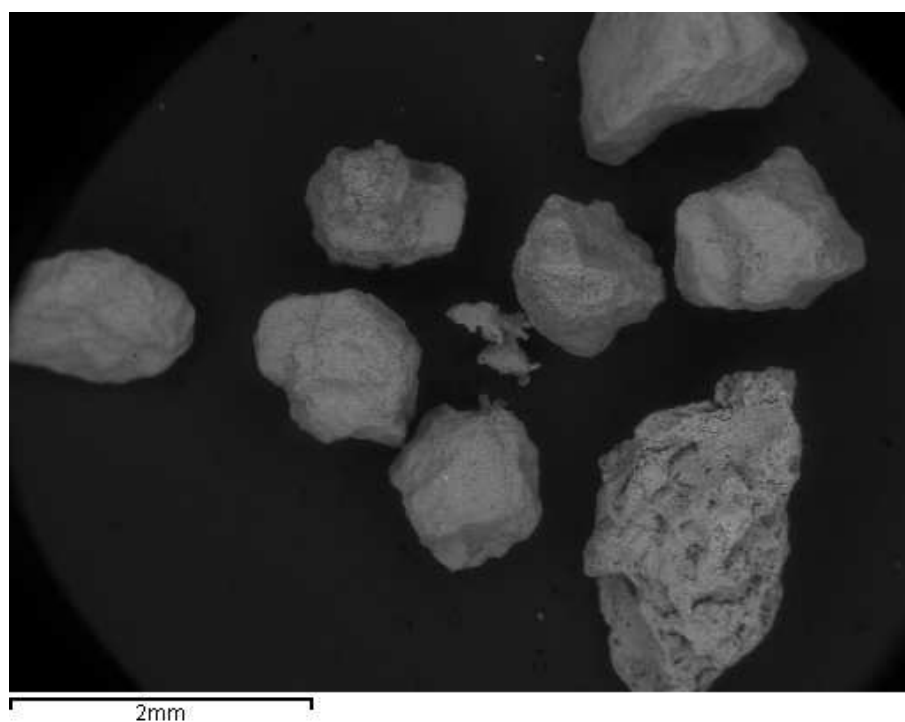


Figure E.5: Micrograph of fluidised bed material sand ($\text{SiO}_2\text{-CaCO}_3$, 50:50) before combustion with fuel

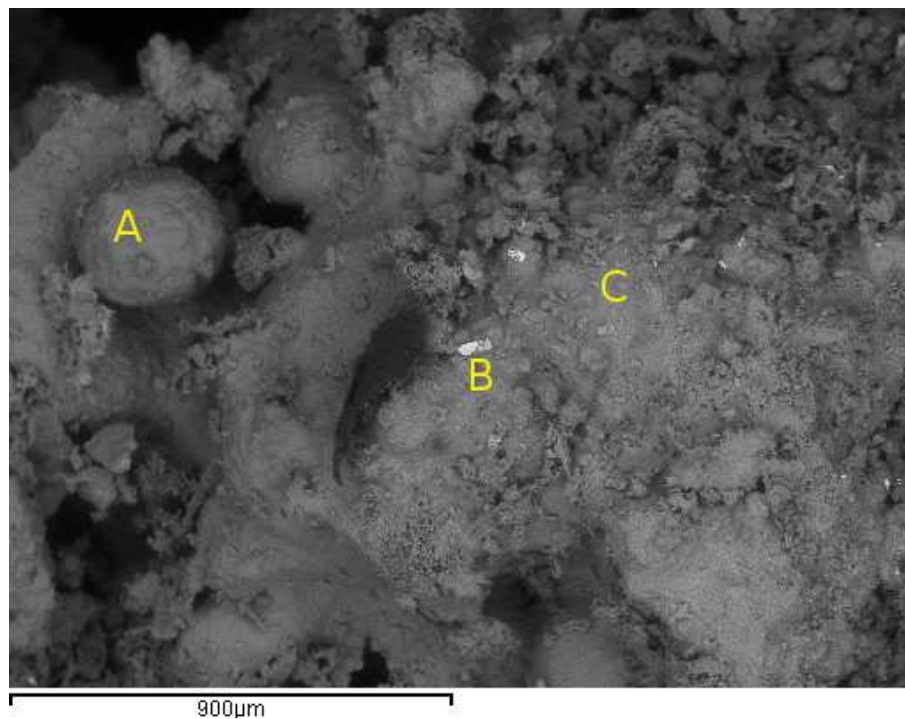


Figure E.6: Micrograph of fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10).

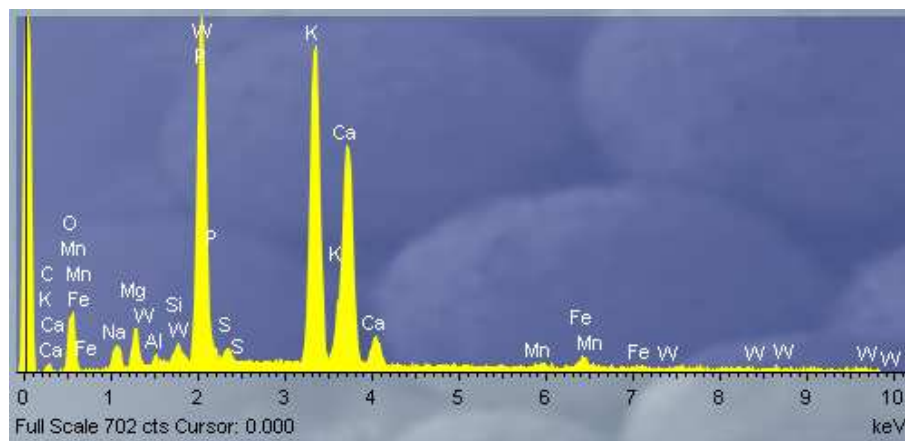


Figure E.7: EDX spectrum of zone A in Figure E.6, fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10).

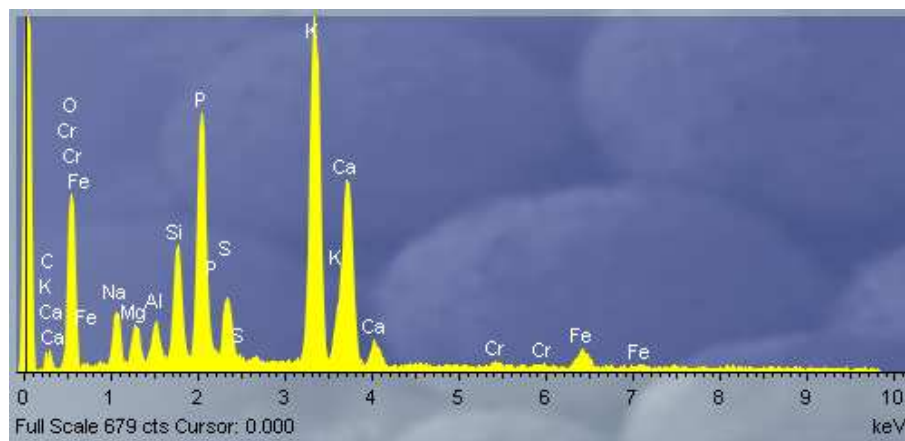


Figure E.8: EDX spectrum of zone B in Figure E.6, fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10).

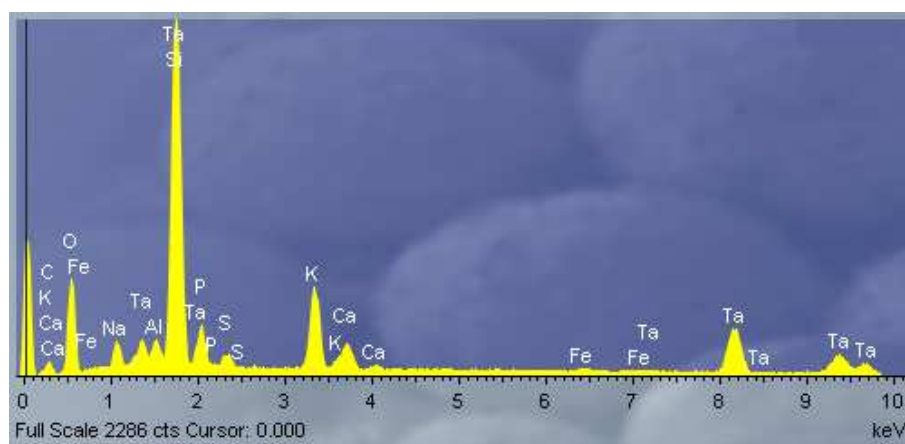


Figure E.9: EDX spectrum of zone C in Figure E.6, fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10).

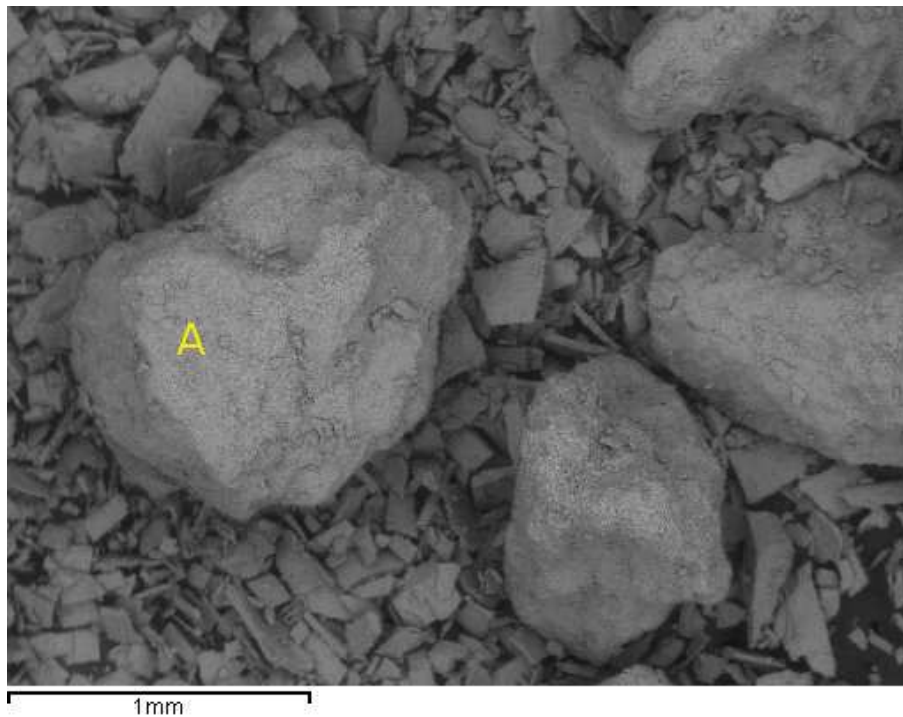


Figure E.10: Micrograph of fluidised bed bottom ash (fluidised bed material, $\text{SiO}_2\text{-CaCO}_3$, 50:50 with fuel miscanthus-MRFR, 80:20). The absence of any agglomeration is clearly evident.

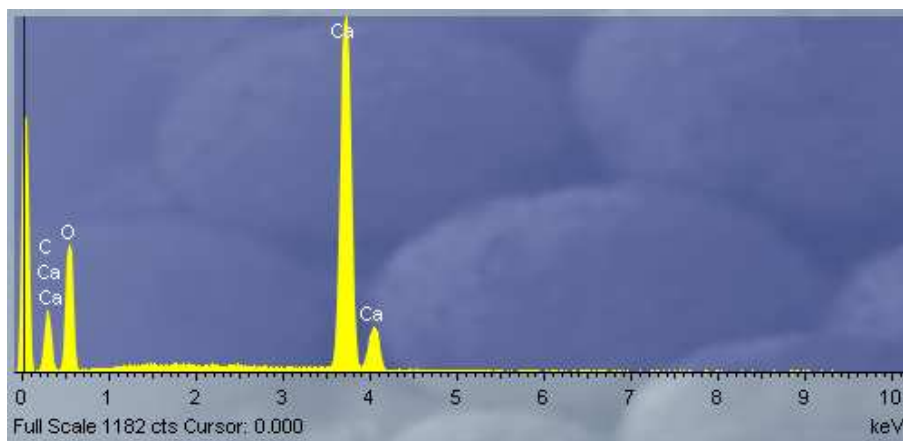


Figure E.11: EDX spectrum of zone A in Figure E.10, fluidised bed bottom ash (fluidised bed material, $\text{SiO}_2\text{-CaCO}_3$, 50:50 with fuel miscanthus-MRFR, 80:20).

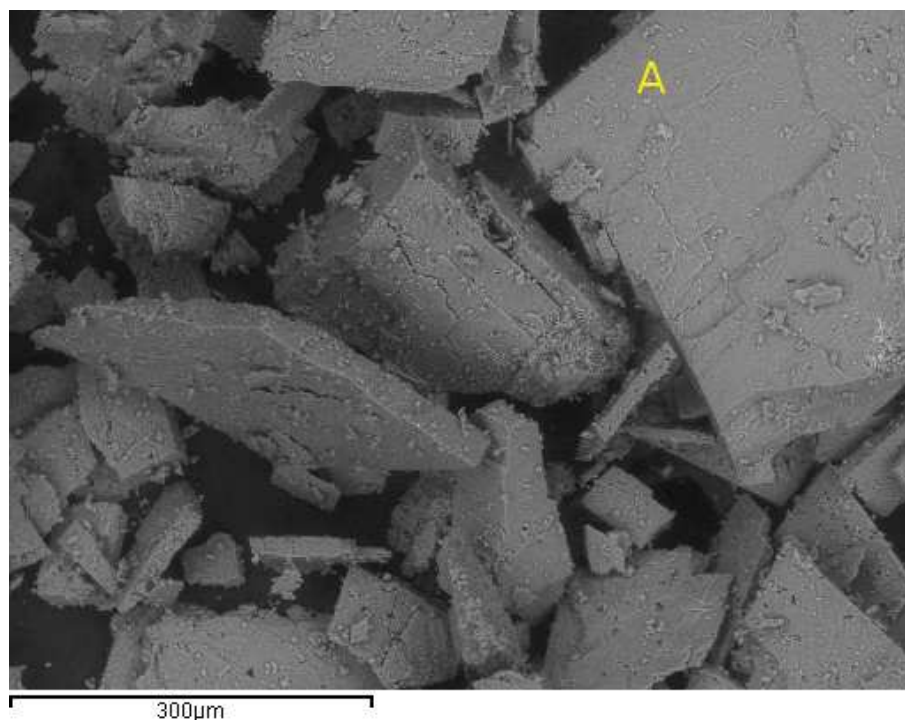


Figure E.12: Micrograph of fluidised bed bottom ash (fluidised bed material, $\text{SiO}_2\text{-CaCO}_3$, 50:50 with fuel miscanthus-MRFR, 80:20).

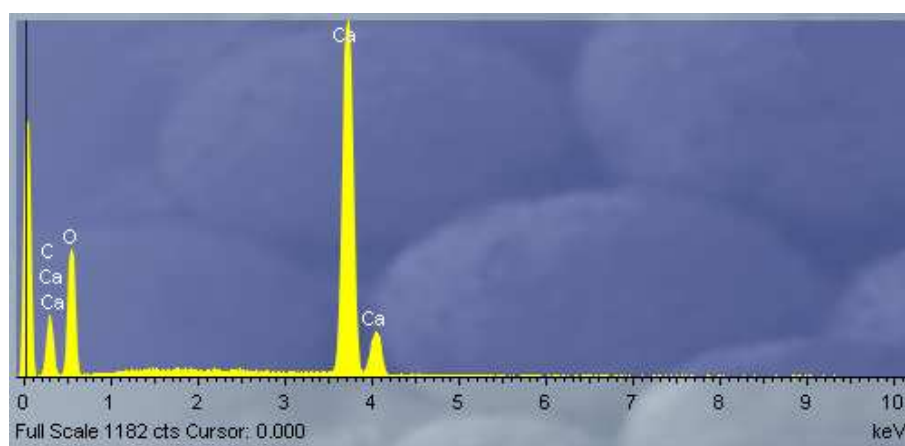


Figure E.13: EDX spectrum of zone A in Figure E.12, fluidised bed bottom ash (fluidised bed material, $\text{SiO}_2\text{-CaCO}_3$, 50:50 with fuel miscanthus-MRFR, 80:20).

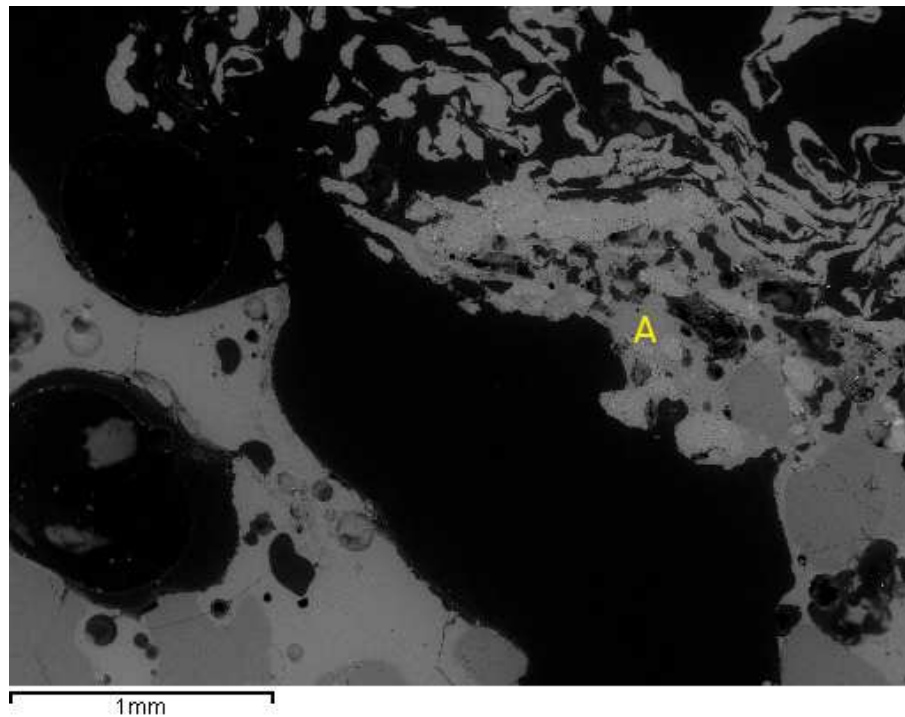


Figure E.14: Cross-sectional micrograph of fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10). The black areas are the background of the sample mount platform, due to epoxy resin used to mount the sample.

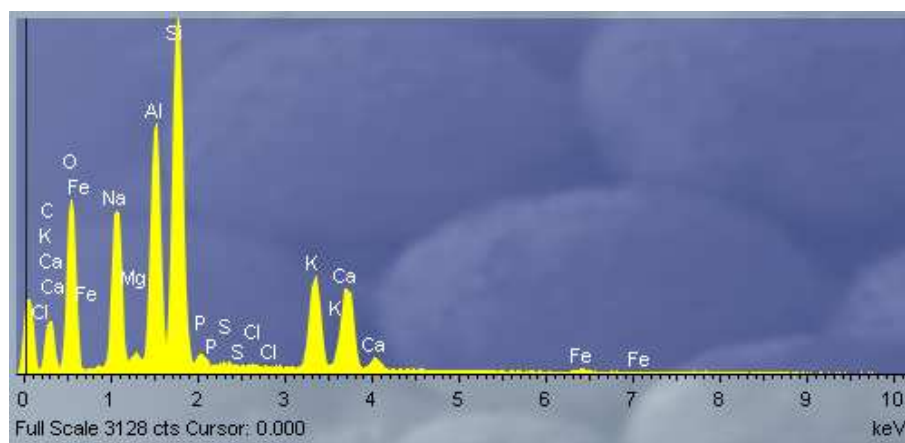


Figure E.15: EDX spectrum of zone A in Figure E.14, fluidised bed bottom ash (fluidised bed material, SiO_2 with fuel miscanthus-MRFR, 90:10).

Appendix F

Computer software

A range of computer software programs were used to enable completion of this project. There are generally characterised as being almost entirely open source (OSI, 2010), or free software (GNU, 2010) to use. Spreadsheet calculation and basic text documents were created using OpenOffice (OpenOffice, 2007) and this PhD thesis was produced using the well-known document formatting and typesetting software, L^AT_EX (L^AT_EX, 2008) in conjunction with supporting documentation (Kopka & Daly, 1995). Computer software was used within a GNU/Linux distribution computer operating system, Mandriva 2007 edition (Mandriva, 2007).

Manipulation of real-time data was required for the FTIR instrument that was used to measure flue gas composition, because it produces data of irregular frequency, preventing direct comparison with data recorded by the thermocouples dataloggers. To enable data visualisation to be performed with temperature and gas emission data, statistics software (R, R Development Core Team (2009)) was used to manipulate the data to create a regular matrix for subsequent plotting of data (Zeileis & Grothendieck, 2005). Data visualisation of gaseous emission data (e.g. Figure 4.3, Figure 4.17) was created using Gnuplot (Williams & Kelley, 2007) and reviewed using OpenDX (IBM, 2008), an open source version of a software product developed by the IBM Deep Computing Institute research centre.

Appendix G

Dissemination

Below is a list of activities to disseminate knowledge, performed by this author throughout the duration of this PhD research project.

René Laryea-Goldsmith. SEM-EDX analysis of fluidised bed material agglomeration during concurrent combustion of biomass and non-recyclable municipal solid waste. Poster presentation abstract. 12th International Waste Management and Landfill Symposium, Cagliari., October 2009a.

René Laryea-Goldsmith. Concurrent combustion of biomass & municipal solid waste. Oral presentation. IChemE Regional Group Milton Keynes, April 2009b.

René Laryea-Goldsmith. Transport of trace metals from concurrent combustion of biomass and non-recyclable waste. Oral presentation abstract. 14th European Biosolids and Organic Resources Conference and Exhibition, Leeds., November 2009c.

René Laryea-Goldsmith. Concurrent combustion of DDGS and MSW PhD research project. Oral presentation. Supergen Bionergy Annual Meeting., March 2010.

René Laryea-Goldsmith, Paul Kilgallon, John Oakey, and Nigel Simms. Conference C92 of the Solar Energy Society, Energy in the city. In Michael Hutchins, Judy Turton, and Tony Day, editors, *Combustion of biomass and*

municipal solid waste to supply combined cooling, electricity and heating, pages 173–178, Abingdon, June 2010a. The Solar Energy Society. Article and oral presentation. ISBN 0904963764. Joint meeting of the Solar Energy Society and The Centre for Renewable Energy in Buildings.

René Laryea-Goldsmith, John Oakey, and Nigel Simms. Bioten conference. In A V Bridgwater, editor, *Combustion of biomass and municipal solid waste to supply combined cooling, electricity and heating*, Birmingham, September 2010b. Poster presentation.

René Laryea-Goldsmith, John Oakey, and Nigel J Simms. Gaseous emissions during concurrent combustion of biomass and non-recyclable municipal solid waste. *Chemistry Central Journal*, 2010c. Article in preparation. [On-line]. Available from: <http://journal.chemistrycentral.com>.