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Fate of nitrogen/trace metals species during combustion and gasification of biomass

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ABSTRACT

This thesis focused on the fate of nitrogen and trace metals species from combustion and gasification of biomass. The effect of process parameters on the release of these species during pilot-scale combustion and gasification of biomass was investigated and the information used to identify methods for the reduction of these species. The investigation focused on Miscanthus and Dried distillers' grains with solubles (DDGS). The pilot-scale test rigs used were a fluidised-bed combustor and a fixed-bed downdraft gasifier. The two fuels were analysed by means of proximate, ultimate and ash analysis. The process parameters monitored were temperatures, gas flow, gas composition and ash composition and the process parameters studied are bed temperature and equivalence ratio. The different nitrogen content of the two fuels plays an important role in the emission. Both bed temperature and air to fuel ratio have demonstrated to have an important influence in the release of nitrogen oxides in combustion and ammonia in gasification, therefore they can be used to mitigate the emission of these species in the flue gas. Both processes are affected by the high alkali metals content of the fuels for the tendency to form low melting composites. Differences have been highlighted in the metal distribution between combustion and gasification. The different nitrogen and ash content of the two fuels make the results of the present thesis applicable to predict the behaviour of other biomass fuels according to the fuel characteristics. The scale of the tests performed allowed highlighting which methods can be used to control the emission of nitrogen and trace metal species. Moreover, the investigation highlighted major drawbacks in the use of biomass fuels in both fluidised bed and fixed bed technology due to ash properties.

Keywords:
Miscanthus, DDGS, bed temperature, equivalence ratio,

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NOMENCLATURE

GHG = Green House Gases

IPPC = Integrated Pollution Prevention and Control

HHV = Higher Heating Value

LHV = Lower Heating Value

FA = Fuel to Air ratio

AF = Air to Fuel ratio

Φ = equivalence ratio

BFB = Bubbling Fluidised Bed

CFB = Circulating Fluidised Bed

CHP = Combined Heat and Power generation

IGCC = Integrated Gas Combined Cycle

SEM = Scanning Electron Microscope

EDX = Energy Dispersive X-ray spectroscopy

XRD = X-ray Diffraction

RSD = Relative Standard Deviation

1. INTRODUCTION

Since the beginning of the Industrial Revolution in the second half of the 18th Century, man has used fossil fuels for power plants, transportation, heating and cooling buildings as well as manufacturing of various goods. This along with the extensive use of the planet's resources (*i.e.* deforestation), has led to an increase on the concentration of pollutants in the atmosphere.

Among the polluting species, the green house gases (GHGs) are the ones creating most of the concern because they are believed to be the cause of global warming. GHGs are CO_2, CH_4, nitrogen oxides and halocarbons and are produced by different human activities: CH_4 is a by-product of agriculture, natural gas distribution and landfills; nitrogen oxides derive mostly from fertilization and burning of organic matters; and halocarbons are used as refrigerator agents (IPCC, 2007b). Global GHG emissions due to human activities have grown since pre-industrial times, with an increase of 70% between 1970 and 2004 (IPCC, 2007a). To mitigate the global GHG emissions, most of the industrialised countries have committed themselves to a significant decrease in GHG emissions when adopting the Kyoto Protocol in 1997 (Heinimö et al., 2007). Consequently, several technologies, policies and constraints have been applied to various sectors such as energy supply, transport, buildings, industry, agriculture, waste management and forestry. For what concerns the energy supply, one of the most important means is to increase the share of renewable energy sources in the total energy consumption. Renewable energy supplied in 2009 an estimated 16% of the global energy consumption counting traditional biomass, hydropower, wind, solar, geothermal, modern biomass and biofuels (see Figure 1)(REN21, 2011). The EU has set an overall target of 22.1% of renewable derived electricity by 2010 and the proposed share of this target by the UK Government is of sourcing 10% of UK electricity supply from renewable resources by 2010 and double this share by 2020 (www.euractiv.com, 2011).

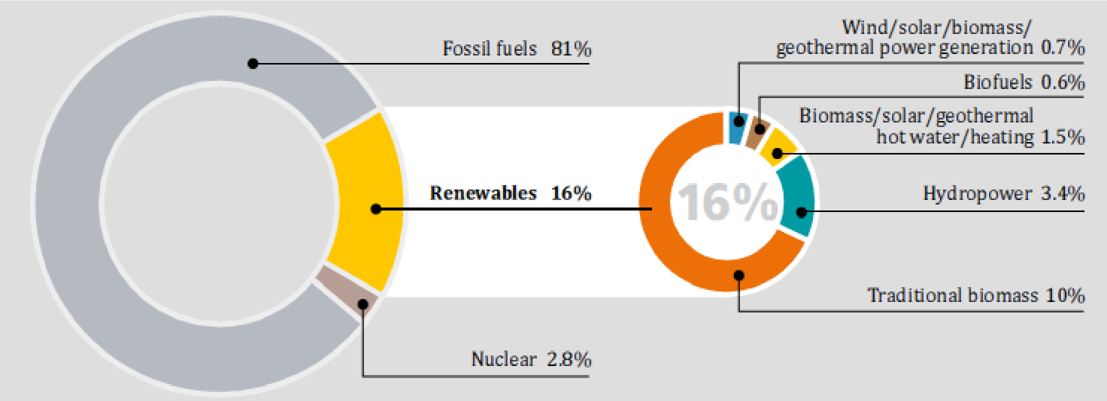


Figure 1. Renewable energy share of global final consumption in 2009 (REN21, 2011).

To encourage the uptake of renewable energies from electricity suppliers the main UK's mechanism is the Renewables Obligation (RO). The RO requires licensed electricity suppliers to resource a specific and annually increasing percentage of the electricity they supply from renewable sources. If they are unable to certificate the amount of renewable electricity they have supplied, the suppliers must pay a buyout fee (James and Howes, 2006). Therefore there is growing interest in the use of biomass energy in response to the Government and EU initiatives for the reduction of GHG emissions, but also to secure the supply of energy in response to increasing prices of gas and electricity.

Biomass, as a renewable energy source, refers to living or recently dead biological material that can be used as a fuel or for industrial production of chemicals. Although fossil fuels are originated from ancient biomass, they cannot be considered a renewable energy source since they are no longer part of the carbon cycle. In contrast, biomass involves a relatively short time scale and the CO_2 emitted during the harvest and combustion processes can be absorbed by the growth of new biomass. Other advantages with the use of biomass are the mobilisation of previously bothersome and environmentally dangerous materials and often less emission of NO_x and SO_2 compared to fossil fuel and coal combustion (Wereko-Brobby, 1996; Quaak et al., 1999). Materials that can be used as industrial biomass include woodworking industry residues (*e.g.* bark, sawdust, and demolition wood), agricultural residues (*e.g.* straw, husks), food industry waste (*e.g.* coffee, grain, sugarcane) and various other industry residues. Industrial biomass can be also grown (energy cropping) using plants such as Miscanthus, switchgrass, hemp, corn, poplar and willow. Biomass fuels and residues can be converted to energy via thermal, biological and mechanical or physical processes. Thermal processing currently attracts the most interest in Europe and Canada while ethanol production is the focus of attention in the USA for security of supply reasons (Bridgwater, 2006). Gasification offers higher efficiencies compared with combustion. Fast pyrolysis is still at a relatively early stage of development but offers the benefits of a liquid fuel with concomitant advantages of easy storage and transport as well as efficiency at the smaller scales (Bridgwater, 2006).

Despite the environmental advantages that biomass presents compared to fossil fuels (reduction of GHGs emission), its use still presents environmental problems due to the presence of components that can lead to the formation of pollutants during thermal conversion processes. The organic components of the biomass always contain – in addition to C, O and H – a small amount of N, S and Cl that can lead to the formation of polluting species such as nitrogen oxides, sulphur oxides and chlorides such as HCl and KCl. Moreover, the inorganic components contain alkali metals, alkali earth metals and heavy metals that can be released and form chemical species threatening either for the environment or for the process itself. The EU Directive (Official Journal of the European Communities,) concerning integrated pollution prevention and control (IPPC) applies to many sectors among which we find bioenergy. In general, wherever consideration is being given to the use of biomass as a fuel, this is likely to require an IPPC permit and it is illegal to carry out activities listed in IPPC regulations without a permit or that do not comply with the conditions in the permit. Nonetheless, the presence of contaminants affects the cost of the process in both combustion and gasification (*i.e.* gas clean-up costs and corrosion costs). The benefits derived from the use of biomass should exceed that of the cost of pollution prevention and control. Moreover, the demand for bioenergy is believed to increase in the future and new fuels are being investigated for energy use. This makes the investigation of major species emissions for these fuels important in order to predict the type and amount of emissions while using technologies that effectively control those emissions.

The project focuses on combustion and gasification of two biomass fuels:

- *Distilled dried grains with solubles (DDGS):* a co-product of the production of ethanol for agricultural products (bioethanol). Their thermal conversion is being studied as an alternative to natural gas for the production of the process heat necessary to run the ethanol plants in order to reduce the costs and improve their net energy balance (Tiffany et al., 2009).

- *Miscanthus:* Miscanthus, together with Phalaris and switchgrass (Hulsbergen et al., 2001), are perennial grasses attracting the attention of research as they belong to the C_4 rhizomatous group using the most efficient type of photosynthesis known (C_4 photosynthesis) and presenting the highest efficiencies of nitrogen and water use (Heaton, 2002). Out of them, *Miscanthus* is the only one proven to grow productively under a range of climatic conditions even at latitudes normally forbidden to C_4 species (which are usually only found in tropical climates).

The potential use of these two materials as biomass fuels has been investigated in several studies, but not enough has been investigated on the thermal conversion of these two biomass fuels. Therefore, the emission of nitrogen species and trace metal species for these two biomass fuels will be studied. Oxidation of N-containing molecules leads to the formation of nitrogen oxides (NO_x) and N_2O, species able to cause serious pollution issues such as acid rain, ground level ozone (O_3), greenhouse effect and reduced visibility. In the case of gasification the oxidation of nitrogen species doesn’t take place, but the precursors NH_3 and HCN can cause problems in the gas downstream. Ammonia can react with chlorides forming NH_4Cl, a compound involved in corrosion processes, or form nitrogen species very difficult to remove from the gas downstream. Hydrogen cyanide can be hydrogenated to ammonia or act as poison in some catalytic processes (Spliethoff, 2010). Discharge of metal ions, even in trace concentration, is an equally serious environmental threat as the fallout of these species from the flue gas can disperse in different parts of the environment and also find their way into the human body by direct absorption through the air, water or via the food chain. A further concern is that trace elements contained in the flue gas could lead to high levels of hot corrosion when the fuel gases are combusted in gas turbines.

The need to meet environmental emission limits and to obtain a product gas that matches the requirements of the intended users have lead to the development of various pollution prevention and control technologies and strategies. Several systems are available for NO_x removal and the application of each type will depend on factors such as the type of combustion system, the type of fuel and its cost. Conventionally, low NO_x burners, staged combustion and gas recirculation or re-burn are used to reduce the NO_x levels; however, with increasingly stringent emissions control, these techniques complement the reduction of NO_x rather than act as the primary means of removal. Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the predominant methods of NO_x reduction. In gasification, virtually no NO_x is formed, but the organic fuel nitrogen is partially converted into HCN and NH_3. Ammonia can be removed in a water scrubber or by catalytic destruction and HCN is removed by catalytic conversion to NH_3; moreover, the Rectisol process removes both NH_3 and HCN by absorbing these species from the raw syngas using refrigerated methanol (Lurgi, 2010). For what concerns trace metals, traditional air pollution control devices such as scrubbers, electrostatic precipitators and bag-house filters can be used for the fine particles, but they cannot capture all the submicron particulate enriched with trace metals: to capture these particles the gas has to be cooled to temperatures at which the above mentioned methods work to remove small particulate. Other systems involve the use of sorbents during the process, sorbents on which the metals can react and be isolated from the environment.

2. Thermal conversion of biomass

Biomass can be converted to usable products by means of different conversion processes:

- *Thermal conversion*: in thermal conversion processes the material is heated to promote its chemical decomposition. There are three types of thermal conversion processes:
    - Combustion is the process where biomass is completed burnt (oxidised) and the heat in the flue gas is converted into electricity.
    - Gasification is the process where biomass is partially oxidised to obtain a gas that can be used in gas turbines or to produce chemicals.
    - Pyrolysis is the process where biomass is heated in absence of oxygen to obtain a liquid product called bio-oil or a gas.
- *Biological conversion*: fermentation and anaerobic digestion are biological conversion processes fermentation and anaerobic digestion. In fermentation processes enzymes or acid are used to hydrolyse the biomass and produce ethanol that is then used as a transport fuel or for synthesis of chemicals (Bridgwater, 2006). Anaerobic digestion is a microbial conversion in the absence of oxygen that produces CH_4 and CO (biogas), gases used for combustion and to provide electricity (Bridgwater, 2006).
- *Mechanical conversion*: the oil contained in biomass is extracted leading to the production of oil to be used as transport fuel (Bridgwater, 2006).

In this project the investigation focuses on combustion and gasification of biomass, therefore the next two sub-sections will describe in more detail these two thermal conversion processes. First, the thermal properties of biomass solid fuels are described and, for completeness, at the end of the section a paragraph will also briefly present the pyrolysis process.

2.1 Thermal properties of biomass

Biomass consists of water, ash and dry-and-ash-free matter; the suitability of biomass as a fuel depends critically on the proportion of the three. The properties that determine the performance of biomass fuels in thermal conversion processes are:

- *Moisture content*
- *Ash content*
- *Volatile matter content*
- *Elemental composition*
- *Heating value*
- *Bulk density*

Because these properties can be quantified differently, definition of them is now given.

2.1.1 Moisture content

The moisture content is the quantity of water present in the material expressed as a percentage of the material’s weight. The moisture content of biomass potentially influences the efficiency of conversion of biomass to power and its value can vary substantially from material to material.

2.1.2 Ash content

The ash content is the quantity of inorganic components present in the material. It can be expressed on a wet, dry and dry-and-ash-free basis, but it’s usually expressed on a dry basis. The inorganic materials in biomass can be divided in two fractions:

- Inherent inorganic material, which exists as part of the organic structure of the fuel and is most commonly associated with the oxygen, sulphur and nitrogen-containing functional groups (Livingston, 2007).

- Extraneous inorganic material, which has been added to the fuel through geological processes, or during harvesting, handling and processing of the fuel (Livingston, 2007).

At high temperatures, the inorganic component can undergo a series of chemical and physical transformation including the fusion or partial fusion of quartz and silica particles and, at high temperatures, interactions to form alkali and alkaline earth metal silicates, the fusion or partial fusion of alumina-silicates, the decomposition of carbonates, oxalates, chlorides, etc. and other inorganic salts, the volatilisation of alkali metals and some heavy metals, particle fragmentation by thermal shock and the rapid release of gaseous species from particles, and the coalescence of intra-particle mineral particles. These processes promote the formation of ash deposits and slagging ash that can influence the efficiency of the thermal conversion process and ash removal systems.

2.1.3 Volatile matter content

The volatile matter content is the part of the biomass that is liberated when the biomass is heated up to 400-500 °C and decomposes into volatile gases and solid char. Biomass fuels are characterised by high volatile matter content (up to 80%) compared to coal which has less than about 40% of volatile matter content (from: http://www.ecn.nl/phyllis/).

2.1.4 Elemental composition

The elemental composition refers to the ash free organic components of biomass. The main components are C, H, and O while N, S and Cl are present in a small proportion.

2.1.5 Heating value

The heating value is a measure of the energy chemically stored in any material: when energy is applied to the material, the chemical bonds are broken liberating this stored energy. The heating value is measured in energy per unit of substance (*e.g.* kJ/kg) and it is calculated with reference to a standardised environment. The standardisation involves the temperature, the state of water (liquid or vapour) and the combustion products. As different standard conditions exist, different heating values can be calculated:

- The higher heating value (HHV) (or *gross calorific value* or *gross energy* or *upper heating value*) is determined by bringing all the products of combustion back to the original pre-combustion temperature and condensing any vapour produced.

- The lower heating value (LHV) (or *net calorific value*) is determined by subtracting the heat of vaporization of the water vapour from the higher heating value. This treats any H_2O formed as a vapour. Therefore, the energy required to vaporize the water is not taken into account.

- The gross heating value accounts for water in the exhaust leaving as vapour, and includes liquid water in the fuel prior to combustion. This value is important for fuels like wood or coal, which will usually contain some amount of water prior to burning.

Both HHV and LHV can be expressed on a wet basis, dry basis and dry-and-ash-free basis. The lower heating value is sensibly correlated to the moisture content; in fact the water contained in the biomass absorbs part of the chemical energy liberated during the combustion process, thus decreases the heating value of the fuel. Also, more water content means less combustible matter which, on a wet basis, decreases the lower heating value per kilogram. Whereas for the higher calorific value the heat of evaporation is recovered completely by the condensation of the water vapour when the gases are brought to the reference state, but still the higher calorific value is affected by the moisture content because it decreases the content of combustible matter per kilograms of fuel.

2.1.6 Bulk density

Bulk density is defined as the weight of material per unit of volume (*e.g.* g/cm^3). It can be calculated on an oven-dry-weight basis (moisture content 0%) or an as-received basis (specifying the moisture content). The bulk density depends on the material with an extreme variation between different solid fuels, but it’s not an intrinsic property of a material and it can change depending on how the material is handled (for example in a pelletisation process).

The characteristics of a fuel affect the choice of the conversion technology used. Despite similarities in heating value, there are differences in moisture content, bulk density, volatile matter content, ash content (and also morphological differences such as size and size distribution) that make biomass fuels really different. Some of them are considered “easy” fuels (*e.g.* wood) as they can work with a variety of equipment, whereas “difficult” fuels (*e.g.* rice husks) can work only with specific equipment.

2.2 Combustion

The most direct process to convert biomass into usable energy is combustion. Combustion results in the complete oxidation of the fuel components; however, the composition of biomass can vary significantly and its combustion is more complex than gas combustion (*i.e.* methane or natural gas) involving more transformations. The combustion process can be divided into four main stages:

- *Drying:* non-flammable CO_2 and water are released.

- *Pyrolysis and reduction*: the temperature increase promotes chemical decomposition of the fuel into combustible gases and solid char.

- *Combustion of volatiles*: at a temperature exceeding their ignition point, the combustible gases burn above the fuel bed. The gas is ignited by radiant heat from already burning fuel particles.

- *Combustion of the char*: the solid char is combusted in the fuel bed.

The most usual oxidiser used in combustion is air and the amount of air theoretically necessary to achieve complete combustion is given by calculating the stoichiometric air. Nonetheless, in real systems, using the theoretical stoichiometric air to fuel ratio does not lead to complete combustion, hence real combustion systems are normally operated with a percentage of excess air. The fuel-air mixture having excess air is called fuel-lean mixture, whereas fuel-air mixture having excess fuel is called fuel-rich mixture and is used in gasification systems. The flue gas containing the energy (heat) produced during the combustion process inside the furnace, is then directed to a heat exchanger where a process medium or energy carrier, such as water steam or air, exchanges the thermal energy with the flue gas (Figure 2).

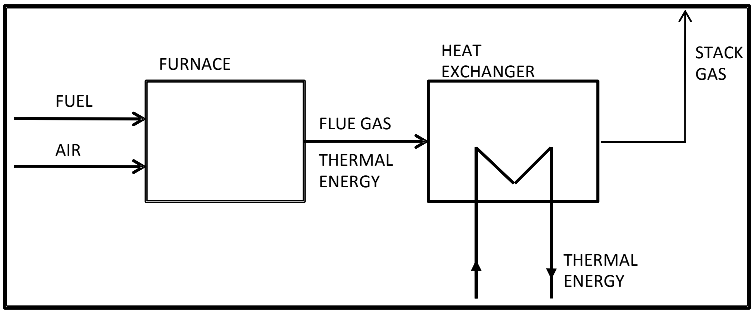


Figure 2. Schematic representation of a combustion process

In practice not all the heat contained in the chemical bonds of the fuel and liberated during the combustion process is converted into usable energy. There are factors causing the loss of part of the energy, they are (Quaak et al., 1999):

- Heat losses due to vaporisation of air and fuel water.
- Heat losses to the environment (by heat transmission through the furnace walls).
- Release of hot ash (the thermal energy stored in the ash thus is not used).
- Unburnt particles in the ash (the chemical energy in these particles is not released).
- Unburnt pyrolysis gases and carbon monoxide in the flue gas (these still contain chemical energy)(Quaak et al., 1999).

The efficiency of the furnace depends mainly on the completeness of the combustion and on the heat loss. If there are unburnt particles of fuel, the combustion is not complete and part of the chemical energy is kept in the fuel.

Usually to reach the best results more air than the theoretical amount is used; the theoretical amount of air necessary to achieve complete combustion is called stoichiometric air. There are several ways to define the fuel-air mixture; commonly, the values used are the fuel to air ratio (FA) or the air to fuel ratio (AF) which can both be expressed as mass or molar basis as follows (Keating, 2007):

Mass basis:

$$AF = \frac{\text{Mass of air}}{\text{Mass of fuel}}$$

$$FA = \frac{\text{Mass of fuel}}{\text{Mass of air}}$$

Mole basis:

$$AF = \frac{\text{Moles of air}}{\text{Mass of fuel}}$$

$$FA = \frac{\text{Moles of fuel}}{\text{Moles of air}}$$

Moreover, the equivalence ratio (Φ) is a dimensionless fuel-air ratio defined as follows (Keating, 2007):

$$\Phi = \frac{(FA_{(moles)})_{actual}}{(AF_{(moles)})_{stoichiometric}}$$

At stoichiometric conditions Φ=1 and optimal combustion is achieved at value near Φ=1.2 (i.e. 20% of excess air). The amount of air exceeding the stoichiometric is referred as the excess air. Moreover, the efficiency of the process depends on the heat exchanger efficiency which in turn depends on how effectively the heat is transferred from the combustion process to the energy carrier (*i.e.* the temperature of the gas as close as possible to the combustion temperature). The number of different technologies used for biomass combustion can be categorised under two types: fixed bed and fluidised bed (Figure 2).

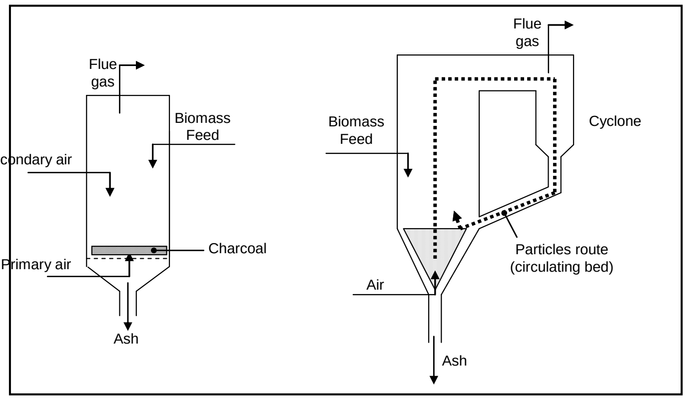


Figure 3. Schematic representation of fixed bed and fluidised bed combustion systems.

2.2.1 Fixed-bed combustion

Fixed-bed combustion systems consist of a grate in a combustion room. At the bottom of the grate primary air is supplied for combustion of the char to sustain the combustion of volatiles, while secondary air is supplied above the bed to combine with the heat generated by the char combustion. The two prominent types of fixed-bed combustion systems are underfeed stokers and grate firing. In the underfeed stokers, the grate is fixed and the feedstock is fed from below the grate while for grate firing there can be several types of grates such as: stationary sloping grates, travelling grates, reciprocating grates and vibrating grate. In stationary sloping grates the fuel burns as it slides down the slope under gravity; in travelling grates the fuel is fed on the side of the grate and is burnt when the grate transports it to the ash pit; in reciprocating grates the grate tumbles and transports fuel by reciprocating movements of the grate’s rods; and finally in vibrating grates the grate has a kind of shaking movement that spreads the fuel evenly.

2.2.2 Fluidised-bed combustion

In fluidised bed systems, the combustion chamber contains a bed of hot sand, limestone, or other non-combustible material; moreover, these materials are not inert and react with the fuel absorbing its components and can be used to reduce the emissions (e.g. limestone is used to absorb sulphur to reduce the emissions of SO_x). By blowing hot air from below the bed through a perforated bottom plate, the sand is forced upwards and a fluid-like behaviour is obtained (fluidisation). In this condition the hot sand acts as the heat-transfer medium (Quaak et al., 1999). The air flow can create two types of bed: bubbling fluidised bed (BFB) and circulating fluidised bed (CFB). In a BFB the sand is suspended above the plate like a bubbling fluid, in FCB the velocity of the air is high enough to drag small particles along with the gas stream. A cyclone separates them and they are redirect to the bed (Figure 2). The intensive mixing in a fluidised bed results in a superior heat exchange rate compared to fixed bed combustion. This enables the completion of the combustion with low excess air factor; also a fluidised bed system has more flexibility to changes in fuel properties, sizes and shapes, and it can work with up to 60% moisture content and 50% or higher ash content. Moreover, CFBs are more flexible than BFBs as the circulation rate can be used as an additional control.

2.2.3 Utilisation of thermal energy of combustion

To generate electricity from the thermal energy obtained by the combustion process a steam cycle can be used. As it can be seen in figure 3, the main components of a steam cycle are furnace, boiler, turbine and feed-water pump.

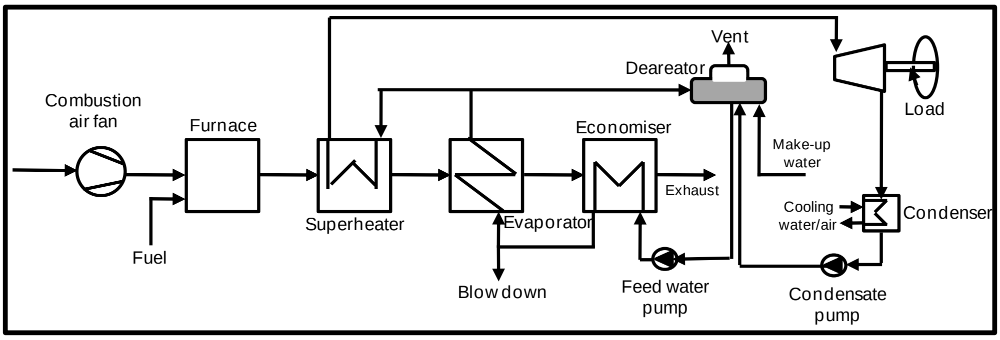


Figure 4. Schematic representation of a steam cycle (Quaak et al., 1999)

The steam cycle can be divided into 5 stages:

- The feed-water is pressurised by the pump and fed into the boiler.
- Inside the boiler the pressurised water is superheated to form pressurised steam.

- The steam is then directed to the steam turbine where it expands lowering the pressure and then passes through the condenser.

- After the condenser the water goes into the deaerator where incondensable gases are removed using some steam from the evaporator.

The efficiency of a steam cycle is the combination of the efficiencies of the components and the electricity used by some of the components (parasitic power). Typical values of the efficiency range from 5 to 40%. Combined heat and power generation (CHP) is the way to recover the loss of thermal energy of the process and boost the efficiency (theoretically) up to 89%. To further increase the efficiency, in CHP (Combined Heat and Power) processes, after electricity is produced by the steam turbine, the heat from the condensation of the steam is recycled in another process or used for district heating.

2.3 Gasification

Gasification is the process that converts biomass into a synthesis gas (syngas) by partial oxidation. The syngas consists of CO and H_2 in different ratios, while the oxidant can be air, pure oxygen or steam. The stages characterising the gasification process are:

- *Drying:* CO_2 and water are released from the fuel at temperatures where they cannot react (200-600 ^{o}C).

- *Pyrolysis and reduction*: the temperature increase promotes chemical decomposition of the fuel into combustible gases and solid char.

- *Combustion of the char*: the solid char is combusted in the fuel bed.

The chemical reactions characterising the gasification process are reported in Table 1. During the gasification, the combustion reaction goes to completion forming CO_2 and solid char: the heat released in this reaction provides the energy for the rest of the reactions in the pyrolysis and reduction stage. The gasification process relies on a balance between these reactions and the composition of the syngas is determined by the relative importance of the reactions. For biomass fuels, neglecting the minor constituents, the overall reaction can be written as:

$$C_xH_yO_m + \mathrm{Air} \quad \leftrightarrow \quad a\mathrm{CO} + b\mathrm{H_2} + c\mathrm{CO_2} + d\mathrm{H_2O} + e\mathrm{CH_4} + f\mathrm{N_2}$$

Table 1. Reactions taking place during gasification of biomass

Reactions	Formulas
Combustion	$C_nH_m + n/2\ O_2 \rightarrow n\ CO_2 + m/2\ H_2O^a$
Boudouard reaction	$CO_2 + C \leftrightarrows 2\ CO$
Water-gas reaction	$C + H_2O \leftrightarrows CO + H_2$
Methanation reaction	$C + 2H_2 \leftrightarrows CH_4$
Steam methane reforming	$CH_4 + H_2O \leftrightarrows CO + 3H_2$

[a] n and m depending on the main constituents of the fuel

As for combustion, the most usual oxidiser used in gasification is air. To obtain partial oxidation of the fuel, the amount of air that has to be provided is only a fraction of the stoichiometric, hence a fuel-rich mixture is used. The value of Φ optimal for gasification is in the range between 0.2 and 0.4 depending on the fuel used and on the process conditions. The types of gasification reactors can be grouped into 3 categories: fixed-bed gasifiers, fluidised-bed gasifiers and entrained-flow gasifiers. Fixed-bed and fluidised-bed systems work as described in paragraph 1.2.2., while in entrained-flow gasifiers a dry pulverized solid, an atomized liquid fuel or a fuel slurry is gasified with oxygen (much less frequently with air) in co-current flow. The need for a pulverised fuel makes the entrained-flow technology less suitable for biomass fuels than for coal for the high costs of fuel pulverisation.

2.3.1 Fixed-bed gasification

Fixed-bed gasifiers are usually fed from the top and have different configuration depending on the way the fuel is brought into contact at the gasification stage (Quaak et al., 1999). In updraft (or counter current) gasifiers, the air is blown from the bottom and the gas leaves from the top (Figure 4a). The main advantages of the updraft system are its ease of operation, low temperature of the exit gas, high gasification efficiency and that it can accept high moisture contents and different fuel sizes. The main disadvantage is the high tar concentration in the product gas because the tar is swept along with the air flow and does not undergo any thermal decomposition.

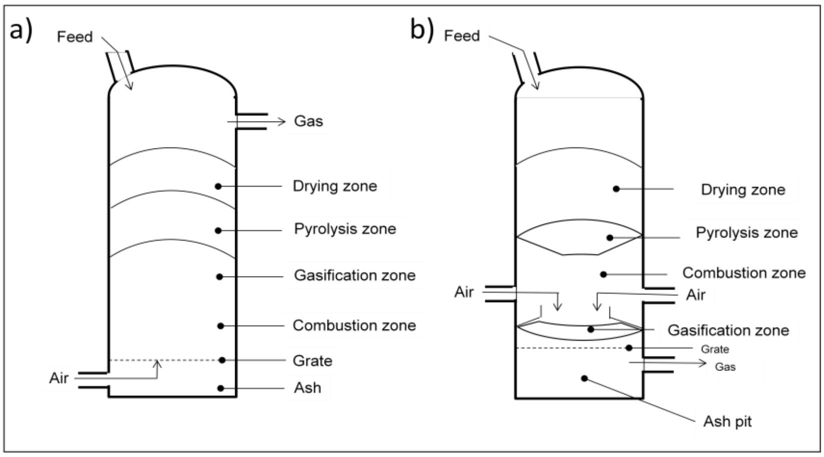


Figure 5. Schematic representation of updraft and downdraft fixed-bed gasifiers

In downdraft (or concurrent) gasifiers the air is fed from the top or from the sides and the gas leaves from the bottom (Figure 4b). In this case the gasification gas is formed in low and hot reaction zones near the burning charcoal that provides the heat for the thermal cracking of most of the tar; low tar in the exit gas is the main advantage for downdraft gasifiers. Disadvantages include the high amount of ash in the product gas, the low gasification efficiency due to too high exit gas temperature and the fact that it can accept few fuel sizes with low moisture content. Other fixed-bed configurations are cross-draft gasifiers and open-core gasifiers. Cross-draft gasifiers are adapted for the use of charcoal and can be used in small scale systems with a very simple cleaning train, but leads to a very high temperature gas and high tar levels. Open-core gasifiers are designed to be used with fine materials and they avoid bridging of the fuel.

2.3.2 Fluidised-bed gasification

As described in Fluidised-bed combustion, in fluidised bed systems the bed is made of hot sand, limestone or other non-combustible material fluidised by blowing hot air from below the bed through a perforated bottom plate and the velocity of the air flow determines if it’s a bubbling fluidised bed (BFB) or circulating fluidised bed (CFB) (Figure 2). As for combustion, fluidised-bed gasifiers have advantages compared to fixed-bed systems:

- Compact construction due to better heat exchange and reaction rate because of the high mixing rate.
- Flexibility on the use of fuels in different forms and with different characteristics.
- Low melting of ash due to lower reaction temperature.

On the other hand they present some disadvantages:

- High tar and dust in the exit gas.
- High gas temperature with presence of alkali metals in the vapour state.
- Incomplete carbon burnout.
- Complexity of operation.

For use in gas turbines, the gas coming out from the gasifiers has to be pressurised. To prevent the relatively high costs of cooling the gas and then pressurising it, the fuel can be gasified under pressure, producing a gas at the pressure of operation of the gas turbine.

2.3.3 Entrained-flow gasification

In the entrained flow gasifiers a pulverised fuel flows concurrently and reacts with steam and oxygen. The operating temperature is above the ash melting point leading to the destruction of tars and potentially high carbon conversion as well as the ash removed as slag. The issues related to entrained flow gasification are the high consumption of oxygen and the necessity of fuel treatment to get it pulverised. The two best-known types of entrained-flow gasifiers are the top-fired coal-water-slurry feed gasifier, and the dry coal feed side-fired gasifiers. There are also the dry coal feed top-fired gasifiers (Figure 5) (Higman et al., 2003).

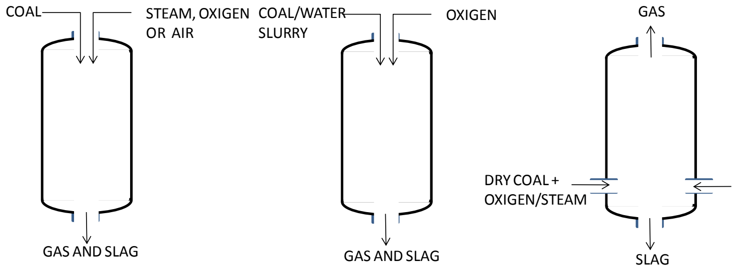


Figure 6. Main types of entrained flow gasifiers

2.3.4 Gasification efficiency syngas applications and treatments

There are several applications for the gasification gas, from heat and electricity production to the synthesis of chemicals. The two most commonly used criteria to define the efficiency of the gasification process are the cold gas efficiency and the carbon conversion, defined in APPENDIX D.

However, because of the different uses of the gas, sometimes the two numbers described above might give a limited description of the process efficiency. For example if a considerable amount of CH_4 is produced during gasification, the gas will have a high cold gas efficiency and it will be a useful gas for power generation; whereas it is preferable to have high content of CO and H_2 in a gasification gas intended for synthesis of chemicals. The most common applications for the synthesis gas are synthesis of ammonia, synthesis of methanol, production of hydrogen, synthesis of CO and oxoalcohols. For power generation, the gas is used in internal combustion engines (spark ignition and injection ignition or in gas turbines). In a gas turbine, compressed air reacts with the fuel (the gasification gas), then the flue gas coming out from the combustor expands in the turbine that drives the compressor and the additional load (Figure 7).

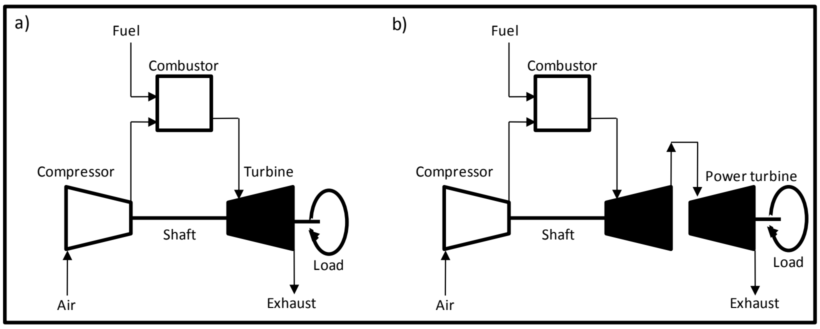


Figure 7. Schematic representation of gas turbines: a) basic gas turbine: b) two shaft configuration gas turbine

The highest electrical efficiency in the thermochemical conversion of biomass is obtained by an integrated gas combined cycle (IGCC), where the gas turbine is integrated with a heat recovery steam generator running a steam turbine producing electricity. Moreover, other specifications of the gas such as the level of contaminants (*i.e.* tar, organic volatiles, nitrogen species, sulphur species, inorganic species and fly ash) change according to its final use. In general terms, before the syngas can be used it has to be cooled and cleaned from tars, dust and alkali metals.

2.4 Pyrolysis

In pyrolysis the biomass is heated in complete absence of an oxidising agent, or with such a limited supply that gasification does not occur to an appreciable extent (partial gasification) (Bridgwater, 1990). The reaction mechanisms of pyrolysis for wood materials can be divided into four stages:

- Partial loss of volatile gases and light tar.
- Emission of CO and CO_2 by breakdown of carbonaceous materials.
- Exothermic reactions emitting CH_4 and C_2H_4, with rising in temperature.
- Complete decomposition.

Depending on the operating conditions, the pyrolysis can be divided into three subclasses: slow pyrolysis, intermediate pyrolysis and fast pyrolysis (Balat, 2008). Depending on the pyrolysis method and reaction parameters, the main product can be liquid, solid or gas. The parameters range for the different pyrolysis processes are summarised in Table 2.

Table 2. Main parameters range for different pyrolysis types

	Slow pyrolysis	Intermediate pyrolysis	Fast pyrolysis
Pyrolysis temperature (K)	550-950	850-1250	1050-1300
Heating rate (K/s)	0.1-1	10-200	>1000
Particle size (mm)	5-50	<1	<0.2
Solid residence time (s)	450-550	0.5-10	<0.5

Slow pyrolysis produces all solid, liquid and gaseous products in significant quantity, while intermediate pyrolysis produces mainly liquid and gaseous products and fast pyrolysis produces mainly gaseous products. The liquid part is composed of a complex mixture of oxygenated hydrocarbons, the solid product is char and the gas product is a fuel gas deriving from partial gasification, containing high levels of hydrocarbons like methane and saturated and unsaturated hydrocarbons (Bridgwater, 1990). Below are described the most common technologies used for pyrolysis processes are described below:

- Fluidised bed: the fluidised bed works as described for combustion systems.

- Ablative: the biomass is brought into contact with a fast moving hot surface such as a hot spinning disc or a rotating cylinder (Boutin et al., 1997).

- Entrained flow: this system has been described above for gasification systems.

- Rotating cone: in the rotating cone technology the biomass particles are fed at the bottom of a rotating cone together with an excess of inert heat carrier particles, so that the biomass is converted while being transported upwards in a spiral trajectory (Prins and Wagenaar, 1997).

- Vacuum moving bed: vacuum pyrolysis is typically carried out at a temperature of 500°C and a total pressure of less than 15 kPa. The biomass is carried in a heated moving bed under vacuum conditions. These mild conditions minimize secondary degradation reactions and enable the recovery of large quantities of pyrolytic oil (Yang et al., 2000).

The conversion of biomass into liquid products called “bio-oil” has advantages in transport storage combustion, retrofitting and flexibility in production and marketing (Bridgwater, 1990).The liquid product can be burnt straight away or more often upgraded to make it compatible with conventional fuel infrastructures. Biomass fast pyrolysis bio-oil can be used directly in diesel engines, in hydrocracking (conversion of the bio-oil into green diesel), gasification (bio-oil and char are slurried together and the slurry is gasified and the syngas is then processed to become green diesel) and fermentation.

2.5 Issues related to minor components

Pollution control has become in recent years one of the most important concerns of worldwide energy industry. The realization of thermal power processes needs to deal with the legislation concerning environmental pollution, hence the monitoring and control of gaseous affluent. The flue gas from combustion of biomass always contains nitrogen and oxygen (deriving from combustion excess air), carbon dioxide, water vapour and a small amounts of carbon monoxide, sulphur oxides, nitrogen oxides, chlorides, volatile hydrocarbons, particulate matter, alkali salts and heavy metals species. The discharge of these species in the atmosphere can lead to environmental issues:

- CO_2 is one of the major contributors to the greenhouse effect.
- Sulphur oxides, along with nitrogen oxides, are the main precursors of acid rain. This contributes to the acidification of lakes and streams, accelerated corrosion of buildings and reduced visibility.
- Chlorides, most commonly HCl or alkali metals salts, contribute to acid rains and represent corrosive species.
- Volatile hydrocarbons include a wide range of organic components that can have negative impact on environment or human health. They include methane and chlorofluorocarbons that contribute respectively to the greenhouse effect and the depletion of the ozone layer.
- Particulate matter, mostly containing alkali metals salts, is the solid-phase materials usually composed by the ash derived from mineral matter in the biomass. These metals can be corrosive or cause smog in the atmosphere.

- Heavy metals can be also present in trace concentration (trace metals) in the combustion flue gas and they are toxic for plant and animal life as well as harmful for human health.

As mentioned before, the two groups of compounds matter of this work are nitrogen species and trace metals species. Environmental issues related to the emission of this species and behaviour of them in thermal conversion processes will be discussed in this report.

2.5.1 Issues related to nitrogen species in combustion and gasification processes

Combustion of N-containing molecules leads to the formation of nitrogen oxides (NO_x), species able to cause serious pollution issues. Most relevant between these problems are:

- *Acid rain:* being NO_x transparent to most of light wavelengths, they have a lifetime of several days, thus can be transported for long distances (Environmental Protection Agency, Research Triangle Park, NC. Clean Air Technology Center, 1999). Then when they come into contact with moisture, they are carried to the ground in the form of nitric acid (HNO_3).

- *Ground level ozone (O_3):* nitrogen oxides and volatile organic compounds can combine, in the presence of sunlight, to form O_3. Being formed in the troposphere (first layer of atmosphere, up to 20 km) it can be breath and can become harmful to human health, causing respiratory diseases.

- *Greenhouse effect:* nitrogen oxides are important greenhouse gases, in particular N_2O.

- *Reduced visibility:* nitrate particles can reduce the visibility by both absorbing light and scattering effect (smog).

In gasification the oxidation of nitrogen species doesn’t take place, but the precursors NH_3 and HCN are dangerous for human health and can cause problems in the raw synthesis gas as follows:

- *Ammonia* can react with chlorides forming NH_4Cl, a compound causing corrosion, or form amines, very difficult to remove from the gas downstream (Higman et al., 2003).

- *Hydrogen cyanide* can be hydrogenated to ammonia or act as poison in some catalytic processes (Higman et al., 2003).

- *Nitrogen oxides* are dangerous in ammonia plants as in the liquid nitrogen washing they can form, with unsaturated hydrocarbons, a harmful resin (Higman et al., 2003).

2.5.2 Issues related to trace metals species in combustion and gasification processes

Thermal conversion processes are among the human activity emitting most of the trace metals into the environment. The long term exposure to these elements can cause adverse health effects (Bridbord, 1977), thus the emission of toxic metals in the atmosphere is regulated (Linak and Wendt, 1993). Elements like arsenic, beryllium, chromium and nickel have been associated with cancer and lung diseases, while elements such as lead, mercury and cadmium can produce disorders to various human organs (Bridbord, 1977). The exposure to trace metals from the environment can occur through the inhalation or through the diet from food contaminated with excessive quantity of toxic metals. Plant-derived biomass fuels contain lower amounts of heavy metals especially if compared to municipal waste or industrial residues that can contain high amounts of pigments (i.e. inorganic elements) and chlorine that increase the volatility of the metals (Linak and Wendt, 1993). Moreover, operational problems can occur when ash materials form depositions in gas-side surfaces (e.g. furnace, heat exchangers and gas turbine’s blades) (Livingston, 2007).

These problems are caused by some compounds of sodium, potassium, phosphorus and also by heavy metals compounds (Livingston, 2007). The most important consequences of the deposition and retention of ash material in the combustion and gasification downstream are listed below (Livingston, 2007):

- *Agglomeration of the ash particles in the fuel bed*: this can lead to poor combustion conditions due to local change in the bed conditions (e.g. temperature of the bed) and to the partial or total loss of fluidisation in fluidised bed operation.

- *Deposition of fused slag material on combustor components (slagging):* this can result in interference with the normal performance of the combustor. If slagging occurs on heat exchanger it can result on reduced heat absorption of the furnace decreasing its efficiency.

- *Formation of fouling deposits*: fouling deposits are ash occurring at lower temperatures than slag deposits, taking more time to form; they also lead to loss of efficiency in gas downstream apparatus.

The accumulation of fused material and the deposition of the ash over time lead to the damage of the combustor by local overheating, ash bridging between tubes and corrosion of the surfaces. The ashes causing fouling and slagging problems contain mainly alkali metal species; therefore due to its high alkali content, biomass has a very high fouling and slagging potential (Livingston, 2007).

As a result, all these species need to be removed from the gas downstream leading to increasing cost for the gas clean-up. The investigation of the mechanisms that govern their release from thermal conversion of biomass helps to find the most appropriate measures to mitigate their emission. Thus, the next sections report the mechanism of release of nitrogen species and trace metals species during thermal conversion processes, along with the measures that can be applied for their reduction.

3. Transformation of nitrogen species during thermal conversion of biomass

The chemical reactions of nitrogen compounds in combustion systems have been intensively studied and NO, NO_2, N_2O and N_2 have been identified as main products. The formation of nitrogen oxides (NO_x) has different sources: it can derive from the fixation of N_2 in the combustion air and can occur by different mechanisms. The molecular nitrogen can react with atomic oxygen, in which case is called thermal-NO formation and follows the reaction sequence showed in Table 3. This process has high activation energies and is relevant at temperatures above 1500 °C. Molecular nitrogen can also react with CH radicals producing NCN or react by the N_2O mechanism (Reactions (4) and (5) respectively in Table 3); NCN and N_2O can be subsequently oxidised to NO or go back to N_2 depending on the reaction conditions. Nitrogen oxide produced by these reactions is called *prompt NO*.

Table 3. Reactions involved in the formation of nitrogen oxides in combustion

Mechanism	Reactions	Label
Thermal-NO	$N_2 + O = NO + N$	(1)
	$N + O_2 = NO + O$	(2)
	$N + OH = NO + H$	(3)
prompt-NO	$CH + N_2 = NCN + H$	(4)
	$O + N_2 + M = N_2O + M$	(5)
N_2O formation from HCN	$HCN + O = NCO + H$	(6)
	$NCO + NO = N_2O + CO$	(7)
NO reduction by NH_3	$2/3\ NH_3 + NO = 5/6\ N_2 + H_2O$	(8)

Furthermore, the oxidation of fuel-nitrogen produces fuel-NO through the mechanism schematised in Figure 8 (Leppalahti and Koljonen, 1995).

Combustion of biomass is generally operated in grates (fixed bed systems) or in fluidised bed systems, where the operation temperature is relatively low and thermal NO formation can be considered small or negligible; hence, the attention can be focused on the fuel-nitrogen conversion. During the pyrolysis stage of combustion, nitrogen-containing species are liberated in part as volatiles in part as a solid char (devolatilisation), then part of the volatiles nitrogen is released as heavy aromatic compounds called tar, while the other part produces light compounds like NH_3 and HCN, species produced also during the combustion of the char, these species are then oxidised to form nitrogen oxides and nitrogen.

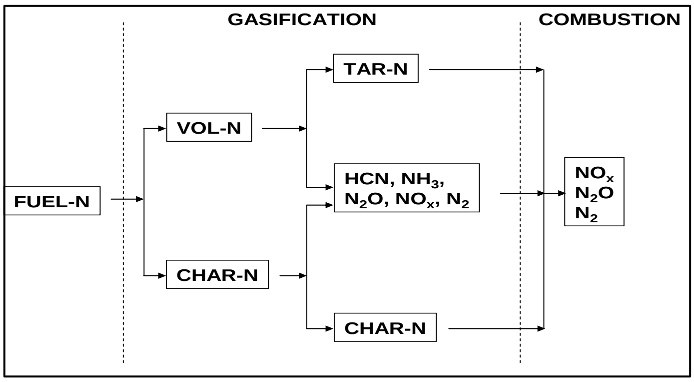


Figure 8. Behaviour of nitrogen compounds in thermal conversion (Leppalahti and Koljonen, 1995)

The distribution of nitrogen between char and volatiles, as well as the volatile nitrogen composition, depends mainly on the fuel type and the temperature. The next sections will describe in more detail the stages of the thermal conversion of biomass.

3.1 Fuel-nitrogen in biomass fuels

The type of fuel used in the thermal conversion process influences the final output, because of the different organic structures in which the nitrogen is bound inside it. For the various type of coal most commonly used there is evidence of nitrogen to be present in heterocyclic structures and in smaller amount as side chains (Pels et al., 1995), while for biomass derived fuels the data set is still poor. Investigation done so far suggests that the primary sources of nitrogen for biomass fuel are proteins, chlorophyll and alkaloids (Figure 9) and several vitamins (Leppalahti and Koljonen, 1995).

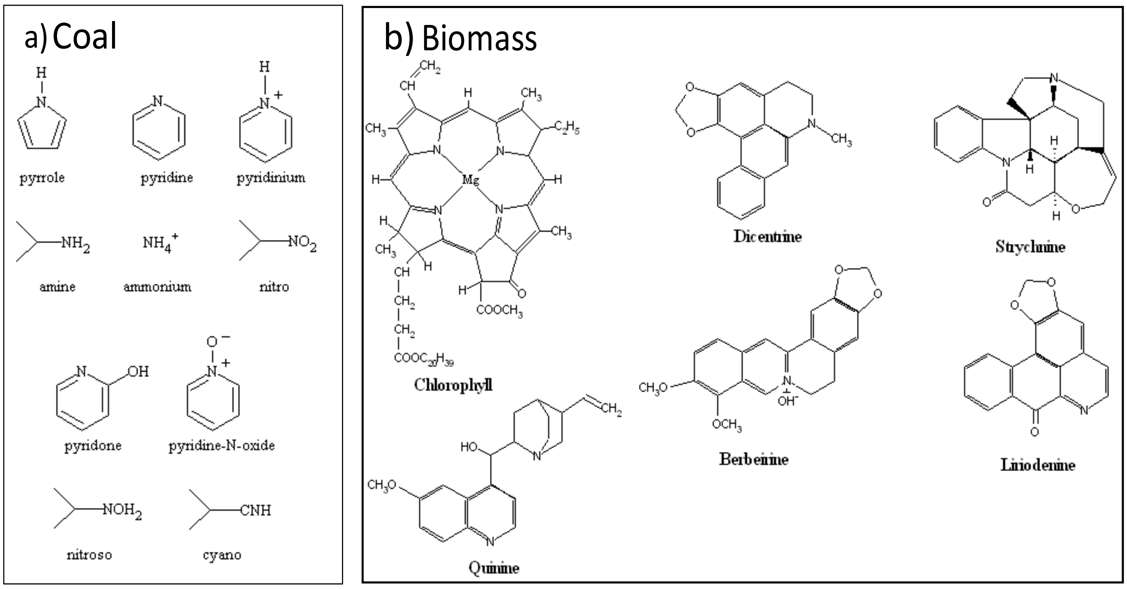


Figure 9. Nitrogen functional forms present in coal (a) and molecular structures of chlorophyll and some alkaloids (b) (Leppalahti and Koljonen, 1995; Pels et al., 1995)

3.2 Devolatilisation

The devolatisation stage is the first of the conversion of fuel-nitrogen and produces char and volatiles; the char is the solid residue containing mainly carbon, while volatiles consist of tar and light gaseous species. The tar is composed by condensable hydrocarbon including single-ring to 5-ring aromatic compound along with oxygen containing hydrocarbons (Li and Suzuki, 2009). The volatile nitrogen species are mainly NH_3 and HCN. The stage of devolatilisation can be divided into two stages as follows:

- In the primary devolatilisation weak aliphatic bonds are broken producing organic fragments constituting the tar. After that, functional groups are decomposed forming CO_2 and water vapour.

- In the secondary devolatilisation further decomposition of the tar and of the char takes place releasing CH_4, CO and H_2 as well as light nitrogen species (NH_3 and HCN) and aliphatic side chains.

The devolatilisation products are dependent on the fuel: biomass, compared to coal, produces more tar/volatiles and less char. Small particles of biomass lead to more tar while larger particles yield smaller amounts of tar. The tar produced from biomass is more reactive than the tar from coal and decomposes at lower temperatures. The parameters influencing the distribution of nitrogen between char and volatiles are fuel type, temperature and residence time: with high oxygen content in the fuel, as well as with high temperatures and residence time, more volatiles are liberated. The data available suggests that biomass fuels release the nitrogen at lower temperatures compared to coal. The light gases produced during the secondary devolatilisation are mostly NH_3, HCN; other species have been detected such as HCNO in minor amounts. Laboratory scale studies have been done on pyrolysis of biomass fuels or model compounds to understand the reactions leading to the formation of these species and the parameters influencing their yield. Differences are found on the distribution of fuel nitrogen between coal and biomass fuel, in terms of partition between char and volatiles and of NHC/NH_3 distribution ratio (Abelha et al., 2008)(Hansson et al., 2004)(Di Nola et al., 2009), but also difference between different biomass fuels (Leppalahti, 1995). This contrast in results doesn’t clarify whether the nitrogen in biomass fuels belongs to protein and amino acids rather than heterocyclic aromatic structures. Analysis of the products from the pyrolysis of proteins found HCN, NH_3 as the main nitrogen containing gases and they correlate the type of protein to the distribution of the final nitrogen between char and volatiles: proteins with no reactive side chains are completely volatized at mild temperature (700-900 °C), while proteins containing reactive side chains tend to form char together with volatiles. High heating rates (i.e. low residence time) appear to increase the HCN/NH_3 ratio for both coal and biomass while NH_3 (Hansson et al., 2003) seems to be the main product of devolatilisation at low heating rates (i.e. high residence time). An explanation to this has been proposed by assuming the hydrogenation of HCN on the surface of the solid matrix that would be increased by high residence times due to more time for this reaction to occur. Assuming that mechanism, also a bigger particle size would lead to the conversion of HCN to NH_3, but more work is needed to endorse this hypothesis. The presence of Ca, K and Fe in the ash can catalyse the formation of HCN, NH_3 and also N_2, in particular Ca and K can promote the formation of ammonia and nitrogen while suppressing the formation of hydrogen cyanide. Iron may instead promote the nitrogen formation from tar and char.

3.3 Behaviour of volatiles in gasification

The devolatilisation or pyrolysis stage has a strong influence on the subsequent fuel conversion process for both combustion and gasification and the pyrolysis products are influenced not only by the fuel composition, but also by process parameters such as pyrolysis temperature, pressure, heating rate and stoichiometric ratio.

Paterson et al. (Paterson et al., 2005b) studied the formation of HCN and NH_3 during gasification of sewage sludge and bituminous coal. The concentration of HCN was found to increase with increasing temperature which is consistent with other works where the formation of HCN is favoured at higher temperatures. Paterson et al. also claim that in a pilot scale gasifier, the concentration of HCN was found to be much lower due to the higher residence time that favours the destruction of HCN according to reaction (9). On the other hand the concentration of NH_3 decreases with the temperature, explained by re-equilibration of the reaction (10).

$$HCN + H_2 \rightleftharpoons NH_3 + C \qquad (9)$$
$$2NH_3 \rightleftharpoons N_2 + 3H_2 \qquad (10)$$

3.4 Volatiles oxidation

As seen in the previous paragraph, the two main light volatile nitrogen species produced in biomass combustion are NH_3 and HCN. Hence, reaction mechanisms for nitrogen oxides, N_2O and N_2 production from fuel-nitrogen involve the oxidation of these two molecules. HCN and NH_3 are oxidised through reactions with oxygen atoms and OH and H radicals (Figure 3).

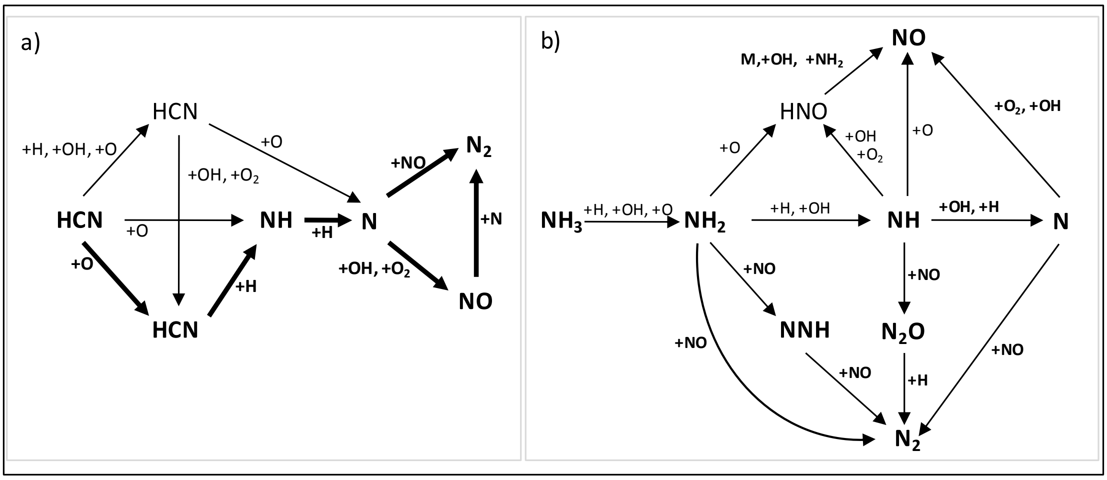


Figure 10. Possible reactions of oxidation of: a) HCN and b)NH3.

On the other hand, NO_2 has been found to be formed by reaction (11) which is usually followed by rapid NO_2 removal through reactions (12) and (13); in presence of high radical's concentration these reactions will remove quickly NO_2 and convert it back to NO. The main reactions for the formation of N_2O are (14) and (15); the N_2O produced then rapidly reacts with hydrogen to form N_2 and hydrogen oxide.

Table 4. Reactions involving nitrogen oxides

Reaction	Label
$NO + HO_2 \leftrightarrow NO_2 + OH$	(11)
$NO_2 + H \leftrightarrow NO + OH$	(12)
$NO_2 + O \leftrightarrow NO + O_2$	(13)
$NH + NO \leftrightarrow N_2O + H$	(14)
$NCO + NO \leftrightarrow N_2O + CO$	(15)
$O + N_2 + M \leftrightarrow N_2O + M$	(16)

The conversion of tar-nitrogen is much more complex to define because the tar is formed by a large number of components and because the nature of these components is dependent on the fuel composition and on the pyrolysis conditions. What is known is that the initial reactions of the tar lead to the loss of side chains of carbon hydrogen and oxygen and higher temperatures are required for significant release of gaseous nitrogen. At temperatures above 1100 ^{o}C HCN is liberated while at lower temperature also NH_3 and HNCO are detected. Also, tars from biomass fuels present different tar-nitrogen reactivity, but anyway the general thermal stability seems to follow this order pyrrolic<pyridinic<cyanoaromatic.

3.5 Char oxidation

The overall mechanism for the formation of NO from char-N is fairly established with the first step being oxygen reacting with the nitrogen fixed in the char surface to produce NO (reaction (17)); the NO produced may then be chemisorbed in a free carbon site (reaction (18)), then the chemisorbed nitrogen may react with NO to form molecular nitrogen (reaction (19)).

Table 5. Reactions of oxidation of the char-nitrogen.

Reaction	Label
$C(N) + O_2 \rightarrow NO + C(O)$	(17)
$2C_f + NO \rightarrow C'(N) + C(O)$	(18)
$C'(N) + NO \rightarrow N_2 + C(O)$	(19)
$C(N) + ½ O_2 \rightarrow C(NCO)$	(20)
$C(NCO) + NO \rightarrow C_f + N_2O + CO$	(21)

The evidence supporting this mechanism are that an increase of NO yield from char oxidation is noted with increasing particle size (i.e. increasing char surface), increasing bulk gas NO concentration, increasing pressure and increasing char reactivity. All these conditions in fact lead to a longer residence time of NO on the particles surface. The oxidation of the char-nitrogen can lead also to production of N_2O; one mechanism proposed involves the homogenous reaction between HCN and HCNO with subsequent reaction of NCO radical with NO (reactions (6) and (7)). The second hypothesis is a heterogeneous mechanism where NCO absorbed on the char surface reacts with gaseous NO (reaction (21)). The relative importance of one of the two mechanisms depends on the char characteristics and reaction conditions.

3.6 NO_x reduction

The nitrogen oxides produced during the stages of volatilisation and oxidation can then undergo reduction both in the gas phase and by reacting with the char. NO is reduced in the gas phase by reaction with NH_3 in the presence of oxygen (reaction (**8**)); this reaction is the same exploited for the selective catalytic reduction of nitrogen oxides as reported in chapter 5. N_2O can be reduced to molecular nitrogen by reacting with H radical or OH radical (reactions (22) and (23)); the reaction with H radical is kinetically favoured between the two, but reaction (23) becomes important at low temperatures typical of fluidised bed combustion (Johnsson, 1994).

Table 6. Reactions of reduction of nitrogen oxides (Johnsson, 1994; Jensen et al., 1995)

Reaction	Label
$N_2O + H = N_2 + OH$	(22)
$N_2O + OH = N_2 + HO_2$	(23)
$NO + (-C) = CO + ½ N_2$	(24)
$NO + 2(-C) = (-CO) + (-CN)$ $2(-CN) = 2(-C) + N_2$	(25)

NO and N_2O can also be reduced by reaction on the char surface to produce molecular nitrogen. The mechanisms of these reactions have not yet been understood. One mechanism proposed involves the reaction between NO and a carbon site to release N_2 and leave chemisorbed oxygen on the char surface (reaction (24)). Another proposed mechanism assumes the absorption of NO by the char into 2 sites and then the reaction of the two nitrogen atoms to form N_2 (reaction (25)). In both cases the oxygen may be liberated as CO: in support of these hypothesis is the evidence that the presence of CO promotes the reaction (Glarborg et al., 2003).

4. Nitrogen species sampling and analysis

The technique used in the literature to measure the concentration of nitrogen species from combustion and gasification sources are as follows:

- *Fourier transformation infrared (FTIR) spectroscopy:* FTIR is a really effective way of analysing nitrogen species as they all are IR active molecules. Besides, all the major components of combustion and gasification gas are also IR active, except oxygen and N_2, allowing multi-component analysis. However, FTIR instruments require the gas to be previously cleaned from tars and particulates that can sensibly reduce the performance of the instrument and the quality of the analysis.

- *Gas Chromatography coupled with mass spectroscopy (GCMS):* this instrumentation is effective for the measurement of main gases and hydrocarbons, but not particularly suitable for nitrogen species.

- *Chemiluminescence*: nitrogen oxides can be analysed by units operating on the principle of chemiluminescence. This type of analyser does not allow multiple analyses of all the gas components.

- *Absorption train + gas-specific electrode:* in this technique the sampling system consists on a train of impinger bottles containing absorption solutions consisting of 0.1M of H_2SO_4 for NH_3 and 0.1M NaOH for HCN (Yu et al., 2007). The analysis is carried out *in situ* by means of gas-sensitive electrodes. This technique has been used successfully in works dealing with the analysis of nitrogen-species (Yu et al., 2007), but it can only give an average concentration of the analysed species. Moreover, other species and N-containing tar can be absorbed interfering with the analysis of the volatile species.

- *Grab sampling + GCMS analysis:* in this case evacuated sampling containers such as flasks, cans, bags and gas syringes are used to trap the gas. The gas is then analysed using GCMS. As mentioned above, GCMS is not a sensitive technique to be used for nitrogen compounds.

- *Indicator tubes*: indicator tubes are tubes filled with crystals that turn their colour when reacting with a specific gas. Despite not giving accurate concentration measurement, they can be used to keep track of the concentration in different periods of the process, hence measure the change in concentration as the process conditions change.

In the combustion tests performed for this work, nitrogen species are analysed by means of a FT-IR spectrometer (Protea-Protir 204 M/C Transportable FTIR). The instrument provides a continuous reading of the gas composition including both major species such as CO_2 and H_2O as well as minor species in ppm concentration; a built in O_2 sensor also provides the concentration of oxygen.

All the minor species are reported in Table 7; the nitrogen-species comprise not only oxides, but also NH_3 and HCN. For a pilot-scale combustion tests this gives an exhaustive analysis of the behaviour of the nitrogen-species during the process.

Table 7. Minor species analysed by the FTIR analyser

NO	HCHO	CO	C_4H_{10}
NO_2	CH_4	SO_2	Phenol
N_2O	C_2H_6	HCl	COS
NH_3	C_3H_8	HF	SF_6
NO_x	Benzene	HCN	TOC[a] (Indicative)

[a] Total organic components

To measure the quantity of nitrogen species in the gasification tests indicator tubes have been used, to sample the gas at specific times during the process in order to get the concentration of the nitrogen species as the gasification conditions were changed.

5. Methods for the reduction of nitrogen species

There are several technologies for the reduction of nitrogen oxides from combustion; a summary of these technologies is given in Table 8 (United States Environmental Protection Agency, 1992). Even if the emission fuel-NO_x tends to increase with increasing nitrogen content its release is not proportional but depends mainly on the local combustion conditions.

Table 8. Summary of the NO_x control technologies (United States Environmental Protection Agency, 1992).

Modification of combustion conditions	Modification of combustion equipment	Flue gas treatment	Fuel modification
Low excess air	Low-NO_x burners	Selective catalytic reduction	Use of additives
Off stoichiometric or staged combustion	Burner spacing	Selective non-catalytic reduction	Fuel denitrification
Flue gas recirculation	Load reduction	Non-selective catalytic reduction	
Reduced air preheat	Catalytic combustion		
Steam/Water injection	Air to fuel adjustments		
	Ignition timing retard		

The techniques for the reduction of NO_x in combustion of solid fuels such as biomass and coal are those based on the modification of combustion conditions and on the flue gas treatment. There are four modifications to apply to the combustion conditions for the reduction of NO_x emissions:

- Low excess air: the level of nitrogen oxides in the flue gas is lower at low excess air values. The limit for how low the excess air can be set is given by the minimum amount of excess air guaranteeing combustion efficiency and minimising the production of tar and CO.

- Off-stoichiometric combustion or air staging combustion: in this technique the fuel is burnt in two stages. In the first stage the combustion is carried in fuel-rich conditions and in fuel-lean conditions in the second stage. In the first fuel-rich zone, the fuel-nitrogen is converted into molecular nitrogen so the fuel-NO_x formation is suppressed, leading to a lower level overall (Mahmoudi et al., 2010).

- Fuel staging combustion: as in the air staging, also the fuel can be introduced in two stages. In this case the first stage is in fuel-lean conditions and the second stage is in fuel-rich conditions. In the second stage the hydrocarbons of the fuel react with NO to produced HCN that then reacts with $O^·$ and $OH^·$ radicals forming molecular nitrogen (Mahmoudi et al., 2010).

- Flue gas recirculation: a portion of the flue gas can be re-circulated in the combustion zone reducing the temperature and lowering the excess air level (Mahmoudi et al., 2010).

The use of the technologies based in the modification of combustion conditions can lead to a reduction of up to 50% of the NO_x produced (Mahmoudi et al., 2010). However, to comply with the regulations, normally a further reduction of NO_x concentration in the flue gas is needed; with the treatment of the flue gas the reduction can go up to 95% of the NO_x produced (Mahmoudi et al., 2010). The three methods for the reduction of NO_x emissions by treatment of the flue gas are:

- *Selective catalytic reduction (SCR)*: in this method nitrogen oxides reacts with ammonia in the presence of oxygen; the reaction is promoted by a solid catalytic bed between 523 and 673 K. Nitrogen oxides are reduced to molecular nitrogen as follows (Mahmoudi et al., 2010):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (26)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (27)$$

The most common catalysts used are TiO_2 and V_2O_5. This method can lead to a reduction of 90% of the nitrogen oxides; this performance depends on temperature, NH_3 to NO ratio, oxygen concentration, catalyst loading and the type of catalyst support used.

- *Selective non-catalytic reduction (SNCR):* in SNCR the nitrogen oxides react with ammonia or urea ($CO(NH_2)_2$) and are reduced to molecular nitrogen. When using ammonia the reactions taking place are reaction (15) and (16), while when using urea the reaction taking place is as follows:

  $H_2N\text{-}CO\text{-}NH_2 + 2NO + 1/2O_2 = N_2 + CO_2\ H_2O$ (28)

In SNCR the reactions take place in homogeneous phase and the efficiency relies upon temperature, reagent/flue gas mixing, reagent to NO ratio and reaction time; reduction of NO emissions can vary between 30 and 90% (Mahmoudi et al., 2010).

- *Non-selective catalytic reduction (NSCR):* the NSCR involves the use of the three ways catalysts, typically used in the automotive industry. The three ways catalyst is composed by a metallic or ceramic support, a layer of metal oxide as promoter or stabiliser of the process and a noble metal as the active species. NSCR can lead to a reduction of up to 95% of NO_x, but works efficiently only at specific air to fuel ratio (close to stoichiometric) (Mahmoudi et al., 2010).

For the reduction of the ammonia produced during the gasification there are two possible approaches as follows:

- *Catalytic destruction*: the catalysts used are dolomite, nickel-based steam-reforming catalysts and iron-based catalysts. These catalysts can be used up to temperature around 900 °C and can remove up to 99% of the ammonia. The advantage is that this method can be used at high temperature, thus the heat of the product gas is maintained. However, the investigation so far has been conducted on bench scale gasifiers and their feasibility has to be proven at larger scales (Stevens, 2001).

- *Wet scrubbing:* if the gas is cooled before its use the ammonia can be removed using wet scrubbers where the gas is treated with a liquid spray that absorbs ammonia. The ammonia can then be recycled and used for the reduction of NO_x eventually formed during the process (Stevens, 2001).

6. Transformation of trace metals species during thermal conversion of biomass

The mechanism that leads to the emission of trace metals in the gas stream of thermal conversion processes is reported in Figure 11: the inorganic composites of the fuel either volatised as metal vapours or in ash particles. As the temperatures get lower, the vapours can condense to form aerosol or be absorbed on an ash particle, while the ash particles can undergo fragmentation to form aerosols.

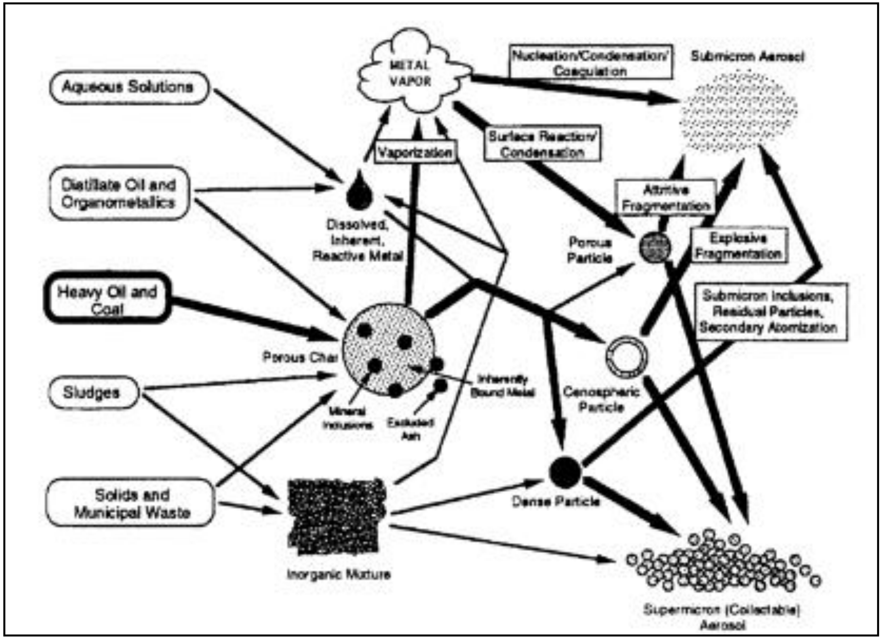


Figure 11. Schematic diagram of the processes involved in the formation of fly ash and aerosol during thermal conversion processes (Linak and Wendt, 1993).

6.1 Forms of trace metals in biomass

Biomass fuels are derived from biological materials and metals such as Si, Na, K, Fe, Al, Cu, Mn, Fe, Zn and Mo occur naturally in their composition in the form of micronutrients and minerals necessary during their life. Other elements including As, Cd, Hg and Pb are non-essential trace elements present in the environment that living organisms uptake from soil, water or air and tolerate up to a certain concentration, without being effected in their normal growth (Table 9). Moreover the fuel handling can potentially become a source of trace metals as the processes of grinding, pelletising and transporting the fuels can bring them into contact with particles that can eventually be carried and take part into the process.

Table 9. Normal and toxic concentration of metals generally found in plants leaves

	Concentration in leaves (□g/g)	
Element	Normal Range	Toxicity
Ag	0..01-0.8	1-4
As(III)	0.02-7	5-20
Cd	0.1-2.4	5-30
Cu	5-20	20-100
Cr	0.03-14	5-30
Hg	0.005-0.17	1-3
Ni	0.02-5	10-100
Pb	5-10	30-300
Sb	0.0001-2	1-2
V	0.001-1.5	1-2
Zn	1-400	100-400

6.2 Distribution of trace metals emitted during thermal conversion processes

The distribution of trace metals volatised during combustion and gasification varies between fuel and fuel and is influenced by the process conditions. Clarke (Clarke, 1993) presents an overview for coal combustion and gasification; the trace metals are divided into groups according to the similar behaviour they show during the processes; the three groups are as follows (Clarke, 1993)(Sekine et al., 2008):

- Group 1: elements concentrated in coarse residue;
- Group 2: elements that are volatised during the process but then condense in the downstream;
- Group 3: elements that are depleted in all solid phases;

The first group includes elements such as V, Cr, Mn, Co and Ni, in the second group are elements such as Zn, Se and Sb and finally the third group comprise elements like Hg. Elements that are organically bound or have organic affinity are oxidised during combustion and therefore volatised due to temperature raise during oxidation or due to reaction with Cl, F, Na and S (which induce volatility) (Querol et al., 1995). Miller et al. (Miller et al., 2003) confirmed this carrying out experiments on combustion of wood-bark injecting HCl and SO_2 finding both influencing the behavior of trace elements, in particular reducing their retention in the biomass ash. On the other hand, metals that are present in minerals tend to have a really low mobility. The fly ash is enriched with elements having affinity with calcium oxide or with sulphide. The slag is enriched with iron oxide and trace elements with affinity to iron such as Cu and Mn. The slag is enriched with all kind of elements that are volatile at combustion temperature and then condense or are adsorbed in calcium oxide in the gas downstream where temperatures get lower. To compare the behaviour of the trace metals, some authors using the enrichment factor defined as follows:

$$EF = ([X]_s/[Al]_s)/([X]_c/[Al]_c)$$

Where $[X]_s$ and $[X]_c$ is the content of the metal in the fly ash /slag and in the coal, while $[Al]_s$ and $[Al]_c$ are the corresponding aluminium content (Aluminium is a non volatile metal taken as reference to normalise the rest). Metals with high volatility will show EF<1 and $EF_{flyash} > EF_{slag}$ (Querol et al., 1995). When considering biomass combustion the attention of the investigation is more on alkali metals, for the higher concentration of them in biomass than coal and also for the fouling and corrosion problems they create. The release of Na and K has similar mechanisms and is strongly dependent on the temperature and fuel composition (van Lith et al., 2008). At temperatures between 800-850 °C the release is more likely to come from organically bound alkali metals, while at higher temperatures is due to the decomposition of alkali carbonates (van Lith et al., 2008). On the other hand, the metals volatised during coal gasification differ from those of coal combustion; this has been explained by the reducing conditions found in gasification (Font et al., 2005; Helble et al., 1996). The reducing conditions were found to favour the formation of sulphides and chlorides with subsequent volatilisation of elements like Pb, Zn, and Fe (Font et al., 2005). Moreover, very toxic metals such as As and Hg would remain in the vapour phase at temperatures of 773-873 K, the operating temperature of most of the hot gas clean-up systems, thus potentially remaining in the product gas (Helble et al., 1996). The literature concerning gasification of biomass is still mostly based on thermodynamic modelling; the experimental work done confirms the emission of heavy metals such as Cd, Pb and Zn in the fly ash (Vervaeke et al., 2006).

6.2.1 Bed agglomeration in fluidised-bed operations

As the combustion experiments performed in this work are carried out in a fluidised-bed, the phenomenon of bed agglomeration deserves a more detailed discussion. The agglomeration of the fluidised bed occurs when the alkali metals and the silica form low melting compounds on the surface of the bed sand particle (Chirone et al., 2006); this particle can then stick together initiating the agglomeration process. The main factor for the initiation of the agglomeration process is the temperature: burning char creates unavoidable hot spots where low melting compounds melt and make the particles stick together, then the agglomerated particles create hot spots were higher melting compounds melt in an auto accelerated process (Figure 12) (Olofsson et al., 2002). The metals compounds most commonly involved in this process are alkali metals compounds as well as calcium oxides as follows (Olofsson et al., 2002):

- Potassium forms silicates ($K_2O{\cdot}nSiO_2$) that have melting points ranging from 764 to 1015 °C.

- Sodium silicates ($Na_2O{\cdot}nSiO_2$) having melting points ranging from 793 to 1088 °C.

- Calcium oxide (CaO) melts at over 2500 °C and $CaO{\cdot}SiO_2$ melts over 1600 °C; however when is added to the Na_2O-SiO_2 system it can form a eutectic of Na_2O-$CaO{\cdot}5SiO_2$ and $3Na_2O$ with a melting point of 755 °C.

- Iron oxide (Fe_2O_3) can react with alkali to form products with a melting point higher than 1135 °C, diminishing the alkali available to react with silica.

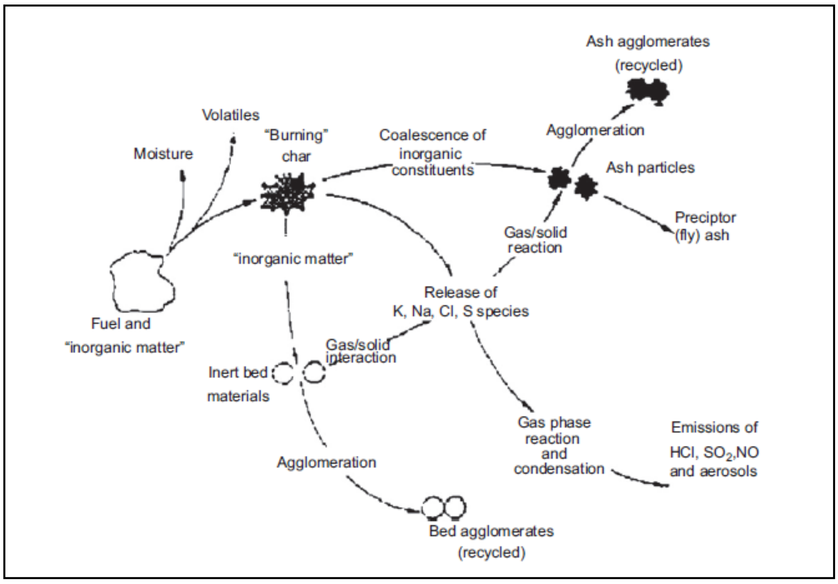


Figure 12. Mechanism of agglomeration

There are several measures that can be adopted in order to counteract bed agglomeration. These measures will be discussed in detail in paragraph 13.2.1 when discussing the best approach to reduce nitrogen oxides.

6.3 Thermodynamic modelling of trace metals in thermal conversion

Because of the complexity of the reaction involving trace metals, the investigation of the fate of trace metals is usually performed by thermodynamic equilibrium calculations, in order to understand and validate experimental data. Thermodynamic calculations are carried by software that minimise the total Gibbs free energy of a given system. The results from the thermodynamic models allows to classify the metals according to what species are formed in oxidative or reducing conditions and also to know which species are expected to condense at certain temperatures (Furimsky, 2000; Thompson and Argent, 2002a). This information can be used to predict the distribution of the metals between the product as well as the reaction leading to the formation of the species formed (Thompson and Argent, 2002a; Thompson and Argent, 2002b).

7. Trace metals sampling and analysis

The most used analysis techniques for trace metals in the flue gas is inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Both techniques rely on the use of a high-temperature argon plasma to generate positive ions; optical emission spectrometry or mass spectrometry detect and measure the concentration of the ionised species. ICP-OES has been used for the continuous measurement of metals in the flue gas (Clarkson et al., 2003); however this involves the use of a mobile laboratory (SPECTRO Analytical Instruments (Kleve, Germany)) and is suitable for industrial-scale operations, but is not cost-effective for investigation at lower scales. A more cost effective approach is to sample the gas in washing bottles connected in series with suitable solutions able to absorb the metals. The solutions collected can then be analysed by means of ICP-OES and ICP-MS as described above. In this case the measurement gives only an average concentration of the metals in the flue gas.

The sampling of ash samples can be done by the same systems used for the gas clean-up (cyclones and electrostatic precipitators) as described in the next section. The ashes sampled can be analysed with different techniques described below:

- *Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM/EDX):* SEM/EDX provides with the analysis of the elements on the surface of the material under the microscope.

- *X-ray diffraction (XRD):* XRD is a very effective analysis technique if the material analysed is in a crystalline form, while is less effective on analysing amorphous solids.

The analysis given by SEM/EDX is a elemental analysis of the surface, while XRD gives the composition of the material. Therefore XRD is preferable for the analysis of the ashes to know not only the elements, but also the species they form. If possible, the use of the two instruments on the same samples can give a better understanding of their composition.

In the combustion tests performed in this work, sampling of ashes and gas was performed in different parts of the system. Bed ash was collected for each test performed and subsequently analysed by SEM/EDX and XRD. The fly ashes and the trace elements contained in the flue gas are sample using a standard method for the determination of metals emission from stationary source (EPA METHOD 29), and then the absorbing solutions are analysed by ICP-MS for all the elements, while the fly ash captured with the filter was analysed by SEM/EDX and XRD.

8. Methods for the reduction and abatement of trace metals species

As described in the previous sections, most of the trace metals are present in the flue gas in the form of particles of different dimensions. There are 4 systems used to remove the particulate matter from the gas stream as follows (Stevens, 2001):

- *Cyclone filters:* this filter use centrifugal force to separate the solids from the gas; the gas is redirected into a circular path where the solids cannot follow the same path of the gas and are separated by inertia. Cyclone filters are extensively used as a primary gas clean-up measure, as they effectively remove particles above 5 μm and work over a wide range of temperatures; however, they are ineffective with submicron particles and with vaporised metals (Stevens, 2001).

- *Barrier filters:* these filters include a range of porous materials that stop the particles and allow the gas to pass. Theoretically, barrier filters can be designed to remove particles of any size, but as the porosity of the material decreases the differential pressure across the filter gets higher; this can create technical problems in systems handling high loads of gas. Therefore the particle removal is limited to the size of 0.5 μm. The particulate matter accumulated in time is periodically removed, normally by flowing clean gas in the direction opposite to the gas flow (Stevens, 2001).

- *Electrostatic filters:* this filters work by passing the gas through high voltage electrodes that impart an electric charge to the particles while leaving the permanent gases intact. The charged particles are then collected on the surface of collector plates of the opposite polarity. The plates are then periodically cleaned by means of mechanical action (if working at 500 °C or more) or by wet scrubbing with a thin layer of water passing on the surface (if working up to 65 °C). This type of filters are big and have high operational costs, therefore they are normally used in industrial scale facilities.

- Wet scrubbers: as described in the previous section for nitrogen species, also particulate matter can be removed by bringing into the gas contact with a liquid spray. This method can remove up to 99.9% of particles over 2 μm and up to 95-99% of particles above 1 μm (Stevens, 2001).

Despite the use of these measures, some species (especially alkali species) can remain in the gas as vapour potentially escaping all the removal techniques described. To avoid it, the gas is allowed to cool below 600 °C, where this species can condense forming particles or condense on the surface of other particles; at that point the systems for the particle removal may be used (Stevens, 2001).

9. Project outline

The project is funded by the UK Engineering and Physical Sciences Research Council (EPSRC) which supports and leads the SUPERGEN initiative focused on “Powering the Future”. The Centre for Energy and Resource Technology at Cranfield University is one of ten UK academic partners in the SUPERGEN consortium on “Biomass, Bio-fuels and Energy Crops”, which is supported by a group of industrial companies.

This project focuses on combustion and gasification of two solid biomass fuels:

- Dried distillers’ grains with solubles (DDGS).
- Miscanthus.

The importance of these two fuels is emphasised in the following paragraphs.

9.1 Energy cropping and Miscanthus

In a plan for sustainable biomass production, the greenhouse balance is not the only criteria to be considered. A key consideration in fuel crop systems is their energy balance, defined as the ratio between the energy inputs and outputs in the whole life cycle of the plant and its regeneration. Heaton et al. (Heaton, 2002)) define a series of requirements that make an energy crop “ideal”:

- Maximisation of the amount of biomass produced per unit area.
- Efficiency in the use of light.
- Water content and water use efficiency.
- Nitrogen and nutrient use efficiency.

- Minimisation of cultivation operations (harvesting and fertilizing).
- Minimisation in land changes and farm machinery.
- Environmental benefits.

Inefficiencies in these points usually lead to more energy input, this causes the use of fossil fuels and hence the emission of greenhouse gases in the atmosphere. Existing food crops used as biomass fuels are not ideal as most of them are annual crops requiring large inputs for plantation and cultivation every year (Venendaal et al., 1997)(Hulsbergen et al., 2001). That is why the attention of research has shifted to perennials grasses, particularly on Phalaris, Miscanthus and switchgrass (Venendaal et al., 1997), as they belong to C_4 rhizomatous group using the most efficient type of photosynthesis known (C_4 photosynthesis) and presenting the highest efficiencies of nitrogen and water use (Heaton, 2002)). Of these, Miscanthus is the only one proven to grow productively under a range of climatic conditions even at latitudes normally unsuitable for C_4 species, which are usually found in tropical climates.

9.2 Dried distillers grains with solubles (DDGS)

Dried distillers grains with solubles (DDGS) are a residue of the production of bioethanol by the dry-grind process. Dry-grind ethanol plants use grains such as corn, wheat, barley, rice and oat to produce ethanol. The process begins with grinding these grains to extract the sugars which are then fermented and ethanol is recovered; the centrifugation and drying of the by-products produces DDGS as the main product. DDGS contains a relatively high concentration of proteins; hence it has been usually used as livestock feed. However, as the production of bio-ethanol increases there is a surplus on the production of by-products, thus DDGS can be used as the source of process heat and electricity instead of natural gas or coal. Therefore, dry-grind plants have the potential to reduce their operating costs and improve their net energy by using DDGS (Tiffany et al., 2009).

Therefore the potential use of Miscanthus and DDGS as biomass fuels has been investigated under different aspects (Lewandowski et al., 2003)(Tiffany et al., 2009; Lewandowski and Heinz, 2003; Collura et al., 2005; Collura et al., 2006; Jeguirim et al., 2010).

This work intends to investigate these two biomass solid fuels for the emission of nitrogen species and trace metal species in pilot-scale combustion and gasification tests. The combustion facility is a pilot-scale bubbling fluidised bed combustor, while the gasification tests use a fixed bed downdraft gasifier. The monitoring of the analysed species is performed using different sampling procedures and analytical techniques.

10. Aims and objectives

NOx and trace metals species formed during thermal conversion processes are pollutants whose emission has to be reduced to comply with regulations and to reduce the costs of the process. There is an extensive knowledge on the formation of nitrogen and trace metal species from thermal conversion of solid fuels deriving from the investigation of coal. Moreover, in the last decades the investigation on biomass has been increased due to the need to substitute fossil fuels for the production of energy. Some biomass fuels have attracted the attention of the investigation more than others due to their potential benefits on the environment and on the energy production costs: among those are DDGS and Miscanthus (see paragraphs 9.1. and 9.2.). Several systems are available for the reduction and removal of these pollutants and the application of each system will depend on factors such as the type of process, the type of fuel and the cost. Thus, the thermal conversion processes have to be investigated and pilot-scale study of processes proves basic reliability of the proposed processes and technologies. This thesis, using the agreed Supergen fuels, explores the effect of process parameters on the release of nitrogen and trace metal species during pilot-scale combustion and gasification.

This thesis aims to:

Explore the effect of process parameters on the release of nitrogen and trace metal species during pilot-scale combustion and gasification of biomass and use the information to identify methods for the reduction of these species.

The Objectives of this thesis are:

- To determine whether relationships involving nitrogen and trace metals species developed for coal translate to biomass.

- To relate the nitrogen species evolved to the nitrogen forms found in different biomass fuels.

- To provide data from which to quantify the reduction in nitrogen species and trace metals achievable through process control methods.

- To identify the potential options, benefits and constraints on the use of process control methods.

To achieve these objectives, the following methodology was developed:

- Analysis of the fuel composition: proximate, ultimate and ash analysis of the fuels is carried out to correlate the fuel content to the thermal conversion output.

- Combustion of Miscanthus and DDGS in a pilot-scale fluidised bed combustor: the combustion is performed at different levels of excess air and at different bed temperature to investigate the effect of these process parameters on the emission of nitrogen oxides.

- Gasification of Miscanthus and DDGS in a pilot-scale downdraft gasifier: the gasification is performed at different levels of equivalence ratio and different bed temperature to investigate the effect of these process parameters on the emission of NH_3 and HCN.

- Sampling and analysis of all the ash residues and of the flue gas: these thermal conversion residues are sampled and analysed for the trace metals content in order to investigate the volatility of the metals and their affinity to other elements.

11. Experimental set-up

The combustion and gasification tests performed for this project are carried out using the facilities available at the "Centre for Energy and Technology Resource" laboratories at Cranfield University.

The combustion facility is a pilot scale fluidised bed combustor equipped with various systems for the monitoring of the process, including temperature measurements, gas flow measurements, mass and heat balance, ash production and gas composition.

The gasification facility is a fixed bed downdraft gasifier equipped with monitoring systems for temperature, gas flow, ash production, tar production and gas composition; dedicated sampling systems and more specific analysis were used for the sampling and analysis of nitrogen and trace metals species.

11.1 Combustion equipment

The combustion of Miscanthus and DDGS pellets was performed in the Bubbling Fluidised Bed combustor of 100 kW_{TH} of capacity showed in Figure 30 (Appendix A). Preheated air is introduced from below the bed through air distribution nozzles and the fuel is fed from above by a screw feeder. The combustion facility is equipped with systems for the monitoring of combustion parameters such as temperatures, pressure, flow rates and gas composition. The facility is also equipped with water cooled heat exchangers, a cyclone and an induced draft (ID) fan before the gas goes to the stack.

Components of the flue gas such as CO_2, O_2, H_2O, CO, NO, NO_2, N_2O, SO_2, HCl, HF and VOCs are analysed by a high resolution multi-component FTIR online gas analyser (Protea-Protir 240 M/C mobile FTIR analyser, Protea, Cheshire, UK); the analyser is fitted with a heated line keeping the gas at 180 °C. For details on this system see APPENDIX A. The resolution of the instrument is 1 cm^{-1} which is in the range accepted as reasonable for quantitative accuracy in open path and extractive measurement of biomass burning and combustion gases (Griffith and Jamie, 2000).

Finally, the measurement based on this type of instrument are normally expected to be have a tolerance of ± 5% which is acceptable for the scopes of this work.

To obtain the distribution of trace metals, the sampling is performed in different parts of the system. Bed ash is collected and then analysed by SEM-EDX which gives the elemental composition of the ash. The SEM-EDX analysis is affected by a variability of 0.1 % and has an accuracy of 1.0 %. However, due to the difference on the ash samples we expect to have a larger variability in the measurement which nevertheless is acceptable for the aim of this work. The trace elements contained in the flue gas are sample using a standard method for the determination of metals emission from stationary source (EPA METHOD 29) showed in Figure 37 (Appendix A) and then the absorbing solutions are analysed by ICP-MS for all the elements. The ICP-MS analysis variability is reported in tables 21 to 23 in paragraph 12.1.6.4, expressed as the relative standard deviation (RSD).

11.2 Gasification equipment

For the gasification tests, a pilot-scale downdraft gasifier was used as represented in Figure 38 (Appendix C). The biomass is fed from above in batches, adding fresh fuel on top of the reacting layers of the bed. The rig is equipped with 4 nozzles from which either air or N_2 can be fed. Hence, this system allowed feed air or N_2 at different bed height or from above the bed. By using this system, the temperature was raised by feeding air where needed and decreased by feeding N_2; on the other hand, when the temperature for gasification was reached, the system allowed the equivalence ratio to be controlled.

The concentration of CO_2, CO, CH_4 was measured by IR gas analysers (Siemens Ultramat 2) and H_2 was measured by a thermal conductivity analyser (Siemens Calomat 2). For both instruments the tolerance of the measurements is no more than ± 5%. The concentration of NH_3 and HCN was measured using Dräger tubes (ammonia 5/b 81 01 941 5 to 100 ppm, ammonia 0.5% to 10 Vol%, nitrous Fumes 2/a 5 to 100 ppm, nitrous fumes 20/a to 500 ppm, nitrous fumes 50/a 250 to 2000 ppm). The tolerance in the measurement is of ± 10%. For details on this system see APPENDIX B.

To obtain the distribution of trace metals the sampling is performed in different parts of the system. Ash samples were collected from above the grate, from the ash pit below the grate and from the cyclone.

11.3 Fuels Properties

The two biomass fuels used for combustion and gasification tests are Miscanthus and DDGS; however the type of Miscanthus used is different for the two processes. The Miscanthus used in combustion was in the supply of Cranfield University, while the Miscanthus used in the gasification tests was provided by E-on. The reason why the Miscanthus provided by E-on was used is that this fuel is commercially used and represented a more reliable fuel to be used to develop the experimental methodologies in the downdraft gasifier. The characteristics of the three fuels are summarised in Table 10. All the fuels are in the form of pellets of 6 to 8 mm of diameter.

Table 10. Proximate, ultimate and ash analysis of the fuels

Proximate analysis (% (wt) as received)	Miscanthus 1	DDGS pellets	Miscanthus 2 (E-On)
Total moisture	11.60	7.40	10.20
Ash	6.50	3.9	2.80
Volatile matter	63.90	73.2	71.1
Calorific value (MJ/Kg) [a]			15.9
Gross calorific value [a]	16.21	18.60	18.77
Net calorific value [a]	14.94	17.21	17.48
Ultimate analysis (% (wt) as received)			
Carbon	41.51	44.18	44.59
Hydrogen	4.85	4.94	5.12
Nitrogen	0.40	5.90	0.40
Oxygen	35.08	32.95	36.89
Sulphur	0.04	0.52	0.01
Chlorine	0.04	0.18	0.01
Ash analysis (% weight)			
SiO_2	42.01	1.01	31.58
Al_2O_3	1.10	0.05	3.78
Fe_2O_3	0.41	0.12	1.09
CaO	6.12	4.82	25.91
MgO	1.66	9.23	2.95
TiO_2	0.07	0.01	0.23
Na_2O	24.12	4.34	1.14
K_2O	11.16	28.45	9.01
P_2O_5	1.89	45.80	5.56
SO_3	2.26	2.58	1.90
Cl	1.07	0.03	0.07

[a] As defined in paragraph 2.1.5

11.4 Combustion tests program

The test program for combustion consists of a minimum of 3 tests for each fuel in which the excess air is changed. The 3 values of Φ 1.2, 1.5 and 2.0 correspond to 20%, 50% and 100% excess air and are indicative of three ranges that go from a large excess of air to conditions close to stoichiometric.

The bed temperature changes whilst maintaining the same value of excess air are used to study the effect of the bed temperature on the emissions.

On the other hand, the trace metals sampling is performed in tests providing the most stable combustion conditions in order to have long sampling times and collect samples containing relatively high concentration of metals, making the analysis more reliable.

Table 11. Combustion test program

Φ / FUEL	1.2	1.5	2.0
MISCANTHUS 1	M.C.1.	M.C.2.	M.C.3.
DDGS	M.C.1.	M.C.2.	M.C.3.

11.5 Gasification test program

The gasification test program consists of a minimum of three tests per fuel at different values of equivalence ratio: the first test is performed at 0.18-0.22 of equivalence ratio, the second test at values between 0.28-0.32 of equivalence ratio and the third at values between 0.38-0.42 of equivalence ratio.

This approach is been adopted to investigate a range of different process conditions knowing that the change in equivalence ratio would also provide with different bed temperatures at which to study the gas composition and the behaviour of nitrogen species and trace metals in the ash.

Φ FUELS	0.18-0.22	0.28-0.32	0.38-0.42
MISCANTHUS 2 (E-on)	M.G.1.	M.G.2.	M.G.3.
DDGS	D.G.1.	D.G.2	D.G.3.

12. Results

12.1 Combustion

This section describes the results obtained from the combustion of the two fuels Miscanthus and DDGS.

The first section reports the combustion results and highlights the operational issues encountered during the investigation that limited the range at which the chosen parameters could be investigated.

Following sections describe the evolution of the analysed nitrogen species (NO, NO_2, N_2O, NH_3 and HCN) during combustion of the two fuels; the analysis of the evolution of these species during start-up stage gives an indication of what nitrogen oxides precursors the two fuels tend to liberate. At steady state conditions, the emission of nitrogen oxides is discussed as a function of the fuel type, bed temperature and excess air level.

Finally, the evolution of trace metals is reported focusing on their distribution along the gas path with the analysis of ash samples taken at different positions and analysed with different techniques. Moreover the flue gas is sampled to find the concentration of trace metals emitted in the vapour phase.

12.1.1 Operation of the combustion rig

The outputs of the combustion tests completed are reported in Table 12; the table shows the average gas composition obtained in the combustion tests performed at different values of excess air and corresponding bed temperatures.

Comparing the gas composition of the 3 tests involving Miscanthus, the test labelled M.C.1 is the one presenting the lowest concentration of O_2 and highest concentration of CO_2 and H_2O. This is due to a better combustion achieved during test M.C.1, which for the same reason presents a higher average bed temperature. The worse average gas composition and lower average bed temperatures on the rest of the tests are due to disruption in the operation of the combustion rig caused by bed agglomeration and de-fluidisation. The phenomenon of agglomeration, (see paragraph 6.2.1.) is caused by the reaction of the silica composing the bed sand with alkali metals of the fuel ash; the composites produced by these reactions have low melting temperatures. The melting material on the sand particle surface makes the particles stick together and form agglomerates that cause de-fluidisation of the bed and hot spots. Figure 13 shows an example of bed temperature profile during combustion: the peak in the graph shows when the de-fluidisation of the bed takes place and a hot spot is formed causing the de-stabilisation of the bed temperature for the rest of the test; the picture beside was taken after an aborted combustion tests and shows how extended bed agglomeration can lead to complete loss of fluidisation.

Table 12. Average gas composition from the combustion tests

FUEL	TEST NUMBER	□	BED TEMPERATURE (^oC)	GAS COMPOSITION		
				O_2%	CO_2%	H_2O%
Miscanthus	M.C.1.	1.5	760	2.9	13.2	16.5
	M.C.2.	2.0	747	11.8	8.3	8.1
	M.C.3.	1.6	867	12.3	5.9	7.0
DDGS	D.C.1.	1.3	801	7.9	11.4	11.0
	D.C.2.	1.06	818	8.4	8.0	9.6
	D.C.3.	1.7	780	10.9	6.3	7.7

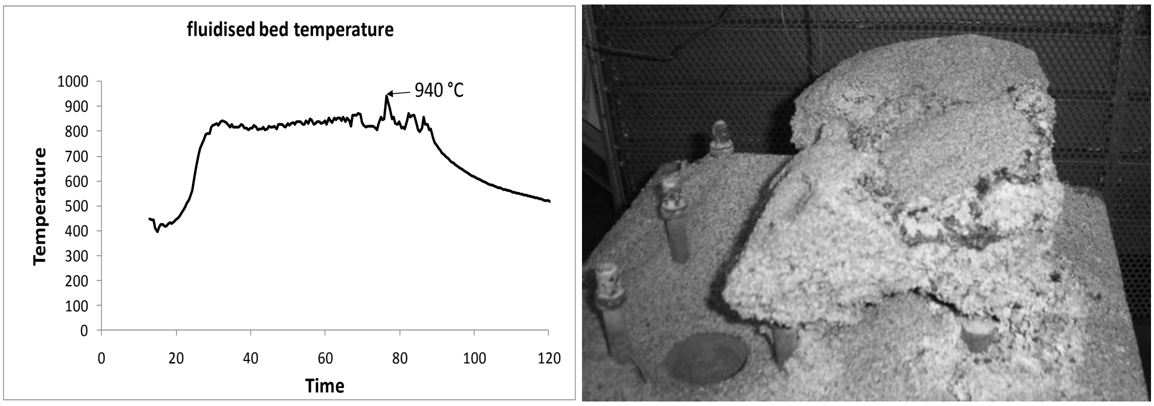


Figure 13. Picture of the agglomerated bed material formed on the air distributing nozzles by fuel melting ashes over 900 °C.

The literature about combustion of biomass reports useful empirical indexes for the prediction of phenomena like slagging, fouling and agglomeration. The alkali index gives information about slagging; values above 0.34 Kg/GJ show that the fuel is certainly going to slag or foul.

The base to acid ratio is an index for the probability of fouling: The higher the index is the more probable is the fouling. For coal the minimum value for coal is 0.75. The index for agglomeration is the bed agglomeration index: For values lower than 0.15, bed agglomeration occurs. The values of Na_2O for Miscanthus and K_2O for DDGS (Table 13) make these two fuels very likely to cause these phenomena. Table summarise this situation.

Table 13. Miscanthus and DDGS calculated indexes.

Index name	Formula	Miscanthus	DDGS
Alkali index	$\frac{\text{Kg } (K_2O + Na_2O)}{\text{GJ}}$	1.41	1.31
Base to acid ratio	$\frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)}$	1.01	43.89
Bed agglomeration index	$\frac{\%Fe_2O_3}{\%(K_2O + Na_2O)}$	0.012	0.004

These indexes strongly agree with the experimental result, as above 900 °C the ash of both fuels starts to melt and form clusters of agglomerated material that collect over the air-distribution causing the complete defluidisation of the bed. The resulting material is a white crystal that collects on the surface of the sand particles causing them to bridge.

However, in the reported tests the problem could be overcome by stopping the fuel feed and normal fluidisation regime re-established for the completion of the scheduled tests.

12.1.2 Fate of nitrogen species during combustion

Table 14 summarises the average concentrations of NO_x and N_2O for the tests conducted, together with the average temperature of the fluidised bed and the in bed excess air % at which those concentration were obtained.

The concentration of NO_x has been calculated as the sum of NO a NO_2 assuming an oxygen content in the flue gas of 6% according to the calculations reported in APPENDIX D.

The concentration of NO is for DDGS two to three times higher than Miscanthus. For both the fuels the major nitrogen oxide produced is NO, while NO_2 is set at negligible concentration (lower than 5 ppm). On the other hand, N_2O has a different behaviour between the two fuels: Miscanthus produces no N_2O (lower than the detection limit), whereas DDGS combustion produces relatively high concentration of this gas (40 ppm).

The behaviour of the nitrogen species during combustion can be discussed by analysing the results from the two tests M.C.1 and D.C.1 (Figure 14 and Figure 15) as follows.

During the start-up stage for Miscanthus there is an increase in the NO concentration, followed by a stabilisation to smaller values as the process proceeds and reaches a steady-state. However, a slight increase can be noticed due to the effect of the increasing temperature (see paragraph 12.1.4 for details).

On the other hand DDGS liberates a relatively high level of HCN and N_2O during the start-up stage of the process; as the process continues these species are replaced by NO; however the level of N_2O remains relatively high. As previously seen for Miscanthus, the increase on NO concentration is caused by the raising bed temperature, whereas N_2O tends to decrease as the bed temperature increases (see paragraph 12.1.4 for details).

Changes in temperature and stoichiometry are the cause of the changes in concentration of NO and N_2O. The emissions of nitrogen oxides during fluidised bed combustion are very dependent on combustion conditions such as the distribution of volatile matter, of char, of oxygen and of possible catalysts within the bed and freeboard. The parameters which have a major influence in this are excess air level, fuel nitrogen and operating pressure and temperature (Glarborg et al., 2003; Sanger et al., 2001; Winter et al., 1999)(Jensen et al., 1995; Valentim et al., 2006; Hämäläinen and Aho, 1995).

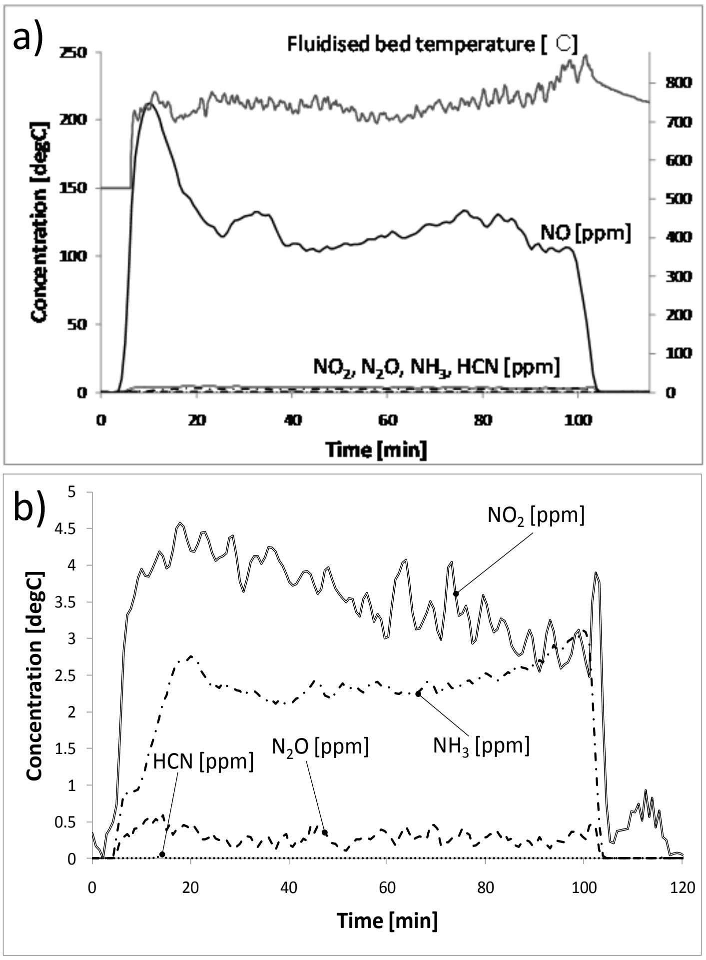


Figure 14. Nitrogen species emission from the combustion of Miscanthus: a) major nitrogen species; b) minor nitrogen species.

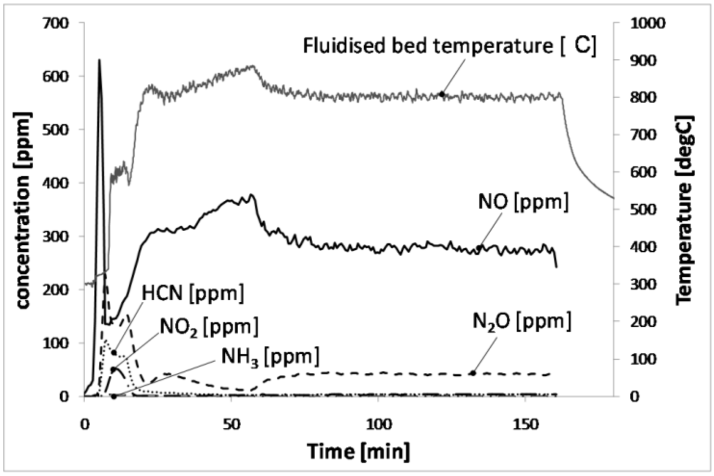


Figure 15. Nitrogen species emission from the combustion of DDGS

Table 14. Mean value of nitrogen oxides emission from combustion tests.

FUEL	FUEL-N AS FIRED (weight%)	TEST NUMBER	EQUIVALENCE RATIO Φ	BED TEMPERATURE °C	FUEL-N (%) CONVERSION TO NO_x	NO_X EMISSIONS IN ppm AT 6% O2 DRY GAS BASIS (273 K)	FUEL-N (%) CONVERSION TO N_2O	N_2O EMISSIONS IN ppm AT 6% O2 DRY GAS BASIS (273 K)
Miscanthus	0.49	M.C.1.	1.5	760	14.1	228	0.03	0
			2.0	747	14.6	134	1.28	1
		M.C.2.	1.8	709	15.0	143	1.2	1
			1.7	731	12.0	136	1.0	1
			1.6	867	9.3	239	1.0	1
		M.C.3.	1.5	840	3.3	227	0.4	1
			1.6	799	3.4	202	0.5	1
DDGS	5.57	D.C.1.	1.3	801	3.2	394	0.2	7
			1.6	841	2.2	447	0.1	2
		D.C.2.	1.2	813	3.0	484	0.02	16
			1.06	818	4.2	272	0.4	11
			1.6	813	2.6	404	0.6	12
		D.C.3.	1.4	820	4.2	529	0.02	46
			1.7	780	3.0	373	0.4	92

12.1.3 Effect of the fuel type on nitrogen species

As mentioned in the introduction, most of the nitrogen oxides emitted in fluidised bed combustion of biomass and coal are derived from the fuel. The nitrogen containing compounds found in coal and biomass break down during combustion, producing simpler compounds, mainly NH_3 and HCN. Many pyrolysis studies on model compounds or proteins have shown that the concentration of NH_3 and HCN depends on the type of nitrogen containing compounds present in the fuel (Hansson et al., 2003), (Pels et al., 1995). For coal, where nitrogen compounds are N-aromatic and N-polyaromatic rings, it has been found a high HCN/NH_3 ratio. In biomass the nitrogen containing structures are amino-acids, proteins, chlorophyll, alkaloids and several vitamins (Leppalahti and Koljonen, 1995). The breakdown of these structures tends to give a lower HCN/NH_3 ratio than those typical for coal (Hansson et al., 2004; Leppalahti, 1995). The relative concentration of NH_3 and HCN has an influence on the concentration of the nitrogen oxides produced at the end of the combustion.

In the tests performed the concentration of NO differs between the two fuels. For Miscanthus combustion, NO concentration ranges between 107 ppm and 135 ppm. For DDGS combustion, NO concentration ranges between 270 ppm and 366 ppm. This can be easily explained by the difference in nitrogen content between the two fuels; as shown in Table 10, the nitrogen content of DDGS is about 8 times bigger than Miscanthus. Moreover, as mentioned before, DDGS produces nitrous oxide (N_2O), normally not expected to be found during combustion of biomass, but important for the combustion of coal as reported by Naruse et al.(Naruse et al., 1992). This effect is attributed to homogeneous reactions involving the volatile matter, especially if more HCN is present. From Figure 15 it can be noticed how, in the case of DDGS, more HCN is produced during the volatiles liberation stage. The presence of HCN in the volatile gases and the relatively high concentration of nitrogen in the fuel may then be the reason for the high production of N_2O at the lowest temperatures, as confirmed by what reported by Johnsson (Johnsson, 1994) where the most important reaction where found to be the 2 reactions below:

$HCN + O = NCO + H$

$NCO + NO = N_2O + CO$

The participation of NO in this reaction could also explain the decrease of this gas at the lower temperatures where considerable N_2O is produced.

12.1.4 Effect of bed temperature on nitrogen species

One of the process parameters that have a major influence in the nitrogen oxides release during combustion is the temperature. In this project the fluidised bed temperature has been varied between 700 and 870 °C. As already mentioned, temperatures above this limit caused agglomeration of the bed sand and no test at higher temperatures has been possible. The effect of an increasing temperature on coal and biomass is to increase the yield of volatiles as well as the rate of devolatilisation. In Figure 16 and Figure 17 the concentration of NO is reported as a function of the temperature for Miscanthus and DDGS. For both the fuels high temperature leads to higher concentration of NO. This effect is observed also for coal and other types of biomass. It is due to the higher rate of devolatilisation of the solid fuel due to higher pyrolysis temperature. At temperatures around 700 °C, coal liberates about 33% of fuel-N into the volatiles, while the devolatilisation reaches 75% at 1000 °C. Biomass seems to release the nitrogen more readily than coal as about 80% of the nitrogen is released during pyrolysis at temperatures above 600 °C (Glarborg et al., 2003).

Figure 17 and Figure 18 report the effect of the bed temperature on the conversion of fuel nitrogen to NO and N_2O. It can be noticed that despite the nitrogen content is much higher for DDGS (Table 10), reflecting on the concentration of NO in the flue gas, the yield of conversion of fuel nitrogen to NO is higher for Miscanthus (18 to 19%) than DDGS (6 to 8 %). This is in agreement with what observed by Winter et al. (Winter et al., 1999) studying the combustion of various biomass fuels. Fuels with high nitrogen content show low conversion whereas fuels with low nitrogen content show high conversion. The explanation to this phenomenon is that fuel with high nitrogen content will release more NH_3 or HCN that can act as reduction agent on NO by the following reaction:

$2/3\ NH_3 + NO = 5/6\ N_2 + H_2O$

The same reaction that is used in the selective catalytic reduction of NO_x.

For what concerns N_2O, it's not present during the combustion of Miscanthus and the conversion is constantly 0%, while for DDGS the conversion of N_2O decreases with rising temperature as the reactions involving its formation (Table 3 reactions (6) and (7)) become less important.

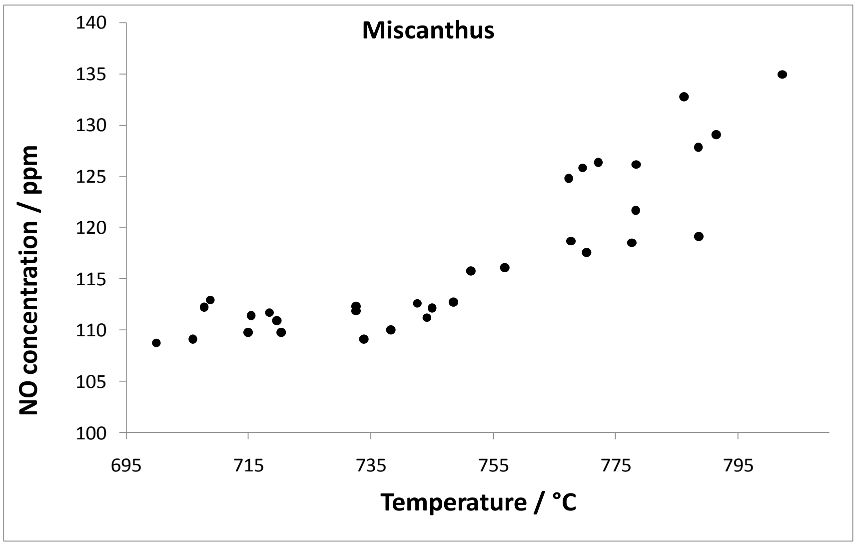


Figure 16. Effect of the temperature on the concentration of NO_x in the combustion of Miscanthus

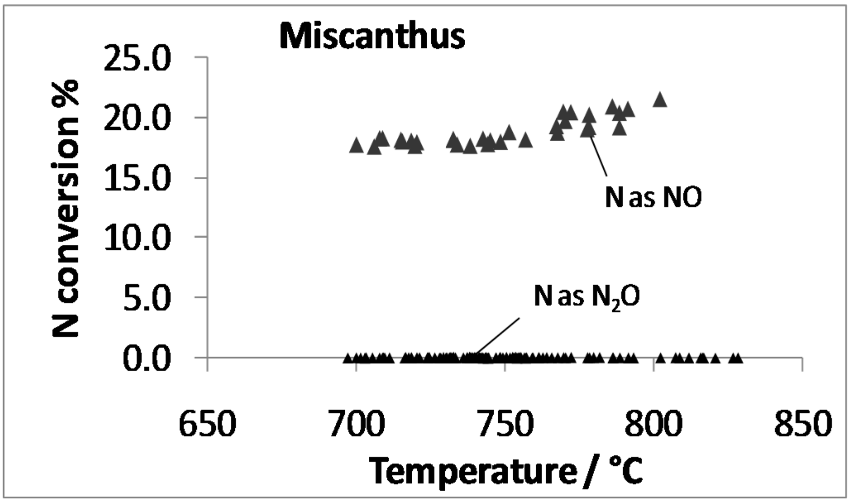


Figure 17 Effect of the temperature on the conversion of fuel-N to NO_x in the combustion of Miscanthus

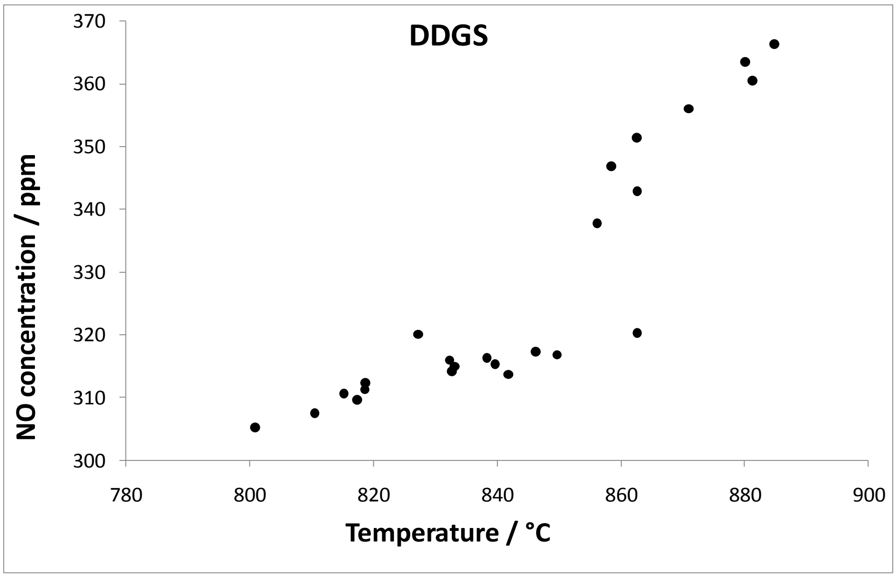


Figure 18. Effect of the temperature on the concentration of NO_x in the combustion of DDGS

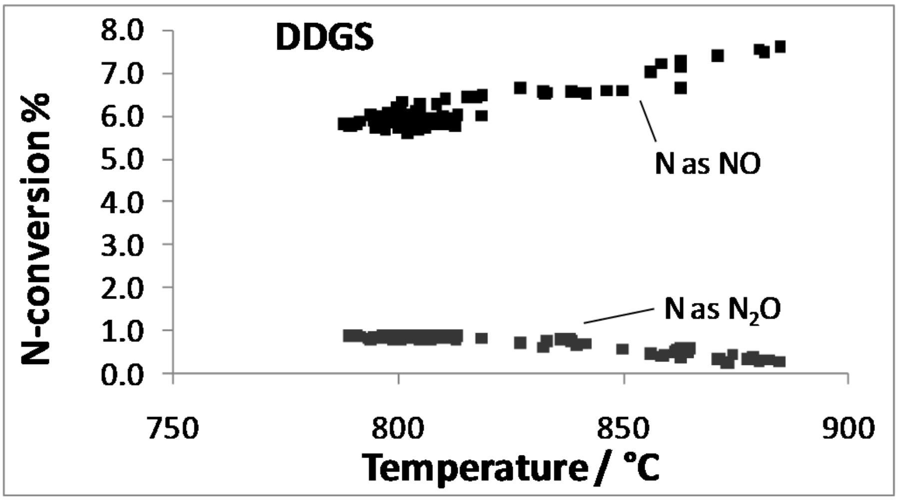


Figure 19. Effect of the temperature on the conversion of fuel-N to NO_x in the combustion of DDGS

12.1.5 Effect of excess air on nitrogen species

The concentration of NO is a function of the amount of air used during combustion. To achieve complete combustion in real systems, the air to fuel ratio has to exceed the stoichiometric conditions.

A useful dimensionless number to express the air to fuel ratio is the equivalence ratio (ϕ) defined in paragraph 2.2.

The general relationship between NO production and excess air level is usually an increase in the concentration of NO to a maximum level, to then decrease in the second part of the curve. The first part of the curve is due to the increase in conversion of fuel-N with increasing oxygen level. In the second part of the curve, although the oxygen keeps increasing, the NO concentration decreases due to a dilution effect (the NO concentration also decreases due to an effect of reverse reaction of formation). The value of the excess air at which NO concentration reaches the maximum depends on the combustor design and operating conditions. The literature regarding biomass and coal combustion reports various examples of the relation between nitrogen oxides concentration and excess air level. Xie J.J et al. (Xie et al., 2007) studied the emission of sulphur and nitrogen oxides for circulating fluidised bed combustion of coal and co-firing with biomass. They report the NO and N_2O concentration change with between 1 and 1.6 ϕ. The NO concentration increases with increasing excess air level for both coal and co-firing, while N_2O is not affected by changes in air to fuel ratio. Sanger et al (Sanger et al., 2001) investigated the nitrogen oxides emission for combustion of sewage sludge. For the dry sludge, at small oxygen volume in the flue gas (i.e. excess air) the NO_x level rises with increasing oxygen volume. On the other hand, for volumes of oxygen over 10% the level of NO seems to start to decrease. Same trend is reported in the work from Glaborg et al. (Glarborg et al., 2003) where the conversion of NH_3 to NO_x is related to the equivalence ratio. Also in this case the level of NO seems to have an increasing gradient for small values of excess air, to then stop growing after a certain point.

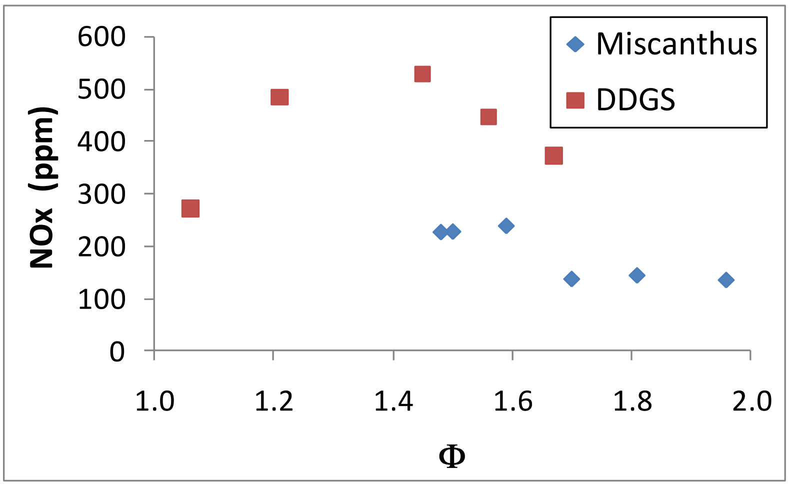


Figure 20. Effect of the equivalence ratio on the concentration of NO.

The relation between nitrogen oxides concentration and Φ for the two fuels investigated is reported in Figure 20. A first consideration concerns the testing of Miscanthus at Φ lower than 1.14 that has not been possible due to bed agglomeration problems. For the conditions tested, Miscanthus production of NO tends to increase with increasing Φ until a certain point where the concentration of NO decreases as the Φ rises. On the other hand, the combustion of DDGS could be carried out at the lowest levels of Φ. Once again the trend of NO concentration suggests that NO increases with increasing Φ, reaching a maximum to then start to decrease as effect of the dilution. The range of Φ at which the maximum NO concentration is reached is between 1.21 and 1.45 for DDGS and around 1.50 for Miscanthus.

12.1.6 Fate of trace metals species during combustion

In this section the release of the trace metals during the combustion experiments is discussed: first is the analysis of the bed residue by means of SEM/EDX, which allows knowing the metals that are less volatile and that are involved with the creation of bed agglomerates.

Then, the content of the fly ash collected by the flue gas sampling system (see APPENDIX A) is analysed by SEM/EDX, where more volatile metals are found, is analysed. Finally the gas absorbed in the HNO_3 solutions of the metals sampling systems and analysed by ICP-MS are discussed.

12.1.6.1 Analysis of the bed residues samples

Table 15 shows the analysis of the bed silica sand before the combustion test: this can be taken as a reference to analyse the results of the analysis of the yellow silica residue left after combustion showed in Table 16; this helps to understand whether or not the sand has changed composition after the combustion. However, being the analysis of the silica sand left after the combustion tests made by SEM/EDX, the composition is given as elemental analysis rather than as metals oxides; nevertheless, the proportion between the elements can be used to compare the composition of the samples. In this case the EDX analysis shows the presence of Si and O in a ratio close to ½ , consistent with the formula SiO_2. Moreover, the rest of the composition of the bed residue samples resembles that of the clean sand with Al and Fe. Thus, the yellow silica sand recovered from the bed after combustion doesn't show significant differences with the clean sand before the combustion.

The second sample recovered from the combustion experiments consists of white granules of the same shape and dimension as the bed sand. These particles are also present in sintered small blocks easy to breakable with one's bare hands that can be defined as slag, in accordance with previous studies (Lindstrom et al., 2007). The analysis of this bed residue has been performed by SEM/EDX.

Table 17 shows the EDX analysis of this material for both fuels: again, the ratio between Si and O close to ½ suggests that it is a silicate. However, the silicates produced by the two fuels have different characteristics: the one derived from the combustion of Miscanthus is characterised by relatively high levels of Na followed by K and Ca, whereas the residue of DDGS combustion has higher levels of K and P and lower Na and Ca. Despite the difference in chemical composition these two materials coating the surface of the bed sand have similar physical characteristics and they both create bed agglomeration issues.

Table 15. Analysis of the trace metals content of the bed sand used

Clean sand Elemental oxide analysis (%) – as analysed	
SiO_2	95.4
Al_2O_3	0.1
Fe_2O_3	1.0
TiO_2	<0.1
CaO	<0.1
MgO	<0.1
Na_2O	<0.1
K_2O	<0.1
P_2O_5	<0.1

Table 16. SEM/EDX analyses of the silica sand residue left after combustion

	Miscanthus yellow silica	DDGS yellow silica
O	60.51	60.06
Na	0.00	0.28
Mg	0.00	0.00
Al	2.14	0.55
Si	32.54	34.75
P	0.00	0.00
S	0.00	0.00
Cl	0.00	0.00
K	2.90	0.17
Ca	0.17	0.19
Fe	1.76	4.02
Cu	0.00	0.00
Total	100.01	100.01

Table 17. SEM/EDX analyses of the slag residue left after combustion

	Miscanthus white silica	DDGS white silica
O	56.15	53.22
Na	8.73	2.06
Mg	0.47	1.86
Al	0.43	0.22
Si	24.62	19.68
P	0.63	8.99
S	0.64	0.21
Cl	0.19	0.00
K	5.16	10.87
Ca	2.09	1.73
Fe	0.88	1.16
Cu	0.00	0.00
Total	99.99	99.99

Regarding Miscanthus the high concentration of Na in the fuel together with the relatively high percentage of it in the bed residue, suggest that Na may be the element most involved in the agglomeration process. In this case the silicates formed are those reported in Table 18: with melting points as low as 793 ^{o}C, the event of agglomeration initialisation in hot spots is highly likely to occur. Moreover, from the EDX analysis, the two metals presenting higher percentage after Na are K and Ca: both these two metals can contribute further to the process of agglomeration. The silicates formed by K are shown in Table 18 and Ca can form a eutectic between Na_2O-$CaO \cdot 5SiO_2$ with a melting point of 755 °C as also reported in paragraph 6.2 (Olofsson et al., 2002).

On the other hand, DDGS has high K and P content and relatively high percentage of them in found in the slag, suggesting that this time K and P may be the elements involved in the agglomeration process. Table 18 reports the potassium-silicates usually reported to be formed in agglomerates (Olofsson et al., 2002). Moreover, calcium and magnesium phosphate rich in potassium have melting temperatures below 700 ^{o}C (Steenari et al., 2009) and they have been found to be produced during the combustion of cereal grain rich in phosphorus (Lindstrom et al., 2007), materials from which DDGS is derived (see paragraph 9.2.2.).

Table 18. Silicates reported to be formed during combustion and causing bed agglomeration

Sodium Silicate	Melting point (^{o}C)	Potassium Silicate	Melting point (^{o}C)
$Na_2O^{\cdot}SiO_2$	1088	$K_2O^{\cdot}SiO_2$	976
$Na_2O^{\cdot}2SiO_2$	874	$K_2O^{\cdot}2SiO_2$	1015
$3Na_2O^{\cdot}8SiO_2$	793	$K_2O^{\cdot}3SiO_2$	740
		$K_2O^{\cdot}4SiO_2$	764

The third sample recovered from the bed material after combustion is the bottom ash: Table 19 reports the analysis of it by SEM/EDX.

The bottom ash recovered from Miscanthus combustion presents high levels of both Na and K, but at the same time the percentage of Si is lower than in the slag residue, while the percentage of Ca is higher. According to what discussed previously, increasing Ca concentration in the presence of high Na concentration may induce the formation of low melting composites, but the low concentration of Si is also an indication that Na is present in different forms. The most common forms of K and Na in the ash are chlorides, sulphates and carbonates which are volatile at normal combustion temperatures. Thus, due to high percentages of S, Cl in the sample the two alkali metals are in the form of chlorine and sulphate that remained in the fluidised bed after combustion, most probably at lower temperature after shut down of the fuel feeding.

DDGS bottom ash has different characteristics: K, P and Mg are the elements at the highest concentration, unlike the slag, the level of Si is much lower. Lindstrom *et al.* report composites such as KPO_3 and KH_2PO_4 to be present in the bottom ash from the combustion of various grains (Lindstrom et al., 2007). These composites along with K_2SO_4 are most probably present in the bottom ash of DDGS combustion;

moreover, the absence of Cl in the sample excludes the presence of KCl in this case.

Table 19. Bottom ash composition analysed by EDX

	Miscanthus bottom ash	DDGS bottom ash
O	52.06	53.30
Na	16.55	1.71
Mg	1.17	4.24
Al	0.48	0.95
Si	9.36	0.76
P	1.37	13.60
S	1.08	1.74
Cl	1.11	0.00
K	10.37	20.09
Ca	5.70	2.43
Fe	0.75	1.02
Cu	0.00	0.00
Total	100.00	100.01

12.1.6.2 Analysis of the fly ash samples

The composition of the fly ash collected in the glass filter of the flue gas sampling system (see APPENDIX A for details) for both the fuels is reported in Table 20. Comparing the fly ash with the bottom ash, some differences can be noticed as follows.

In the fly ash deriving from Miscanthus combustion, the level of Na is sensibly lower, while the percentage of P is higher as well as the percentage of S and Cl; moreover, the relative concentration of K is much higher. Therefore, the volatile components forming the fly ash from the combustion of Miscanthus are potassium chloride (KCl), sulphates (K_2SO_4) and phosphates (K_3PO_4). Nevertheless, also volatile Na salts such as NaCl and NaOH are volatile species usually found to condense in the downstream of biomass combustion processes and finally the percentage of Si indicates the presence of silicates in the fly ash.

Table 20. Fly ash composition analysed by EDX

	Miscanthus fly ash	DDGS fly ash
O	58.82	50.84
Na	3.14	2.71
Mg	1.43	2.83
Al	0.43	0.39
Si	7.38	3.91
P	6.31	14.01
S	2.89	2.45
Cl	6.91	3.19
K	9.60	15.89
Ca	2.97	3.78
Fe	0.00	0.00
Total	99.9	100.0

Likewise Miscanthus, DDGS fly ash composition is dominated by the presence of K, but the concentration of P is also high making potassium phosphates the species most probably forming the majority of the fly ash from the combustion of DDGS. Moreover, DDGS fly ash has Cl in its composition, most probably due to the high devolatilisation of KCl. Also the level of sulphur is increased compared to that of the bottom ash due to devolatilisation of KSO_4. However, the DDGS fly ash presents a low concentration of Si if compared to Miscanthus, but at the same time higher than the Si content in the bottom ash; this denotes the formation of silicates during the combustion of DDGS that are transported by the gas stream.

The analysis of the bottom and fly ash is consistent with the behaviour of minor elements usually observed when combusting biomass. Potassium and sodium silicates are responsible for bed agglomeration and are found in the bottom ash of the two fuels in proportion with the fuel content. On the other hand, potassium is mainly released in the fly ash as a compound of Cl, P and S for both fuels despite Miscanthus having high Na content.

12.1.6.3 Elements Enrichment

The enrichment factor is described in paragraph 6.2. as the ratio between the analysed concentration of a specific element in an ash and the theoretical concentration in the total ash of the same element. Al is used to normalise the results being a non volatile metal in combustion.

Figure 21 and Figure 22 show the trend of the enrichment factor for the main ash elements discussed in the two previous paragraphs.

In the samples collected from the combustion of Miscanthus, there is a remarkable increase in the enrichment in Cl, P and S in the fly ash denoting the devolatilisation of phosphates, chlorides and sulphates. Whereas, the most enriched element in the bottom ash is Fe; Fe and Cl are the most enriched in the slag.

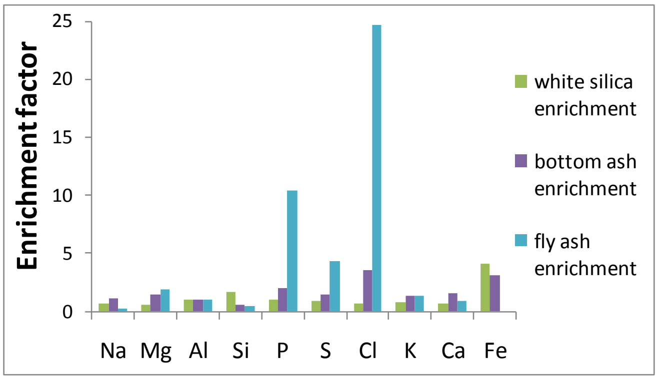


Figure 21. Enrichment factor for the analysed elements in Miscanthus ash samples

On the other hand, the element enriched in the fly ash samples deriving from DDGS combustion is Cl, while Si and Fe are the most enriched in the slag.

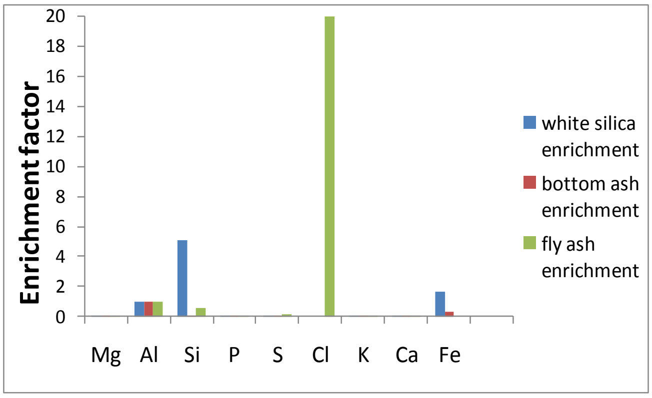


Figure 22. Enrichment factor for the analysed elements in DDGS ash samples

The fact that Fe is enriched in the slag has been found in previous investigations and it has been attributed to the formation of iron oxides in combustion condition that favour the fixation of iron in the bottom ash and slag (Querol et al., 1995). The high volatility of chlorides explains the enrichment in Cl of the fly ash for both the fuels.

12.1.6.4 Analysis of the flue gas samples

The elements discussed so far for the combustion of the two fuels Miscanthus and DDGS are elements present in the fuel ash or that condense along the gas path in the form of fine particles. However, biomass fuels contain also heavy metals in trace concentration deriving in part from the micronutrients and minerals necessary during their life, in part from the environment (see paragraph 6.1.).

The UK Heavy Metal Monitoring Network (Flowers et al., 2006) monitors the concentration of the following heavy metals in air and precipitation: As, Cd, Cr, Cu, Ni, Pb, Se, V, Zn and Hg. For this it has been decided to sample the flue gas using the standard method for the determination of metals emissions from stationary sources (EPA METHOD 29) described in detail in APPENDIX A.

Table 21 shows the concentration of these elements. Miscanthus presents relatively high concentration of Mn and Cu, small amounts of Co, Cd, Ni, Pb and V, while Cr, Zn, As and Hg are absent.

DDGS presents relatively high concentrations of Mn, Zn and Cu, small amounts of Cr, Co, Cd, Ni and Pb; finally V, As and Hg are not present in DDGS composition.

Table 21. Concentration of heavy metals in the two fuels Miscanthus and DDGS

Miscanthus – heavy metals concentration (ppb)		RSD	DDGS - heavy metals concentration (ppb)		RSD
Cr	1.9	0.0	Cr	1.6	3.2
Co	2.6	0.3	Co	0.2	2.5
Cd	2.4	0.1	Cd	0.1	4.4
Cu	1.7	5.9	Cu	14.9	1.4
Mn	1.2	21.0	Mn	154.0	1.1
Zn	2.6	0.0	Zn	44.6	0.3
Ni	4.0	2.7	Ni	0.8	3.2
Pb	0.9	2.1	Pb	1.4	0.7
V	3.8	0.8	V	0.0	0.0
As	0.0	0.0	As	0.0	0.0
Hg	0.0	0.0	Hg	0.0	0.0

Table 22 reports the concentration of the analysed heavy metals in the flue gas from combustion of Miscanthus: the percentage of the element in the flue gas gives an indication of the volatility of the element. In the case of Miscanthus Cd, Cu, Ni, V, and Co are present in the flue gas, while Cr, Zn and Pb are not in the gas phase, despite not being in the bottom ash or in the fly ash composition.

Table 22. Concentration of heavy metals in the flue gas from Miscanthus combustion

Element	Concentration in the fuel (ppb)	Concentration in the flue gas (ppb)	Actual input (□g)	Actual output (□g)	Element % in the flue gas	RSD
Cr	0.000	93.210	0.000	23.300	0.000	6.2
Co	0.270	0.010	3.240	0.000	0.077	1.7
Cd	0.075	0.10	0.890	0.030	2.794	1.0
Cu	5.900	3.220	70.800	0.810	1.137	0.4
Mn	20.980	0.320	251.760	0.080	0.031	0.1
Zn	0.000	0.000	0.000	0.000	0.000	0.3
Ni	2.695	1.140	32.340	0.290	0.881	0.5
Pb	2.130	0.000	25.560	0.000	0.000	0.7
V	0.780	0.060	9.370	0.020	0.160	3.1

Table 23 reports the concentration of the heavy metals in the flue gas from combustion of DDGS: in this case all the analysed species are found in the flue gas; hence the composition of DDGS favours the devolatilisation of heavy metals species more than Miscanthus.

Table 23. Concentration of heavy metals in the flue gas from DDGS combustion

Element	Concentration in the fuel (ppb)	Concentration in the flue gas (ppb)	Actual input (□g)	Actual output (□g)	Element % in the flue gas	RSD
Cr	1.613	10.9	25.810	2.730	10.556	1.00
Co	0.226	3.285	3.620	0.820	22.665	2.80
Cd	0.072	2.825	1.150	0.710	61.278	0.20
Cu	14.933	0.325	238.930	0.080	0.034	0.70
Mn	154.000	6.32	2464.000	1.580	0.064	0.70
Zn	44.567	56.51	713.070	14.130	1.981	0.20
Pb	1.426	4.045	22.820	1.010	4.431	0.60
V	0.043	0.87	0.680	0.220	31.761	2.80

Previous studies on coal show how the elements with organic affinities are oxidised during the combustion process and subsequently devolatised due to the rise in temperature or because of reaction with compounds of Cl, F, Na and S (Querol et al., 1995).

12.1.6.5 Summary of trace elements behaviour in combustion

The analysis of the ashes and the flue gas samples from the combustion tests was performed using SEM/EDX for the analysis of the ash samples and ICP-MS for the analysis heavy metals in the fuel and in the flue gas samples.

The bed residue was divided in two samples:

- The slag: formed by white brittle particles with a tendency to form small agglomerates easy to break with ones bare hands.
- The bottom ash: fuel ash particles left in between the bed particles after the combustion process.

The analysis of the enrichment factor (defined in paragraph 6.2.) allows the investigation of the volatile behaviour of the trace elements analysed.

First of all, the slag samples for both fuels are enriched in Fe and Si indicating the formation of iron oxides and silicates with low volatility.

On the other hand, the bottom ash deriving from Miscanthus combustion is enriched with Fe, Ca, K, Cl, S, P and Mg, while the bottom ash from DDGS retains the composition of the ash analysis.

Furthermore, the fly ash analysis presents a considerable enrichment in Cl for both the fuels, showing a tendency of chlorides to be highly volatile. Moreover, Miscanthus fly ash is also enriched in P and S indicating sulphates and phosphates as the other species with high volatility that tend to condensate in the gas downstream.

Finally, the fuel and the flue gas have been analysed: Miscanthus contains lower levels of heavy metals than DDGS with the exception of Mn; this reflects in the flue gas where Cd, the element showing the highest volatility, is less than 3% of the Cd introduced with the fuel. However, DDGS contains higher concentrations of heavy metals and this reflects in flue gas that contains higher concentrations of heavy metals than that of Miscanthus. The elements showing the highest volatile behaviour are found to be Cd, V and Cr. The sampling system dissolves the flue gas in nitric acid and the analysis of the samples gives only the concentration of the heavy metals’ ions, hence the compounds formed during the devolatilisation of the elements could not be determined.

12.2 Gasification

This section describes the results of the gasification experiments performed with the two fuels Miscanthus and DDGS.

The first section reports the gasification results and highlights the operational issues encountered during the investigation limiting the range at which the chosen parameters could be investigated.

Following sections describe the evolution of the analysed nitrogen species (NH_3 and HCN) during gasification of the two fuels; the emission of nitrogen species is discussed as a function of the fuel type and bed temperature.

Finally, the evolution of trace metals is reported focusing on their distribution along the gas path with the analysis of ash samples taken at different positions along the gasification rig and analysed by SEM-EDX.

12.2.1 Operation of the gasification rig

Table 24 reports the average gas composition obtained in the gasification test performed at different values of excess air and corresponding bed temperatures.

Table 24. Output of the gasification tests

Fuel	Test label	Equivalence ratio, □	Bed temperature, °C	CO_2%	CO%	H_2%	CH_4%
Miscanthus E-on	M.G.1.	0.20	720	12.1	14.2	11.3	1.9
	M.G.2	0.27	750	7.0	9.9	6.8	1.1
	M.G.3	0.33	820	13.6	15.3	11.7	1.3
	M.G.4	0.38	860	12.2	16.5	10.8	1.4
DDGS	D.G.1.	0.20	850	10.9	6.5	4.3	1.0
	D.G.2.	0.22	890	11.2	8.4	5.2	1.2
	D.G.3.	0.27	856	14.0	10.4	5.9	1.7
	D.G.4.	0.40	970	12.5	7.3	4.0	0.7

To take into account the combined effect of air flow, feed rate and duration of the run, the equivalence ratio has been calculated as reported by Zainal et al. (Zainal et al., 2002).

The four tests performed cover the ranges of equivalence ratios scheduled (first test 0.18-0.22, second test 0.28-0.32, third test 0.38-0.42); usually the value of equivalence ratio at which gasification takes place is 0.25 (Reed and Desrosiers, 1979): below this value pyrolysis takes place, while at values over 0.25 gasification takes place depending to the characteristics of the fuel. However if the equivalence ratio is increased too much the process becomes a partial combustion. For this reasons the tests have been conducted in the range 0.2-0.40.

The gas compositions reported in Table 24 corresponds to the average gas concentrations at steady state conditions, after the start-up stage when a stable bed temperature was achieved.

The trend of the analysed species during the gasification of Miscanthus along with the profile temperature of the various thermocouples of the gasifier is shown in

Figure 23. The same parameters are reported in Figure 24 for the gasification of DDGS. The fuel gas obtained when gasifying Miscanthus has a higher calorific value (more CO and H_2) than the gas obtained with DDGS. This difference between Miscanthus and DDGS resides mainly on a different behaviour of the formed ash inside the bed, as the ash formed by DDGS disrupted both the air distribution and the heat transfer. However, for both the fuels the concentration of the main gases is lower than expected (Zainal et al., 2002; Jiang et al., 2003; Gezer et al., 2009).

The start-up of the test was done by using an ignition system placed at the same height of the thermocouple called T2 situated at the bottom of the gasifier (see Figure 38 b); under the grate the thermocouple T1 measures the gas temperature: these two thermocouples the first two temperatures to rise. As the front of the burning fuel advances in height the other temperatures go up and the layers of reacting biomass described in Figure 38b are formed; hence, gasification takes place. During the first stage of the process, more CO_2 is produced until stable conditions are achieved and both CO and H_2 increase.

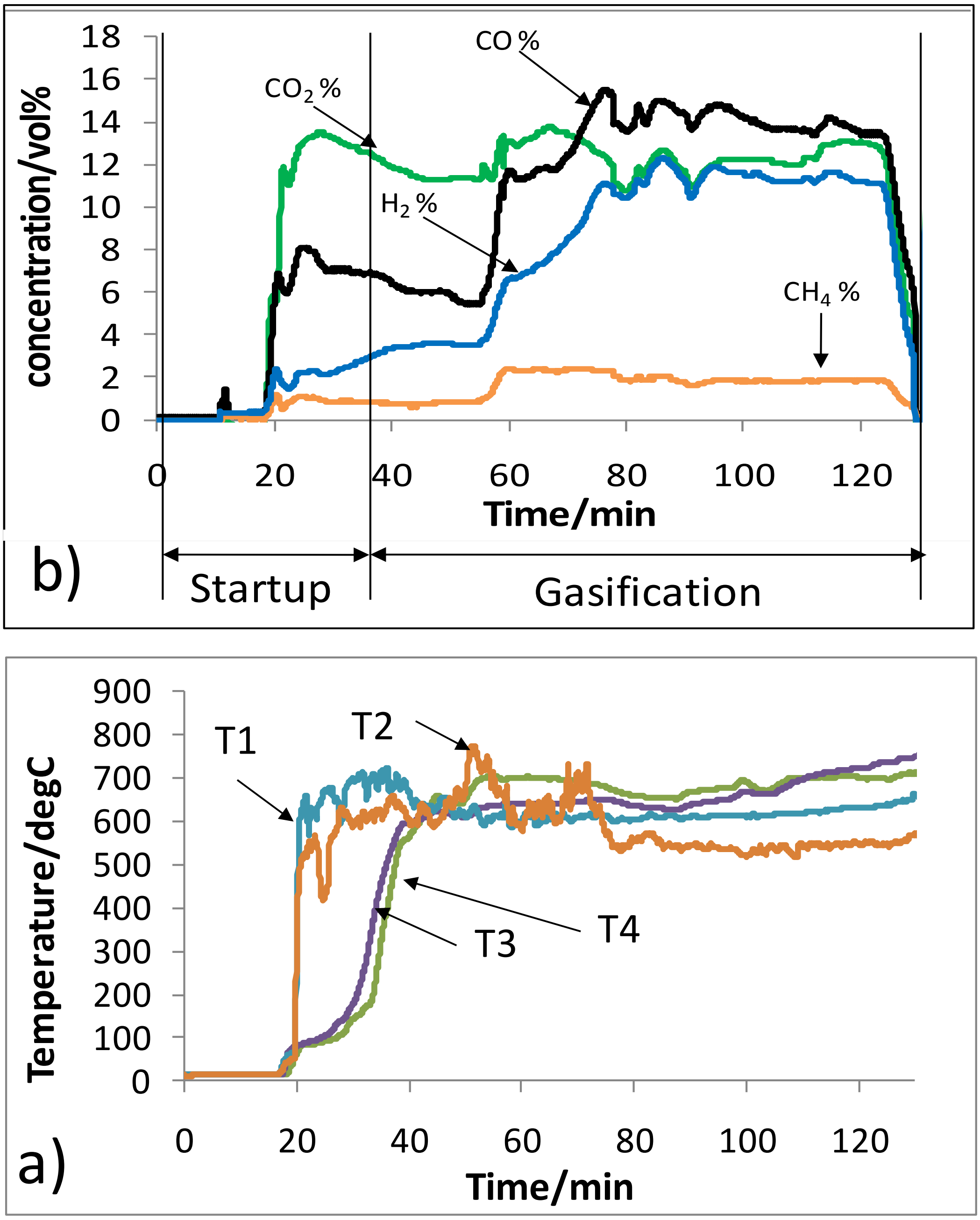


Figure 23. a) Trend of the analysed species for Miscanthus in test number 3. b) Temperatures profiles.

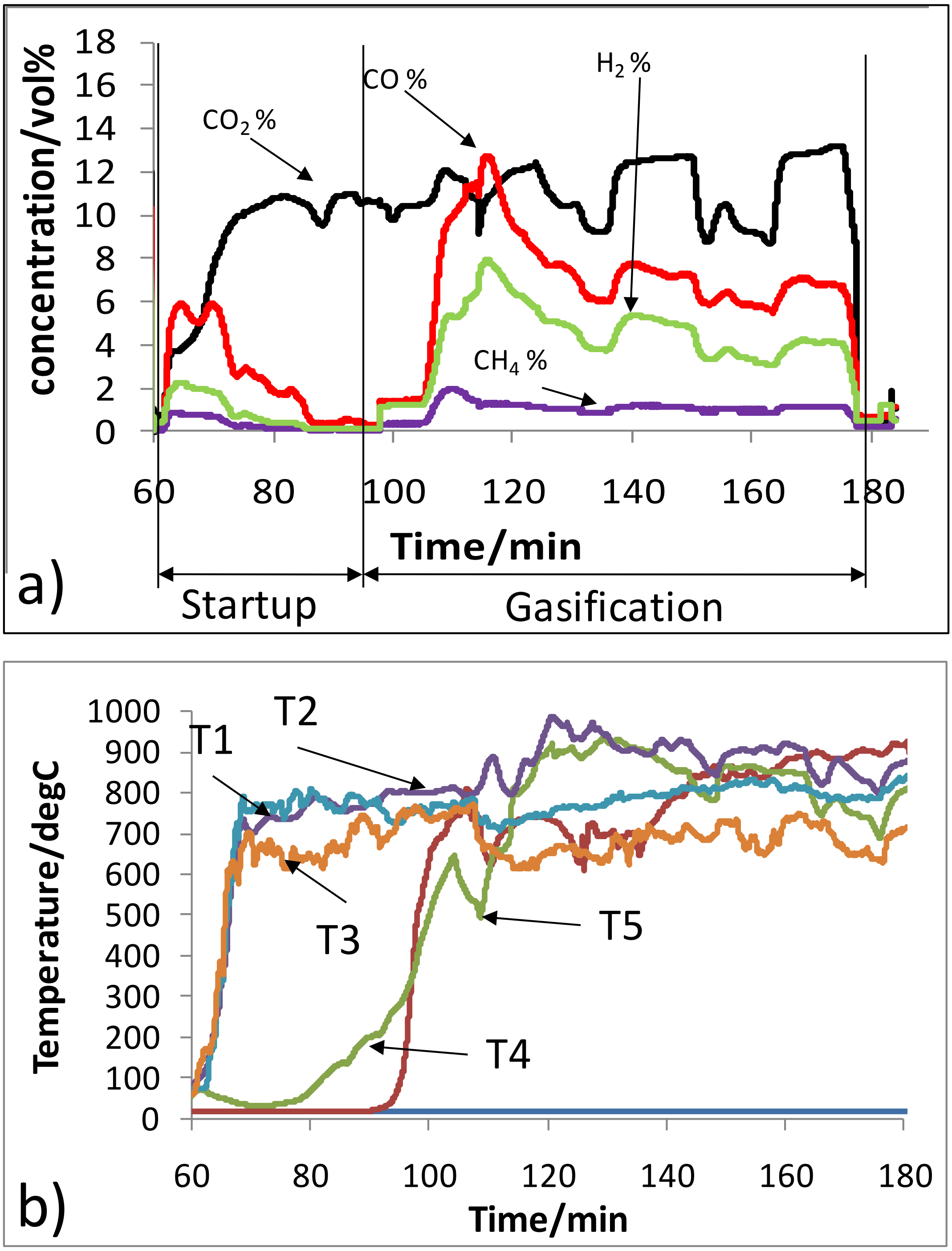


Figure 24. a) Trend of the analysed species for DDGS in test number 5.b) Temperatures profiles.

12.2.2 Gasification efficiency

Table 25 shows the output of the gasification tests conducted for the two fuels in terms of gas yield, calorific value of the produced gas, the cold gas efficiency and the conversion of the fuel carbon to gas; all these parameters are defined in APPENDIX D.

Table 25. Performance of the gasification tests of Miscanthus and DDGS

Fuel	Test label	Gas yield (Nm^3/kg)	Gross Calorific value (MJ/Nm^3) [a]	Cold gas efficiency (%)	Gas Carbon conversion (%)	Φ
Miscanthus	M.G.1	1.25	3.99	31.6	42	0.20
	M.G.2	1.33	2.55	22.0	28	0.27
	M.G.3	2.15	4.74	54.2	78	0.33
	M.G.4	2.38	4.84	61.4	86	0.38
DDGS	D.G.1	0.97	1.77	11.8	22	0.19
	D.G.2	1.18	2.20	17.7	30	0.22
	D.G.3	1.58	2.74	30.0	50	0.27
	D.G.4	2.10	1.71	25.3	52	0.40

[a] As defined in paragraph 2.1.5

From the plot of the gas yield against the equivalence ratio showed in Figure 25, it can be seen how for both fuels the increasing equivalence ratio increases the production of gas.

However, the gas composition is affected in a different way depending on the fuel: when gasifying Miscanthus the production of CO and the calorific value increase with the equivalence ratio, while the best gas composition and calorific value have been obtained from DDGS at lower values of equivalence ratio.

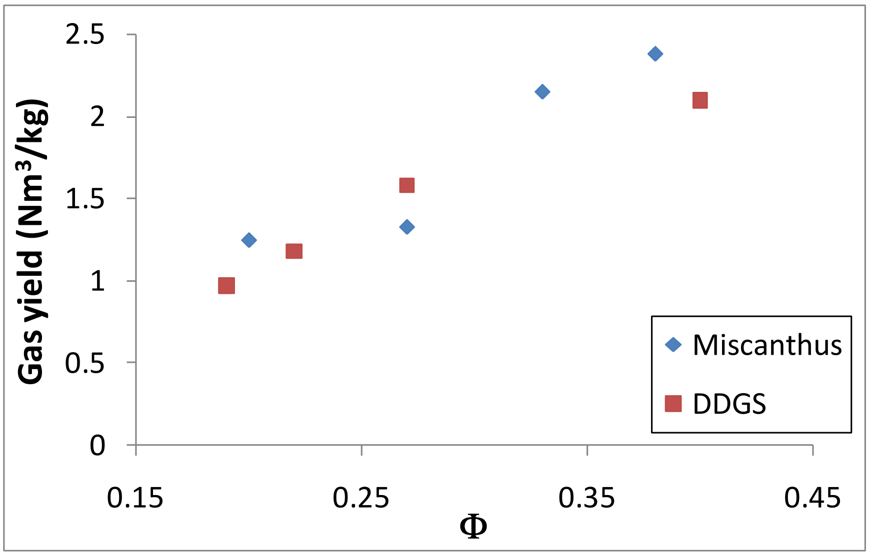
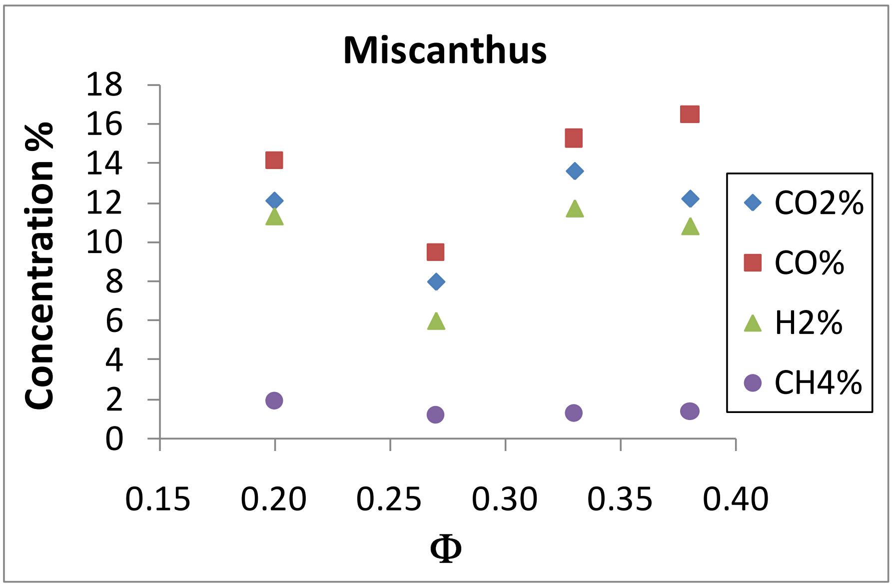


Figure 25. Effect of the equivalence ratio on the gas yield



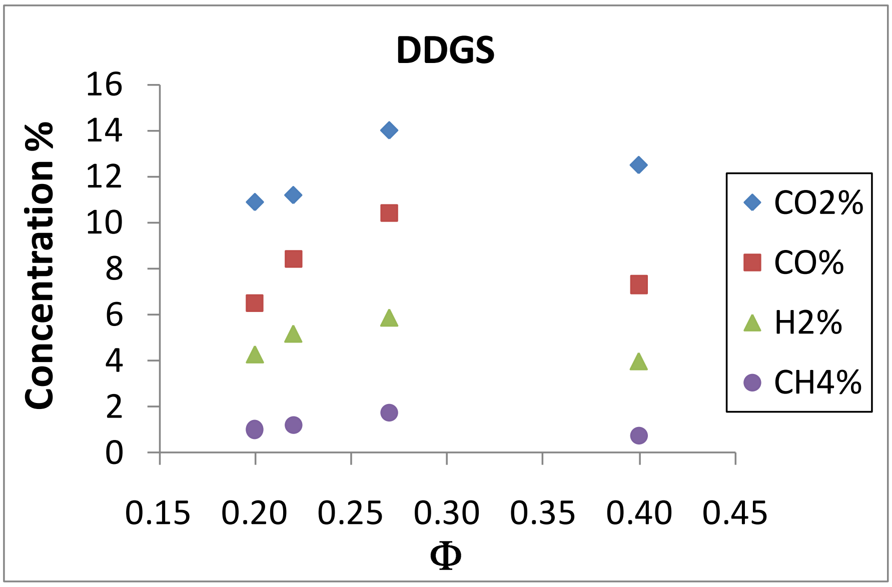


Figure 26. Effect of the equivalence ratio on the gas composition

Hence, among the operating conditions investigated the highest gasification efficiency for Miscanthus has been found at 0.38 equivalence ratio, while for DDGS at 0.27 equivalence ratio. High equivalence ratios are reached by increasing the amount of air input: this creates really high temperatures in the oxidation zone, temperatures at which the gasification efficiency of DDGS drops due to bad distribution of the air and bad heat transfer. On the other hand, Miscanthus pellets can handle higher temperatures than DDGS and at higher temperatures the devolatilisation rate gets higher improving the gas yield.

12.2.3 Fate of nitrogen species during gasification

12.2.3.1 Effect of the fuel type

During gasification the maximum concentration in the fuel gas of NH_3 is hundreds of times lower when gasifying Miscanthus than DDGS (see Table 26). This is due to the difference in the nitrogen content of the two fuels that is 15 times higher for DDGS than Miscanthus (see Table 10). Usually, reported NH_3 content of a syngas are in the order of thousands of ppm (Leppalahti and Koljonen, 1995; Paterson et al., 2005b).

Moreover, the conversion of fuel-N to NH_3 can be calculated for the two fuels. the conversion of fuel: nitrogen to NH_3 is between 4.4% and 4.8% for Miscanthus, while it is 9.8% to 12% for DDGS. The conversion of fuel-N to NH_3 reported in the literature can vary significantly and can be sometimes much higher than found in these tests. However, Leppälahti (Leppalahti and Koljonen, 1995) reports fixed bed gasification of wood showing a conversion of 4% of fuel-N to NH_3 and a conversion of 66-68% of fuel-N to N_2. On the other hand, Yu et al. (Yu et al., 2007) report a conversion to NH_3 of 12.7% of fuel-N in the gasification of Miscanthus. The low conversion of fuel-N to NH_3 could be due to the quality of the fuel in terms of nitrogen bonds in the fuel structure. However, it could be due to the decomposition of ammonia to form molecular nitrogen caused by the re-equilibration of reaction 10 (paragraph 3.3), an effect reported by Paterson et al (Paterson et al., 2005b).

Table 26. concentration of nitrogen species in the gasification tests

Test label	NH_3 (ppm)	HCN (mg/m^3)	Bed temperature (^oC)	Φ
M.G.3.	5	12	830	0.33
	180	5	897	
	100	20	958	
M.G.4.	0	15	856	0.38
	0	15	816	
	0	5	644	
D.G.3	400	>20	867	0.27
	1000	>20	876	
D.G.4	30	>20	972	0.4
	40	>20	957	
	200	>20	1101	

The kinetic of reaction 10 in the gas phase typically leads to a negligible rate of decomposition of NH_3 (Leppälahti, 1993), unless heterogeneous reactions involving the char and ash at the bottom of the stratified bed are involved. The layout and dimensions of the test facility could have led to high residence times in the char and ash, explaining the low conversion of fuel-nitrogen to NH_3, totally absent in test M.G.4.

12.2.3.2 Effect of the bed temperature

The effect of the temperature on the concentration of nitrogen species is reported in Figure 27. For both DDGS and Miscanthus there appear to be a correlation between NH_3 concentration and bed temperature changes with bed temperature. In particular, at a temperature of around 920 ^oC there is maximum concentration of ammonia, decreasing at higher temperatures. On the other hand, HCN concentration is at its lowest when NH_3 is high and at its higher when NH_3 decreases.

Similarly, DDGS presents a maximum in NH_3 concentration at a temperature around 920 ^oC, whereas at higher temperatures the concentration of NH_3 decreases. HCN was produced during the gasification of DDGS and its concentration was constantly over the maximum measurable concentration with the absorbing tube.

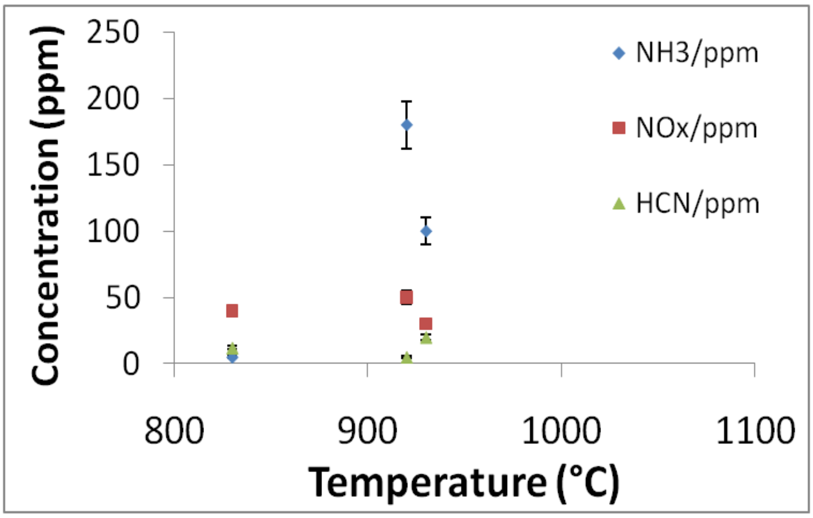


Figure 27. Concentration of nitrogen species as a function of the temperature for the gasification of Miscanthus.

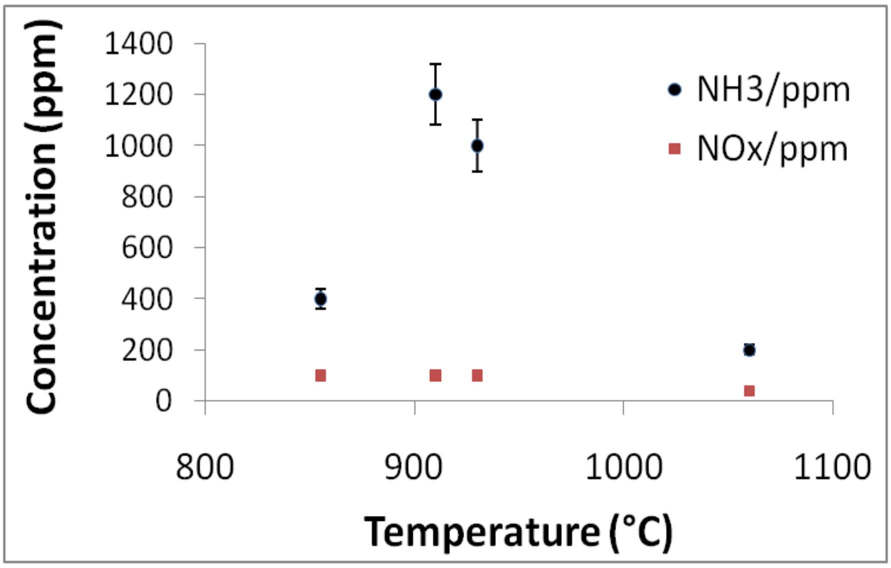


Figure 28. Concentration of nitrogen species as a function of the temperature for the gasification of DDGS.

However, previous investigations agree on the fact that the concentration of NH_3 decreases with bed temperature (Leppalahti and Koljonen, 1995; Leppälahti, 1993; Paterson et al., 2005a). An explanation to this can be found considering that apart from 5 ppm of NH_3 found at 830 ^oC in the test M.G.3., significant amounts of NH_3 for Miscanthus appear only at 897 ^oC (in test M.G.3) and at higher temperature. This would explain why in test M.G.4. where the bed temperature is lower, no NH_3 was registered. Therefore, the temperature seems to have the effect of increasing the devolatilisation of the fuel-nitrogen to produce NH_3 until, the increasing temperature favours the formation of HCN and N_2 through reactions (9) and (10).

12.2.4 Fate of the trace metals during gasification

In this section the release of the trace metals during the gasification experiments is discussed. All the residues are analysed by means of SEM/EDX, which allows knowing the metals that are less volatile and that are involved with the creation of bed agglomerates. The analysed samples comprise the bed ash left over the grate, the ash collected in the ash pot and the fly ash collected from the cyclone.

12.2.4.1 Analysis of the bed residues samples

Table 27 shows the analysis of the bed residue after the gasification of Miscanthus and DDGS: both fuels show high percentage of Ca in this sample and contrary to what one would expect, Miscanthus ash is higher in K and P content than DDGS despite the analysis of the ash of the fuels shows the opposite (see Table 10).

Table 27. EDX analysis of the gasification bed residue

Element	Miscanthus bed ash	DDGS bed ash
O	51.59	62.98
Na	0.52	0.52
Mg	1.72	0.98
Al	1.21	0.72
Si	3.52	1.75
P	4.07	2.09
S	0.89	5.79
Cl	0.00	0.47
K	7.41	5.01
Ca	26.57	15.15
Mn	0.28	0.13
Fe	1.11	3.25

On the other hand, the analysis of the finer ash collected in the ash pot of the gasifier resembles more the ash composition of the two fuels: the concentration of Ca is much higher in Miscanthus ash and the percentage of K and P is higher in DDGS ash. Moreover, the ash pot sample of Miscanthus has essentially the same composition of the bed ash, whereas DDGS ash pot sample has an increased concentration of volatile metals like Na and Mg, while metals normally showing less volatile behaviour such as Al, Ca and Fe are slightly decreased.

Table 28. EDX analysis of the ash collected in the ash pot of the gasifier

	Miscanthus ash pot	DDGS ash pot
O	51.19	55.60
Na	0.07	2.01
Mg	1.78	3.25
Al	2.39	1.81
Si	3.18	1.05
P	4.43	11.38
S	1.68	1.78
Cl	0.00	1.07
K	4.59	15.70
Ca	21.49	6.90
Mn	0.51	0.00
Fe	0.77	1.15

Indeed this difference in the produced ash determined a significant difference on the behaviour of the fuels during their gasification. It has been reported that biomass with high alkali content produce low melting ash crating agglomeration, slagging and fouling as much as in combustion systems. Despite being gasification operated in reducing conditions, the gasification process needs combustion in order to produce the heat needed for the process. Especially in fixed bed gasification the oxidation zone can reach temperatures as high as 1200 ^{o}C.

In the gasification tests performed in this investigation there is not a significant difference in the temperature reached by the reacting fuels during the gasification process: both fuels reach temperatures in the order of 1000-1100 ^{o}C, but the different ash composition of the fuels determines different ash melting point.

Actually, in previous paragraph the reactivity of Ca towards K and Na silicates was the cause of a lower melting temperatures of the ash; however, in this case the concentration of alkali metals in Miscanthus is low and the high Ca content has a different effect. It has been reported that Ca in gasification of biomass can act as anti-agglomeration and anti-sintering agent and as a catalyst for char gasification (Risnes et al., 2003).

On the other hand, the high K and P content of DDGS ash led to serious agglomeration problems due to the characteristics of the potassium rich phosphates as discussed in paragraph 11.1.6. In this case of fixed bed operation the melting ash affects the gasifier normal operations by forming a liquid layer of molten material and by interacting with the refractory walls of the gasifier; this, by disrupting the air distribution affects the heat transfer between bed particles resulting in a discontinuous bed consumption and subsequent fluctuation on the gas composition.

12.2.4.2 Analysis of the fly ash samples

Table 29 shows the result of the EDX analysis of the fly ash collected at the cyclone; for both fuels the concentration of Cl and S is increased in accordance with what happens in combustion systems where the volatile metals species are sulphites and chlorides. However, also Fe concentration is increased in the fly ash, being Fe a non-volatile element in combustion; therefore the reducing conditions of gasification cause a volatilisation of Fe. Indeed, Fe has been found in the reduced form of Fe^{2+} (Font et al., 2005).

Table 29. EDX analysis of the fly ash samples

	Miscanthus fly ash	DDGS fly ash
O	66.90	48.55
Na	0.37	2.89
Mg	0.79	3.44
Al	1.29	0.00
Si	3.26	0.00
P	1.71	6.32
S	2.17	4.48
Cl	0.73	2.73
K	6.65	12.46
Ca	11.79	7.82
Mn	0.00	0.00
Fe	3.03	11.31

Moreover, the percentage of Ca in the fly ash is lower than in the bed ash for Miscanthus as well as the P concentration for DDGS.

12.2.4.3 Elements Enrichment

Also for gasification the enrichment of the elements in the various samples points can be determined in the same way it was done for the combustion tests.

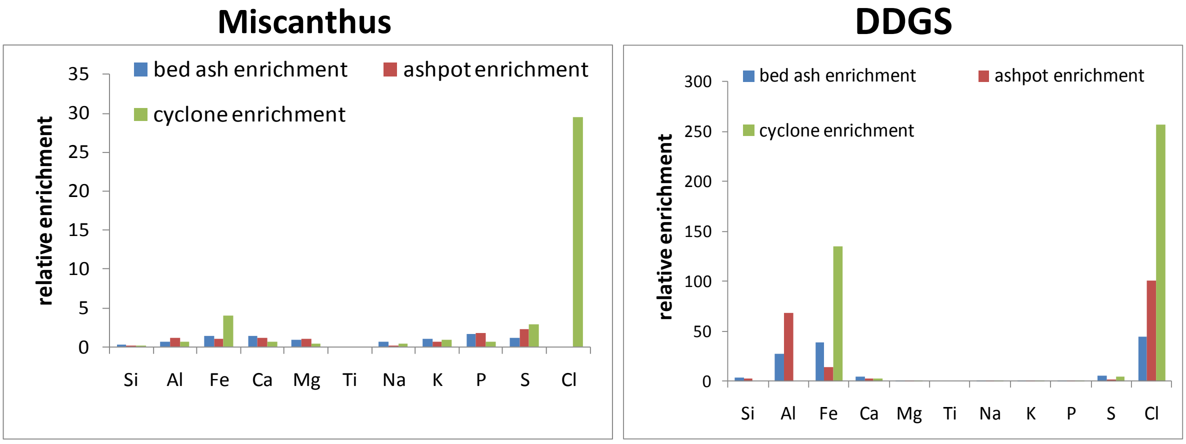


Figure 29. Enrichment factor for the analysed elements in Miscanthus and DDGS ash samples

The bed ash of Miscanthus has essentially the same composition of the ash analysis, while the bottom ash of DDGS is enriched in Al and Cl.

The fly ash of both fuels is enriched in Cl, confirming the tendency of metals to be volatised as chlorides; on the other hand, the enrichment in Fe in the fly ash is different from the behaviour found in combustion where it tends to be among the least volatile species. This suggests the formation of FeCl and the volatilisation of Fe under gasification conditions.

13. Discussion

This section summarises the results for the combustion and gasification tests described in the previous section and applies what has been found to the analysis of the mechanisms involved in the production of nitrogen and trace metal species. Moreover the approach to reduce the emission of these species is described.

13.1 Mechanisms regulating the emission of nitrogen species from combustion

The different nitrogen content of the two fuels plays an important role in the emission their characteristics influencing the amount of NO and N_2O emitted in the flue gas with DDGS producing higher concentration of both.

The analysis of devolatilisation products and final nitrogen oxides produced allows highlighting the most important reactions taking place in the combustion of the two fuels investigated.

Miscanthus devolatilisation and main combustion produce NO as the major nitrogen species. All the other nitrogen species are produced at low level throughout all the process. However, the presence of NH_3 even in small quantities among the minor species suggests it being the main precursor for the formation of NO. Therefore the reactions taking place during the combustion of Miscanthus are those involving the oxidation of NH_3 to form NO as reported in Figure 10b.

On the other hand, the devolatilisation of fuel-N from DDGS produces high levels of HCN as well as N_2O. This species then react leading to NO and N_2O as major products. NH_3 is absent when combusting DDGS, thus the reactions taking place during its combustion involve the oxidation of HCN. Being HCN the main precursor of N_2O this explains the relatively high concentration of this gas in the product even after the start-up stage. The reactions path of HCN to become NO are reported in Figure 10a.

The fact that Miscanthus produces NH_3 as a NO_x precursor, while DDGS releases HCN can be explained by a difference in the nitrogen containing compounds present in the two fuels. As reported in paragraph 3.2 between coal and biomass there is a difference in the partition between char and volatiles and of HCN/NH_3 (Abelha et al., 2008)(Hansson et al., 2004)(Di Nola et al., 2009), but also biomass fuels have been found to differ (Leppalahti, 1995). The difference between the two fuels could be a consequence of different types of protein: proteins with no reactive side chains have been found to be completely volatized at mild temperature (700-900 °C), while proteins containing reactive side chains tend to form char together with volatiles. Volatile proteins liberate readily the nitrogen in the gas phase and tend to produce ammonia, while proteins that decompose more slowly tend to produce cyclic amides that are then converted to HCN (Hansson et al., 2004).

Despite being DDGS the higher nitrogen containing fuel, the conversion of fuel-N to NO is lower for DDGS than for Miscanthus: this can be explained by the reactions involving the volatile species in the gas phase. This is due to DDGS producing more volatile species that tend to react and reduce nitrogen oxide to form molecular nitrogen according to reaction (8).

Both fuels present increasing NO concentration with increasing temperature, in agreement with the expected effect of increased rate of devolatilisation and higher concentration of volatile species in the gas phase. Moreover, in the combustion of DDGS the concentration of N_2O decreases at higher temperatures. The fact that the concentration of NO decreases at lower temperatures when the concentration of N_2O is high suggests that the reactions taking place involve both species as in reactions (6) and (7) where HCN is oxidised by O and OH radicals to form NCO that reacts with NO to form N_2O and CO. At high temperatures the concentration of N_2O decreases as N_2O is oxidised to NO by homogeneous reaction and heterogeneous reactions reported in Table 5.

13.2 Best approach to reduce NO_x produced during combustion

There are several techniques that can be used to reduce the emission of nitrogen oxides from combustion; those that can be used with solid fuels such the biomass fuels used in this thesis comprise modification to the process conditions and treatment of the flue gas.

The modifications to process parameters that can be used are the following:

- *Low excess air*
- *Air staging combustion*
- *Fuel staging combustion*
- *Flue gas recirculation*

Whereas the flue gas treatment can be done using the following techniques:

- *Selective catalytic reduction*
- *Selective non-catalytic reduction*
- *Non-selective catalytic reduction*

All these methodologies are described in detail in chapter 5; the present study has investigated the effect of process parameters on the emission of nitrogen oxides. Therefore, the use of these parameters to reduce the emission of nitrogen dioxide is discussed below.

13.2.1 Use of low excess air levels

One of the systems to reduce the emission of NO_x is to operate at low excess air in fact, as it has been reported in paragraph 11.1.5., the combustion of DDGS results show that at Φ= 1.06 corresponding to 6% excess air level the concentration of NO_x is 272 ppm (or 350 mg/Nm^3), that is the lowest value encountered in the conditions investigated. Therefore, working at low excess air levels has been confirmed as an effective measure to lower the emission of nitrogen oxides. However, the combustion of Miscanthus led to bed agglomeration at Φ<1.4; the agglomeration of the bed is a major drawback for the use of low value of Φ for both fuels. Therefore, the option of operating at low excess air can be considered feasible only if the bed agglomeration issue is resolved. There are several methods to avoid the agglomeration involving operational actions, use of additives and change of bed material. The operational actions that can be undertaken are as follows:

- *Remove heat from the bed:* because the high temperature of the bed is cause of the agglomeration, the heat produced could be removed by having tubes with flowing fluid inside the bed as heat exchanger.

- *Stopping the feeding and let the bed temperature lower*: during the combustion tests carried out for this project a temporary stop of the feeding, which also lowered the bed temperature has sometimes proven to be a suitable method, especially if the agglomeration process was detected before major agglomerates were formed. However, stopping the fuel feed is a disruption to the continuous operation of the combustor and the efficiency of the combustion process is compromised (Bartels et al., 2008).

- *Avoid fuel-rich zones:* the fluidised bed combustion system should be designed to favour the mobility of the bed particles in order to avoid fuel-rich zones where the local reducing conditions can encourage the agglomeration of the bed.

- *Pulsation of the gas flow*: in the present project the air distribution nozzles below the fluidised bed were creating a bubbling fluidised bed unable to break the agglomerates formed. A different air distribution of the fluidisation air creating pulses of air through the bed sand (e.g. spouted bed) would break the forming agglomerates and delay or prevent the agglomeration process(Bartels et al., 2008).

- *Optimisation of the drainage of spent bed material and addition of fresh sand* (Bartels et al., 2008)*:* these systems involve the continuous recycle of the fluidised bed sand with fresh one; the sand particle size is selected by sieving installation and discarded, while fresh sand is added to the bed. However, the spent sand has to be disposed of and represents an additional cost.

- *Use of additives*: there are various additives that have been investigated to counteract the agglomeration process; few major additive groups appear to be hydrated alumino silicates and hydrated magnesium silicates as well as carbonates or oxides of calcium, magnesium or barium (Bartels et al., 2008). All these are silicates containing Al, Mg, Ca and Fe that can significantly reduce the agglomeration tendency due to higher melting point than the silicates formed without an additive (Bartels et al., 2008).

- *Use of alternative bed materials*: the phenomenon of agglomeration is caused by the formation of silicates; therefore, bed materials different than SiO_2 would lower the content of silica in the reaction environment. By doing this, especially when using fuels containing low amounts of Si the agglomeration would be sensibly reduced (Bartels et al., 2008).

Bed agglomeration is caused by many mechanisms involving the formation of low melting eutectics combined with low mobility of the bed material. As described in paragraph 2.5.2 this is a common issue of all biomass fuels. Moreover, there are some indexes (paragraph 12.1.1) that can help identify fuels that will cause agglomeration from the analysis of the ash. Therefore, the use of the described methods for the reduction of bed agglomeration should be considered when performing combustion of biomass fuels having high content of alkali metals.

Finally, the use of low excess air can lower the combustion efficiency increasing the amounts of unburned carbon in the ash, production of high levels of carbon dioxide and tar. Therefore, the low excess air level should be achieved in conditions that avoid the phenomenon of agglomeration as described above and making sure that the fuel is completely combusted.

13.2.2 Use of air staging or fuel staging combustion

Other systems to reduce NO_x emissions comprise staging the introduction of air or fuel in the reaction environment. In the case of combustion air staging, a first fuel-rich zone is created where the fuel-N is reduced to molecular nitrogen and the production of NO_x is suppressed (Mahmoudi et al., 2010), then more air is introduced in a second zone to complete the combustion. On the other hand, on fuel staging combustion part of the fuel is introduced above the combustion zone creating a fuel-rich secondary zone where the NO_x created in the primary zone is reduced through decomposition (Mahmoudi et al., 2010). However, the use of solid fuels in this project doesn’t allow using the fuel staging. On the other hand, the staging of the combustion air is a feasible method to be used in the combustion of biomass: only part of the air necessary for the combustion is introduced to fluidise the bed (primary) and the rest of the combustion air is introduced above the bed (secondary air). Unfortunately the fuel-rich zone created would increase the chance of bed agglomeration.

13.2.3 Use of flue gas recirculation and low combustion temperatures

The use of flue gas recirculation is reported to be not very effective in reducing the nitrogen oxides deriving from the fuel, but instead those produced through thermal and prompt mechanism (see Table 3). The recirculation of the flue gas lowers the temperature and decreases the excess air and the fuel-NO_x that has low thermal sensitivity is not affected. However, in the present investigation, the concentration of NO_x has showed to be affected by the temperature of the bed: in the temperature range investigated a temperature difference of 100 ^oC provokes the increase of 18% in NO_x emission for Miscanthus and 16% increase for DDGS. Hence, using flue gas recirculation to lower the combustion temperature or simply work at the lowest possible temperature can reduce the emission of nitrogen oxides.

13.2.4 Combination of methods for the reduction of nitrogen oxides

The council directive relating to limit values for sulphur dioxide, nitrogen oxides, particulate matter and lead in ambient air defines the oxides of nitrogen as the sum of nitric oxide and nitrogen dioxide and are expressed as nitrogen dioxide in mg/Nm^3 (Official Journal of the European Communities,). The European Directive on the limitation of emissions of certain pollutants into the air from large combustion plants, comprising NO_x states the limits for the operation of new plants in the Member States of the European Union; these values are reported in Table 30 (Official Journal of the European Communities,). In the range of operating conditions investigated, the maximum emission found from the combustion of the fuels investigated is 239 ppm for Miscanthus and 529 ppm for DDGS. Considering the molecular weight of air (28.8 kg/kmol) and the molar volume at STP (22.4 m^3/kmol), the concentration becomes: 307.2 mg/Nm^3 for Miscanthus and 680 mg/Nm^3 for DDGS.

Table 30. Limit values for nitrogen oxides (expressed as NOx) for the operation of new plants put into operation.

Type of fuel	50 to 100 MWth	100-300 MWth	>300 MWth
Biomass	400	300	200
General case	400	200	200

Considering the lowest limit value reported in Table 30 of 200 mg/Nm^3 and the highest emission registered during the combustion of the two fuels of 239 mg/Nm^3 for Miscanthus and 529 mg/Nm^3 for DDGS, a decrease of 16% and 62% respectively is necessary. The low excess air method achieves a reduction of the 16-20 %, while staged air combustion can achieve 30-40% reduction of NO_x concentration. Taking the lowest values of achievable reduction, the level of NO_x reduction can be calculated for the two fuels as follows:

- *Miscanthus*: a reduction of 16% when combusting Miscanthus would reduce the NO_x emission to the desired level of 200 mg/Nm^3. Even if the low excess air method cannot be used with Miscanthus at the conditions investigated, the use of staged air for the combustion would lead to an even better result reducing the emission to 167 mg/Nm^3.

- *DDGS:* A reduction of 16% on 529 mg/Nm^3 would lead to 444 mg/Nm^3 that further reduced of 30% would produce 311 mg/Nm^3. On the other hand, if the highest values of NO_x reduction are achieved, the concentration of NO_x would be reduced from 529 mg/Nm^3 to 253 mg/Nm^3.

Therefore, the reduction of NO_x to the value required cannot be achieved even in the best case scenario for DDGS leading to the adoption of flue gas treatment that can achieve 50-90% of NO_x reduction; thus, combining flue gas treatment with air staging can ensure to meet the emissions limit when combusting DDGS.

13.3 Mechanisms regulating the emission of nitrogen species from gasification

The two fuels present different values of fuel-N conversion to NH_3: the conversion is higher for DDGS than Miscanthus due to higher amount in the fuel. As reported in paragraph 12.1, under combustion conditions the fuel with higher nitrogen content (DDGS) had the lowest conversion of fuel-N to NO, instead in gasification the NH_3 is higher for the high nitrogen-containing fuel.

On the other hand, the effect of pyrolysis temperature on NH_3 concentration is similar for the two fuels as the maximum concentration is registered at the same temperature of 920^{o}C and at higher temperatures NH_3 concentration tends to decrease. Indeed, the more important stage of the gasification determining the amount of NH_3 liberated to the gas phase is the pyrolysis stage: the higher the temperature, the higher is the rate of devolatilisation of nitrogen containing species to form NH_3. At this stage the reaction involved are the same described for the combustion devolatilisation stage, therefore DDGS would be expected to liberate big amounts of HCN; unfortunately the presence of HCN could be only detected but not measured due to the limit in the absorbing tube used. Nevertheless in gasification conditions DDGS liberates NH_3 up to 1200 ppm; Miscanthus instead produced smaller concentration of HCN and NH_3 compared to DDGS.

The decrease in NH_3 concentration at temperatures higher than 920 ^{o}C for both fuels is explained by the decomposition of NH_3 at high temperatures catalysed by char and ash. In fact, the decomposition of NH_3 in the gas phase is negligible even at temperatures as high as 1200 ^{o}C if only homogeneous reactions are considered, whereas heterogeneous reactions involving the solid residues can lead to decomposition of NH_3 at lower temperatures. The configuration of the pilot-scale gasifier used in the present project favours the contact between the gases produced in the pyrolysis zone with the char on the reduction zone (see Figure 38b) and the ash below it.

Therefore, at the lowest temperatures NH_3 is liberated at a lower rate due to lower pyrolysis temperature and due to the lower air input, the residence time of the gas is higher and makes reaction (10) go towards the decomposition of NH_3 and the production of molecular nitrogen and hydrogen. Then, as the temperature and the air input are increased, the pyrolysis of the fuel produces higher amounts NH_3 and the residence time of the gas in the char is lower so that the emission of NH_3 in the produced gas is increased. However, at the highest temperatures the increasing temperature favours the formation of HCN and N_2 through reactions (9) and (10) and the concentration of NH_3 decreases again.

13.4 Best approach to reduce the nitrogen species produced during gasification

The investigation of the two fuels DDGS and Miscanthus in the downdraft pilot-scale gasifier can be used to assess measures for the reduction of ammonia in the produced gas.

The quantity of ammonia that can be tolerated in gasification systems depends on the final use for which the gas is intended. The gas produced in the present project could be used as it is in systems that require minimal gas cleaning: systems like biomass-fired kilns, steam cycle power generation systems and co-firing applications where the biomass fuel gases are burned in coal power stations (Stevens, 2001). These systems have characteristics that allow the minimally treated gas to be used effectively are as follows (Stevens, 2001):

- The end-use can tolerate significant amounts of particulates;
- The system has no special sensitivities to alkali salts;
- The gasifier and end-use technology are closely coupled, which helps retain the sensible heat in the raw gas and also prevents tar condensation in pipes;
- Tars are combusted at the burners;

- Environmental emissions regulations can be met by treating the cool combustion gases after the heat is extracted, or emissions requirements are minimal;

Otherwise, the gas cleaning has to be performed using catalytic destruction or wet scrubbing as described in chapter 5.

Nevertheless, the investigation of the two fuels Miscanthus and DDGS has also highlighted common behaviour of ammonia in this type of gasifier. Therefore, actions on the gasification conditions can reduce the NH_3 content in the produced gas. The investigation of the two fuels DDGS and Miscanthus in the downdraft pilot-scale gasifier has revealed the two following effects:

- The liberation of NH_3 is lower at the lowest bed temperatures and at the highest bed temperatures.

- The decomposition of NH_3 is favoured by high residence time.

As previously explained these conditions favour the decomposition of NH_3 through reaction (10). The feasibility of these two actions on the process is discussed below.

13.4.1 Gasification at low or high temperature

In the current configuration of the gasification rig (Figure 38) the operating temperature is determined by the air input; hence, working at low temperatures implies low air inputs and consequently working at low values of equivalence ratio which lead to lower gas yields and lower cold gas efficiencies.

As an alternative, working at high temperatures favours both the reduction of NH_3 and a better gasification. In the gasifier used operating at high temperatures means operating at high values of equivalence ratio; for Miscanthus this maximises the gas yield and the cold gas efficiency (Table 25); on the other hand, operating at high equivalence ratio values and high temperatures with DDGS does not improve the gasification (Table 25). Moreover, the concentration of HCN seems to increase when raising the temperature and the issues related to the ash melting also become important.

The production of a gas is favoured at high temperatures, but the ash properties of the fuels play an important role in the final production of gas in this type of gasifier. In fact, one of the most important properties is the air distribution through the fuel particles: if the ash starts to melt at the bottom of the gasifier, a layer of molten ash is created that disrupts the air distribution along the bed and also disturbs the heat transfer between bed particles. Therefore, in order to avoid interference of the ash on the gasification process, there should be a system for the removal of the ash from the bottom of the gasifier before it causes agglomeration and starts to disrupt the air distribution and the heat transfer in the bed.

13.4.2 Maximisation of the residence time

The maximisation of the contact between char particles and the gases produced in the pyrolysis stage favours the decomposition of NH_3; hence, a higher residence time of the gas in the char reduction zone helps reducing the amount of NH_3. This in the current configuration of the gasifier involves introducing the air at the lower possible flow rate so that the bed temperature is kept low and the residence time is maximised due to lower gas velocity through char and ash. However, the lower air input means that the equivalence ratio is lower and as described in paragraph 12.2.2 the gasification efficiency is affected. Hence, the residence time does not seem to be a process parameter on which action can be taken to reduce NH_3 conversion.

13.5 Fate of trace metals during combustion and gasification

During the experiments the ash produced by the fuels has been collected enabling to compare the behaviour of the ash main components between the two processes. The analysis of the ash residues enables to know whether the ash components tend to be volatised and carried to the gas downstream in the fly ash particles or the metal species tend to remain in the bottom ash. Moreover, the ash content had an influence in the efficiency of the two processes. These aspects are discussed in the following sections.

13.5.1 Ash components involved in the agglomeration process

The effect of ash content on the ash melting behaviour and the issues caused on the thermal conversion processes have been discussed in previous paragraphs. During the fluidised bed combustion, the silica of the bed material reacting with the alkali metals creates low melting compound that are the main responsible for the initiation of the agglomeration process. The occurrence of the agglomeration process depends on the mobility of the alkali metals, defined as the ability to come into contact with other materials (Bartels et al., 2008). Other ash components such as Ca, Si, P and S can contribute on the mobilisation of K and Na. Ca can form eutectics with lower melting point than the melting point of the of the silicate alone (Bartels et al., 2008); phosphorous, when present in high concentration can combine to form potassium silicates with melting temperatures as low as 650^{o}C (Lindstrom et al., 2007). Also, in gasification the melting ash caused disruption on air distribution and heat transfer between fuel particles.

The methods to avoid the agglomeration during fluidised bed operation are described in paragraph 13.2.1, while in paragraph 13.4.1 the removal of the ash from the gasifier is described as a possible solution to avoid ash melting.

Alkali elements are water soluble and the opportunity exists to remove them by mechanical dewatering and leaching as part of the feedstock preparation process (Turn et al., 1997). However, the process of leaching increases the water content of the feedstock that has to be dried afterwards increasing the cost of the overall thermal conversion process.

13.5.2 Volatilisation of trace metals during combustion and gasification

During the combustion of the two fuels, bottom ash is enriched in Fe due to Fe_2O_3 being non-volatile species during combustion as well as a compound that contributes to the agglomeration process lowering the silicates melting point. The fly ash is composed mostly by sulphates, phosphates and chlorides of potassium: the species usually involved in the volatilisation process are KCl, K_2SO_4 and K_3PO_4.

During the downdraft gasification, the composition of the bottom ash is not altered by the silica; in these conditions the composition of the produced ash resembles the one of the ash analysis obtained in oxidising conditions. However, the fly ash is enriched in elements like Fe and Al that in combustion conditions are non-volatile and found in the bottom ash.

Finally, chlorine is main enriched element in the fly ash from gasification involving the formation of KCl also in reducing conditions. In both processes the formation of chlorides leads to volatilisation of the metals that then condense in the fly ash.

Therefore, both processes are affected by the high alkali metals content of the fuels and given the temperatures necessary for the processes to take place, the volatilisation of alkali species cannot be avoided. Hence, both combustion and gasification require a downstream cleaning system for the removal of alkali compounds described in chapter 8.

13.5.3 Fate of heavy metals from combustion

In the combustion process the heavy metals release in the flue gas was analysed by ICP-MS: the metals analysed are As, Cd, Cr, Cu, Ni, Pb, Se, V, Zn and Hg. These heavy metals are those specified by The UK Heavy Metal Monitoring Network (Flowers et al., 2006) that measures the deposition of these metals in the environment across the UK.

Moreover, there are two Directive of the European Union setting the limit values for the quantity of Pb, As, Cd, Hg and Ni in ambient air. Therefore, the regulated heavy metals have to be monitored for their presence in the flue gas to avoid emitting large quantities in the environment.

The two fuels investigated have been analysed for these heavy metals and they do not contain As and Hg. The combustion of both fuels produced small concentration of the heavy metals with a maximum of 4 ppb of Pb for DDGS. Moreover these levels of heavy metals have been detected in the flue gas after it had been filtered only through the glass filter of the sampling system; the application of further metals removal systems is discussed in the next paragraph.

13.5.4 Removal of trace elements from the flue gas

As described in the previous sections, there are 4 systems used to remove the particulate matter from the gas stream as follows (Stevens, 2001):

- *Cyclone filters:* in the cyclone filters, the solids are separated from the gas by redirecting the gas into a circular path where the solids are separated by inertia.

- *Barrier filters* Barrier filters include a range of porous materials that stop the particles and allow the gas to pass.

The particle removal for these two methods is limited to the size of 0.5 μm and has been successfully applied in the present study for the sampling of fly ash in the present study. The content of the fly ash from both combustion and gasification showed a high concentration of alkali and Cl meaning that the capture of these volatile compounds can be effective using cyclone and barrier filters.

Despite the use of these measures the sampling of the flue gas from combustion demonstrated the presence of heavy metals contained in particles passing through the glass filter and in the vapour phase.

For further reduction of trace metals from the flue gas there are two other methods:

- *Electrostatic filters:* this filters work by electrically charging the particles that are then attracted to the surface of collector plates. The ESP can remove more than 99% of the particulates from the flue gas.

- *Wet scrubbers*: particulate matter can be removed by bringing into the gas contact with a liquid spray. This method can remove up to 99.9% of particles over 2μm and up to 95-99% of particles above 1μm (Stevens, 2001).

14. Summary and Conclusions

In this project the emission of nitrogen species and trace metal species during pilot-scale combustion and gasification of Miscanthus and DDGS has been investigated.

Studying the influence of process parameters such as bed temperature and equivalence ratio in pilot scale combustion and gasification of the two fuels enabled determining which reactions are influencing the emission of nitrogen species in the flue gas. The different nitrogen content of the two fuels plays an important role in the emission; their characteristics influencing first of all the amount of NO and N_2O emitted in the flue gas with DDGS producing higher concentration of both NO and N_2O in the flue gas. Both fuels present increasing NO concentration with increasing temperature, in agreement with the expected effect of increased rate of devolatilisation and higher concentration of volatile species in the gas phase. The effect of excess air on NO_x concentration has been affected by bed agglomeration issues. However the concentration of NO seems to increase with increasing value of excess air until the dilution effect causes the decrease of NO concentration. The two process parameters bed temperature and air to fuel ratio have demonstrated to have an important influence in the release of nitrogen oxides, therefore they can be used to mitigate the emission of these species in the stack gas to reduce the cost related to the gas clean-up.

Moreover, in gasification the different nitrogen content of the two fuels determines the amount of nitrogen emitted emitted in the produced gas. DDGS Low concentration of NH_3, have been found due to heterogeneous reactions involving the char and ash which catalyse the reaction of decomposition of ammonia to form molecular nitrogen.

The analysis of the ashes from the two processes has also been performed. Both processes are affected by the high alkali metals content of the fuels and given the temperatures necessary for the processes to take place, the volatilisation of alkali species cannot be avoided. Hence, both combustion and gasification require a downstream cleaning system for the removal of alkali compounds such as electrostatic filters, bag filters or wet scrubbers after cooling the gas.

Differences have been highlighted in the metal distribution between combustion and gasification. Both in combustion and gasification the fly ash analysis presents a considerable enrichment in Cl for both the fuels, showing a tendency of chlorides to be highly volatile. Moreover, Miscanthus fly ash is also enriched in P and S indicating sulphates and phosphates as the other species with high volatility that tend to condensate in the gas downstream. On the other hand, the enrichment in Fe in the gasification fly ash is different from the behaviour found in combustion where it tends to be among the list volatile species.

This thesis has demonstrated that:

- The gas phase reactions involving nitrogen species developed for coal can be applied to biomass, whereas the devolatilisation of the fuel nitrogen in the pyrolysis stage is highly dependent on the fuel type and differs between coal and biomass. The trace metals content of biomass and coal is sensibly different: biomass contains high levels of alkali metals that play a central role in the ash chemistry, while the concentration of heavy metals is lower for biomass and represent a lesser issue.

- The nitrogen forms of the fuel determine the release of volatile species such as NH_3 and HCN in the pyrolysis stage of the thermal conversion processes. The gas phase reactions involving the volatile nitrogen species are influenced by their concentration in the gas which in turn depends on the nitrogen content of the fuel.

- The release of metals species is related to volatilisation through reaction with Cl S and P. The high level of alkali metals increases the risk of bed agglomeration and ash fusion.

- The reduction of nitrogen species can be achieved by controlling process parameters such as equivalence ratio and temperature. However, the use of these control methods can be achieved only if the process is optimised to avoid issues related to the bed agglomeration and the melting ash.

Both the solid biomass fuels investigated have a great potential to be used for thermal conversion and production of electricity and heat. The different nitrogen and ash content of the two fuels make the results of the present thesis applicable to predict the behaviour of other biomass fuels according to the fuel characteristics. The scale of the tests performed allowed highlighting which methods can be used to control the emission of nitrogen and trace metal species. Moreover, the investigation highlighted major drawbacks in the use of biomass fuels in both fluidised bed and fixed bed technology due to ash properties.

In future investigation, the issue of bed agglomeration should be addressed investigating the use of the methods described in paragraph 13.2.1. To avoid agglomeration is basic in order to extend the investigation to higher temperatures and lower values of excess air in fluidised bed.
Moreover, the fuels should be tested in other combustion and gasification technologies such as fixed bed combustion and fluidised bed gasification to investigate the effect on nitrogen and minor species behaviour.

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APPENDIX A: FLUIDISED BED COMBUSTION RIG DESCRIPTION AND OPERATION

A.1. Rig description

A schematic representation of the combustion rig is shoed in Figure 30.

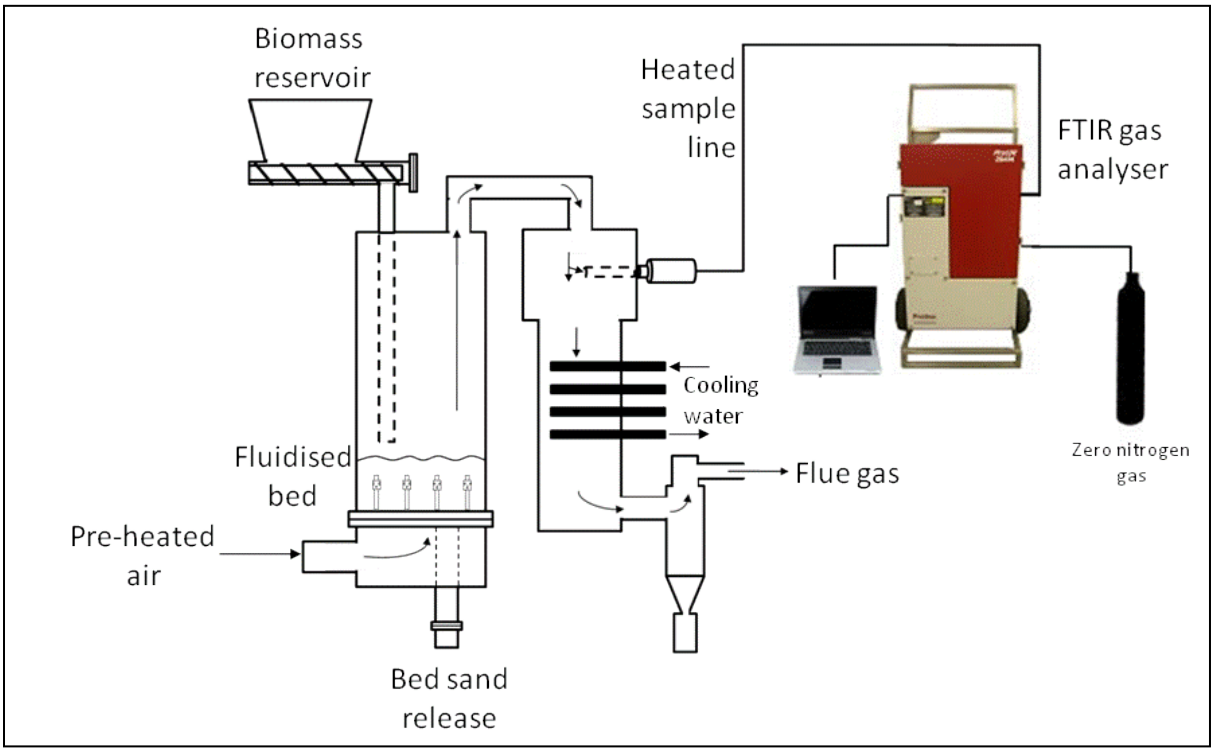


Figure 30. Schematic representation of the combustion rig

Details about the various components of this system are given below.

A.1.1. Screw feeder

The feeding system is a screw feeder; the calibration was performed by measuring the amount of fuel fed during known lapse of time, then the data was interpolated and the feeding rate was calculated using the equation reported in Figure 31.

EXPERIMENTAL

Feeder engine level (%)	Kg of fuel per 5 min of feeding
7	0.9
8	0.95
9	1.05
10	1.1
12	1.3
14	1.45
16	1.6
18	2
20	1.85

CALCULATED

Feeder engine level (%)	kg/h
7	10.8
8	11.7
9	12.6
10	13.5
11	14.4
12	15.3
13	16.2
14	17.1
15	18.0
	16

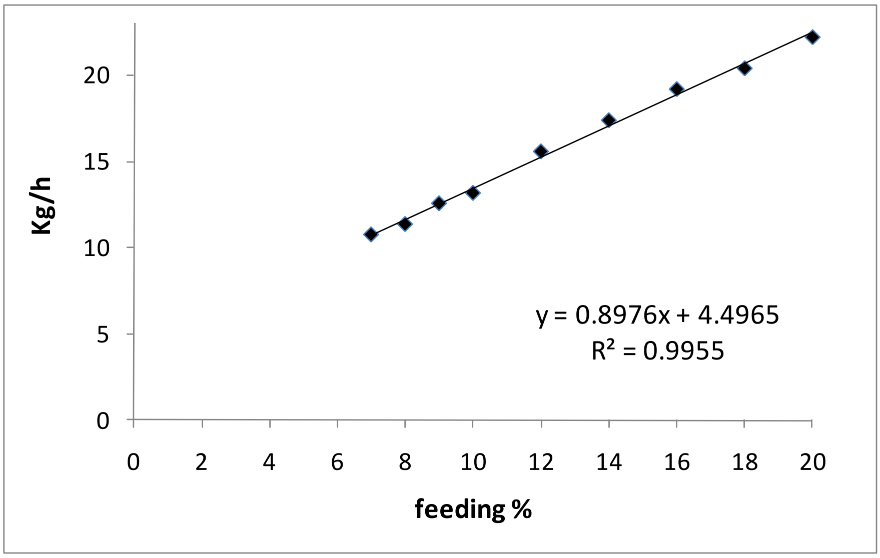


Figure 31. Calibration line for the screw feeding system

A.1.2. Fluidised bed

The fluidisation of the bed is performed by passing pre-heated air through 9 nozzles (Figure 32). The sand used in the bed is silica sand of grade 16/30 and size Range 1.00 - 0.50mm (Garside Sands Eastern Way, Heath and Reach, Leighton Buzzard, Beds LU7 9LF Specialists in Silica Sand). The datasheet is reported in Figure 33 (the sand used is the yellow one).

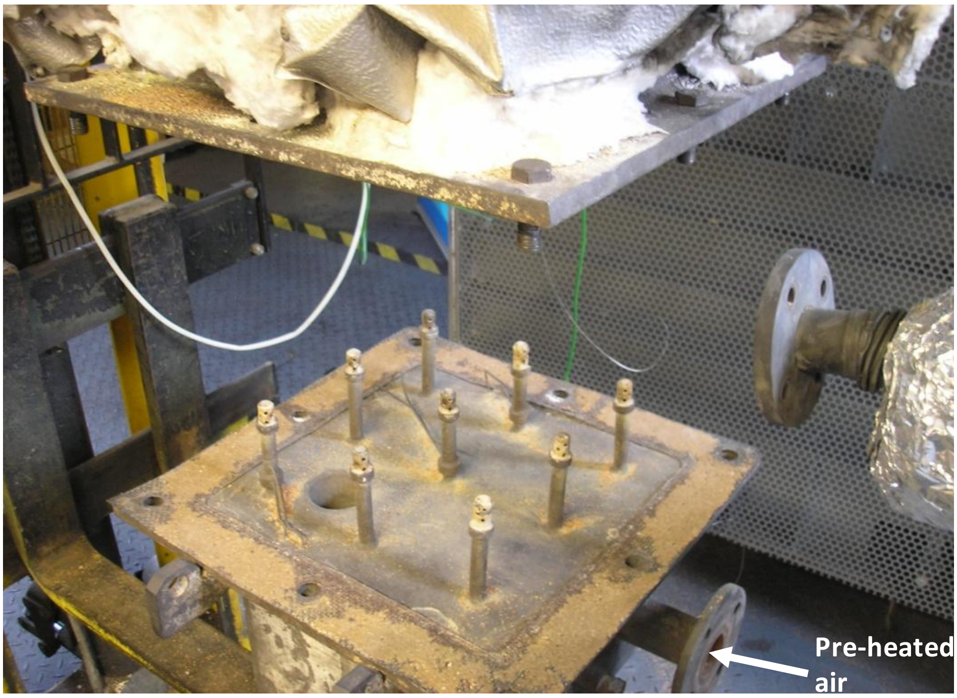
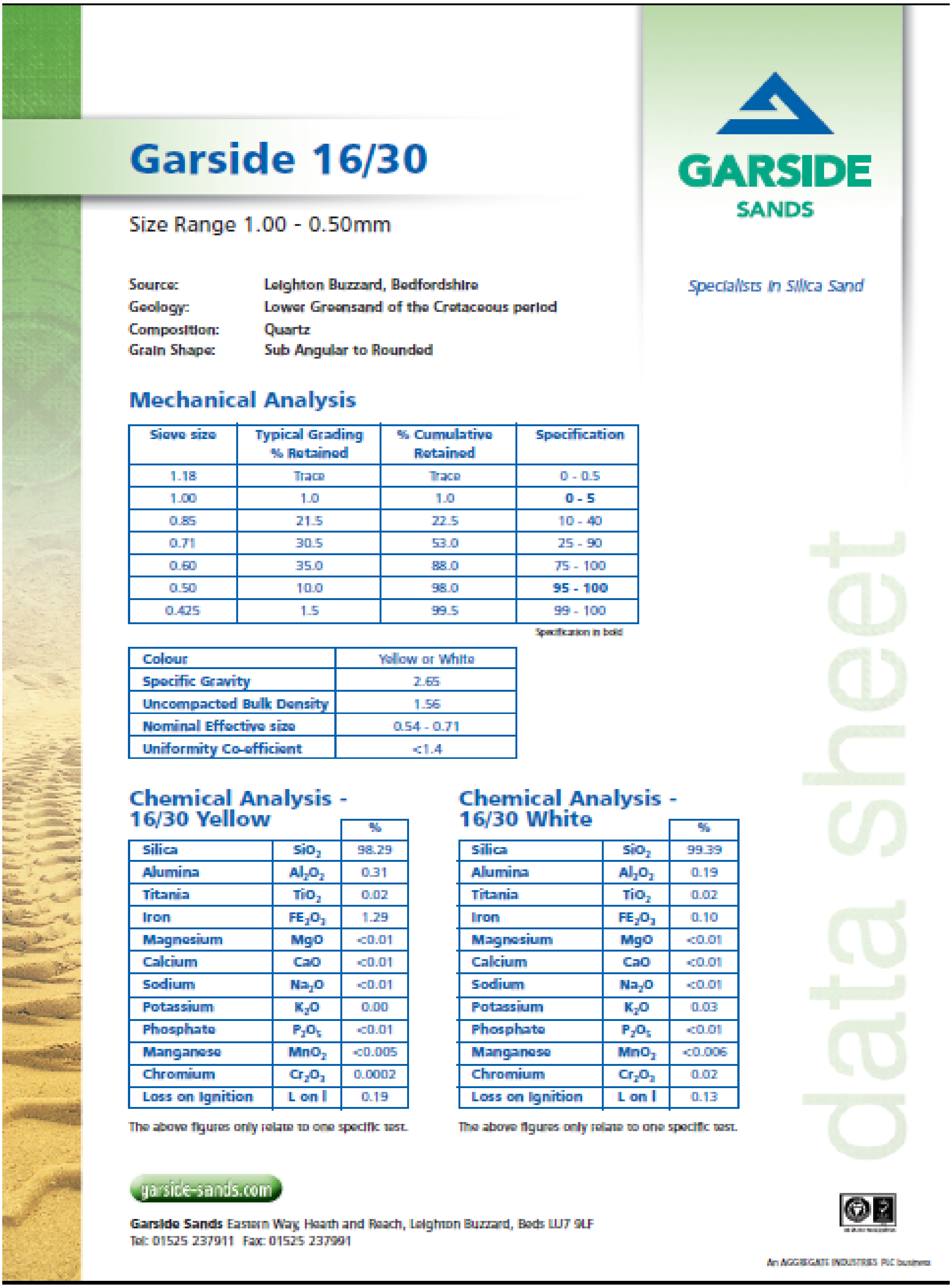


Figure 32. Picture of the 9 nozzles used for the fluidisation of the bed.

The combustion was performed with 25 kg of sand giving a static bed height of 17 cm.



Garside 16/30

Size Range 1.00 - 0.50mm

GARSIDE SANDS

Specialists in Silica Sand

Source: Leighton Buzzard, Bedfordshire
Geology: Lower Greensand of the Cretaceous period
Composition: Quartz
Grain Shape: Sub Angular to Rounded

Mechanical Analysis

Sieve size	Typical Grading % Retained	% Cumulative Retained	Specification
1.18	Trace	Trace	0 - 0.5
1.00	1.0	1.0	**0 - 5**
0.85	21.5	22.5	10 - 40
0.71	30.5	53.0	25 - 90
0.60	35.0	88.0	75 - 100
0.50	10.0	98.0	**95 - 100**
0.425	1.5	99.5	99 - 100

Specification in bold

Colour	Yellow or White
Specific Gravity	2.65
Uncompacted Bulk Density	1.56
Nominal Effective size	0.54 - 0.71
Uniformity Co-efficient	<1.4

Chemical Analysis - 16/30 Yellow

		%
Silica	SiO_2	98.29
Alumina	Al_2O_3	0.31
Titania	TiO_2	0.02
Iron	FE_2O_3	1.29
Magnesium	MgO	<0.01
Calcium	CaO	<0.01
Sodium	Na_2O	<0.01
Potassium	K_2O	0.00
Phosphate	P_2O_5	<0.01
Manganese	MnO_2	<0.005
Chromium	Cr_2O_3	0.0002
Loss on Ignition	L on I	0.19

The above figures only relate to one specific test.

Chemical Analysis - 16/30 White

		%
Silica	SiO_2	99.39
Alumina	Al_2O_3	0.19
Titania	TiO_2	0.02
Iron	FE_2O_3	0.10
Magnesium	MgO	<0.01
Calcium	CaO	<0.01
Sodium	Na_2O	<0.01
Potassium	K_2O	0.03
Phosphate	P_2O_5	<0.01
Manganese	MnO_2	<0.006
Chromium	Cr_2O_3	0.02
Loss on Ignition	L on I	0.13

The above figures only relate to one specific test.

data sheet

garside-sands.com

Garside Sands Eastern Way, Heath and Reach, Leighton Buzzard, Beds LU7 9LF
Tel: 01525 237911 Fax: 01525 237991

An AGGREGATE INDUSTRIES PLC business

Figure 33. Datasheet of the silica sand used in the fluidised bed; the sand used in this project is the yellow one.

A.1.3. Dimensions and operating temperatures

The dimensions and the points where temperature measurements are performed are reported in Figure 34.

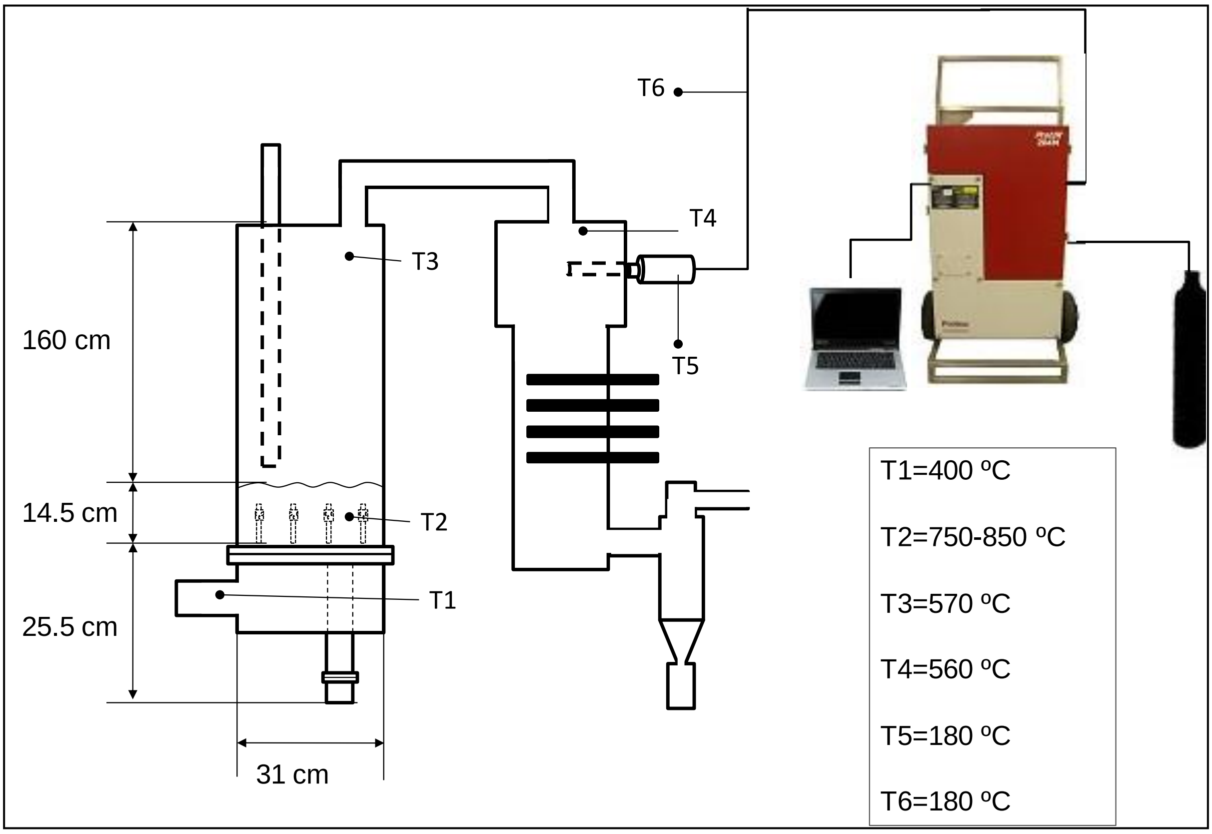


Figure 34 Dimensions of the rig and typical temperatures during operation

A.1.4. FTIR gas analyser

The gas analyser used is high resolution multicomponent FTIR online gas analyser (Protea-Protir 240 M/C mobile FTIR analyser, Protea, Cheshire, UK). The analyser is fitted with a heated line keeping the gas at 180 °C. Table 31 and Table 32 report the species analysed by the instrument along with their detection limits and calibration ranges.

Table 31. Detection limits for the FTIR gas analyser

Detection limits with standard optics					
H2O	< 0.4 %	SO2	0.99 ppm	N2O	<0.5 ppm
CO2	<0.2 %	CO	1.70 ppm	CH4	<0.5 ppm
O2	<0.2 %	HCl	0.43 ppm	C3H8	<0.5 ppm
NO	4.20 ppm	NH3	0.56 ppm	CHOH	<0.5 ppm
NO2	0.82 ppm	HF	0.40 ppm	HCN	<0.5 ppm

Table 32. Calibration ranges for the FTIR gas analyser

H_2O	0 – 40 %	CO	0 – 10000 ppm	C_2H_6	0 – 100 ppm
CO_2	0 – 65 %	HCl	0 – 2500 ppm	CH_4	0 – 10 ppm
O_2	0 – 20.9 %	NH_3	0 – 50 ppm	C_3H_8	0 – 10 ppm
NO	0 – 750 ppm	HCN	0 – 10 ppm	C_4H_{10}	0 – 10 ppm
NO_2	0 – 1500 ppm	N_2O	0 – 100 ppm	CHOH	0 – 10 ppm
SO_2	0 – 1000 ppm	HF	0 – 100 ppm		

A.1.5. Trace metals sampling system

The samples analysed for the presence of trace metals are three:

- The bed residue
- The fly ash
- The flue gas

In the bed three types of samples could be identified and collected for the analysis with scanning electronic microscope (SEM) as showed in Figure 35. Moreover, the slag residue was also found to be the material to cause the agglomeration and sample of agglomerated material were also collected (Figure 36) and analysed with the SEM.

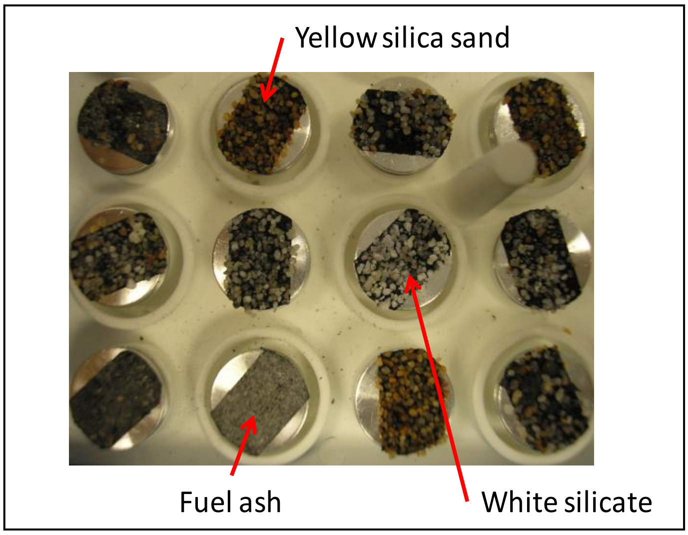


Figure 35. Bed residue samples

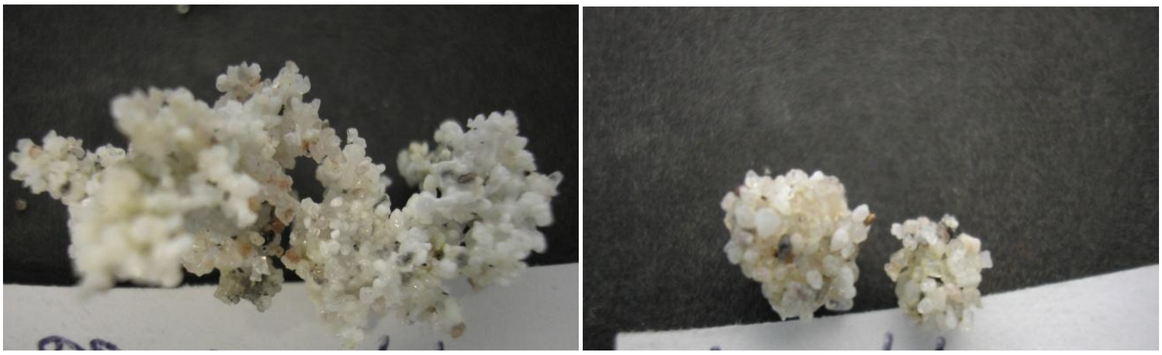


Figure 36. Pictures of the agglomerated slag for a) Miscanthus and b) DDGS

Furthermore, the fly ash samples and the flue gas samples were collected by means of the same sampling system, consisting of a standard method for the determination of metals emission from stationary source (EPA METHOD 29).

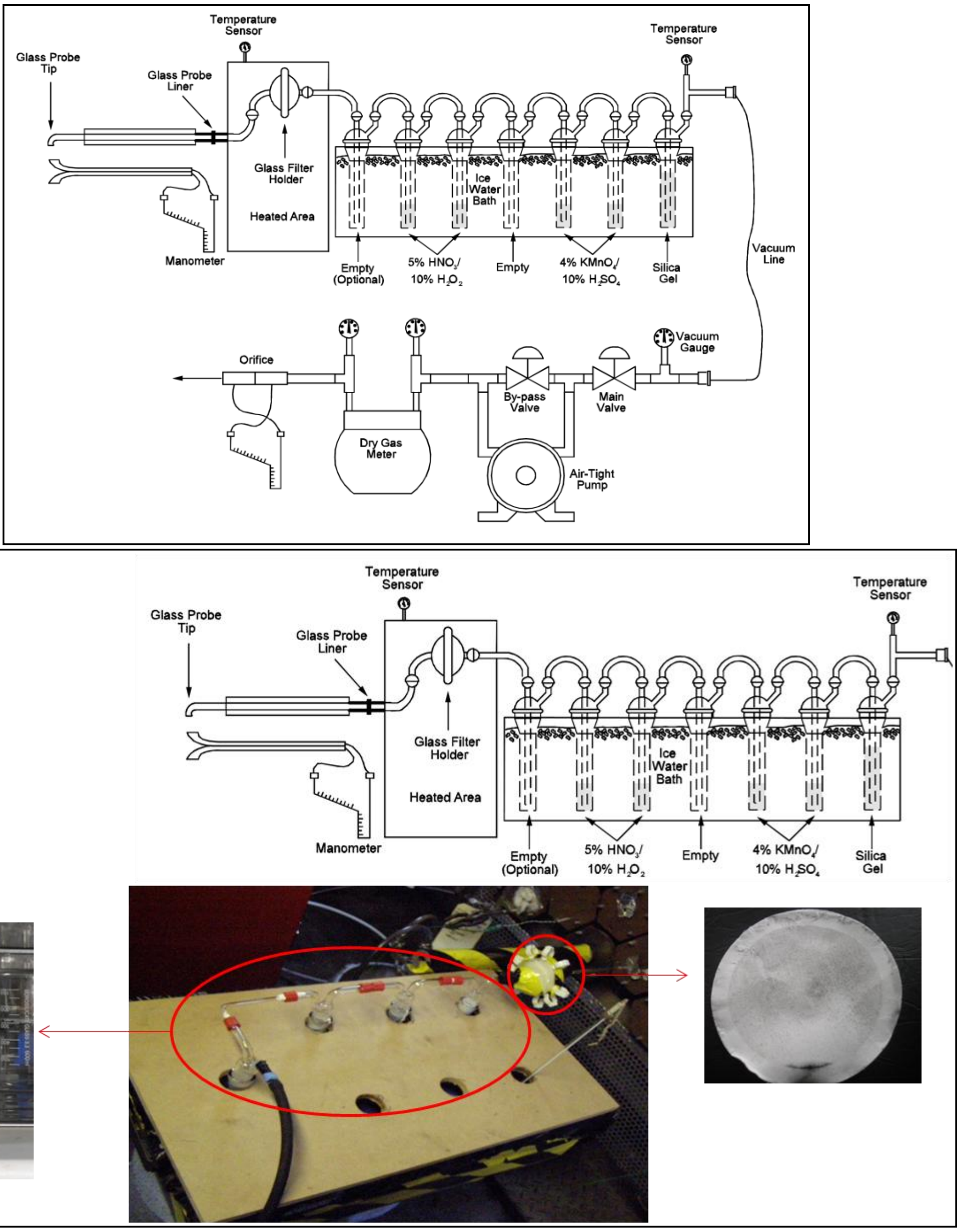


Figure 37. Schematic representation of the sampling train used for trace metals sampling

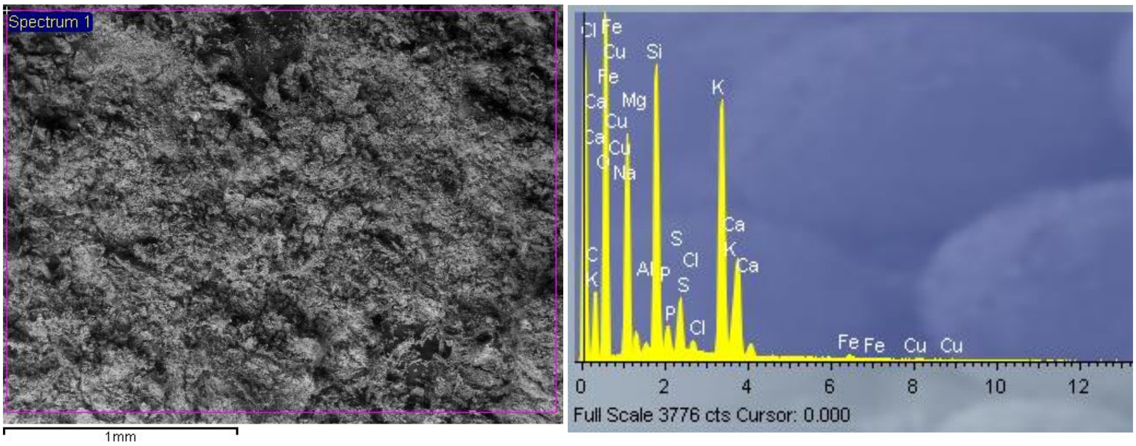
As represented in Figure 37, the system consists of a train of bubblers connected to a pump which withdraws the sampled gas. The gas passes through a glass fiber filter for the collection of the fly ash. The liquid contained in the bubblers dissolves the metals contained in the flue gas. The ash can then be analysed by SEM-EDX, whereas the liquid is analysed by ICP-MS.

APPENDIX B: SEM/EDX ANALYSIS

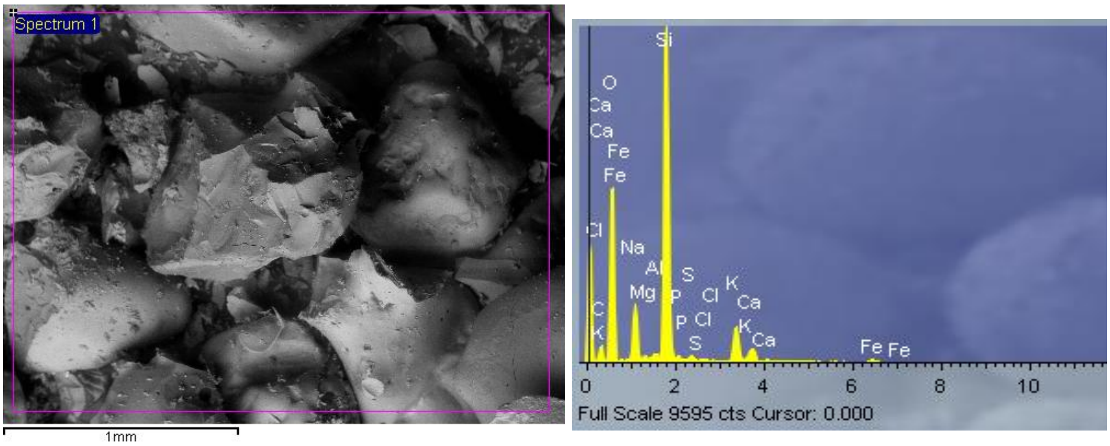
This section reports the images taken by the microscope and the point where the analysis was done and the EDX spectra obtained.

B.1. Combustion ash

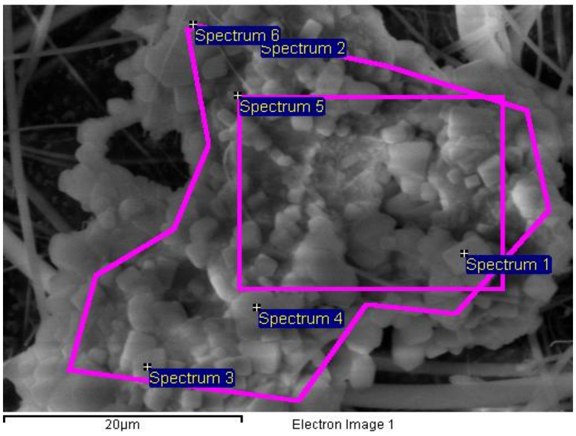
Miscanthus bottom ash:

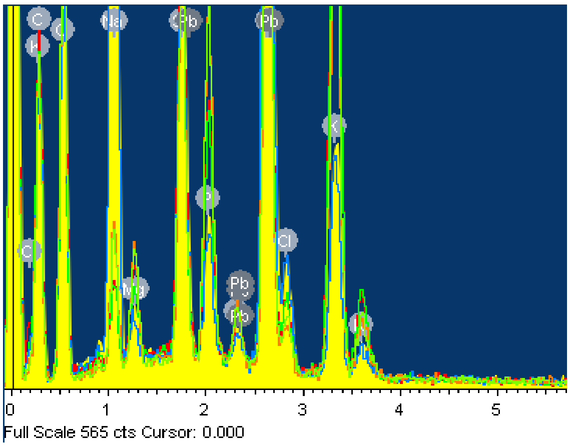


Miscanthus slag:

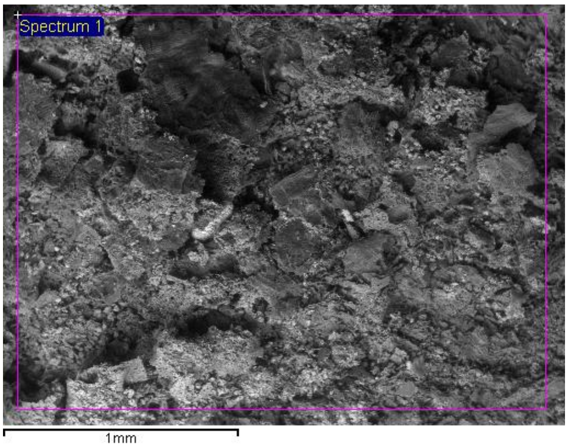


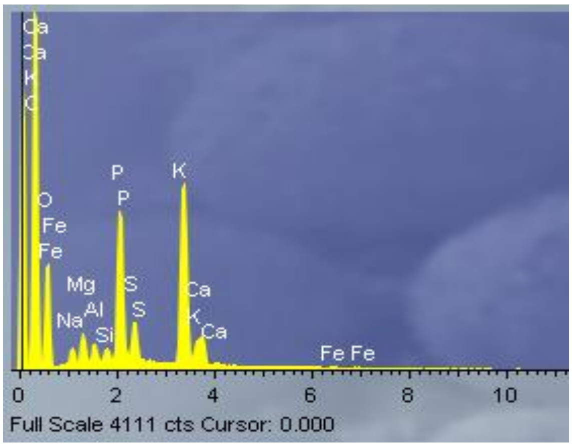
Miscanthus fly ash:



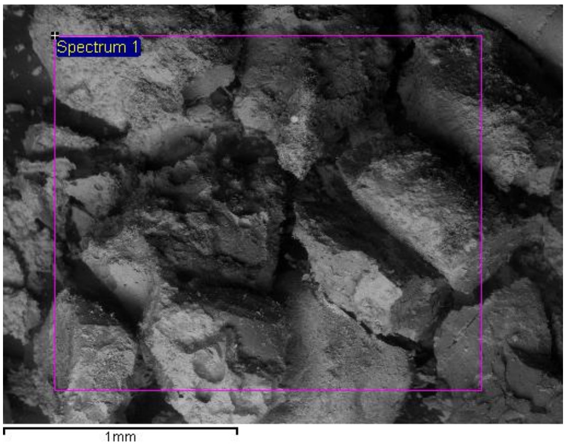


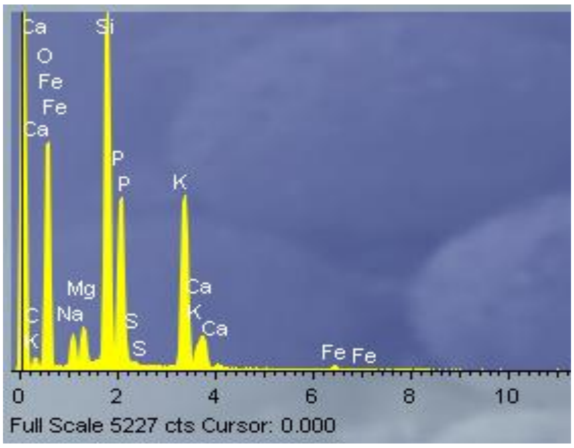
DDGS bottom ash



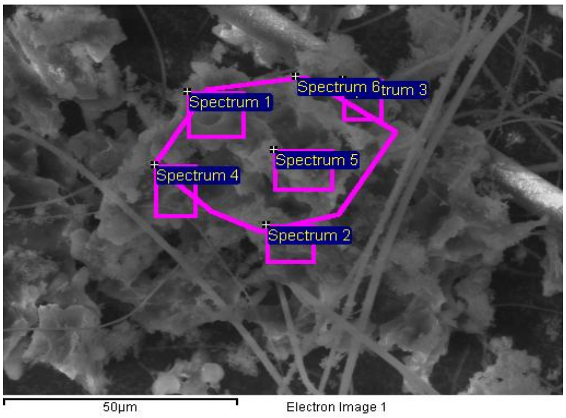


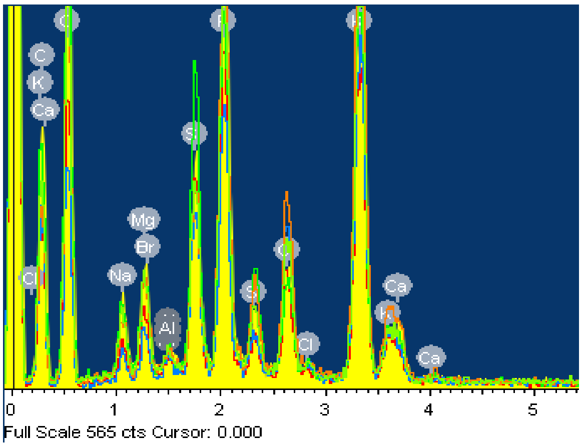
DDGS slag





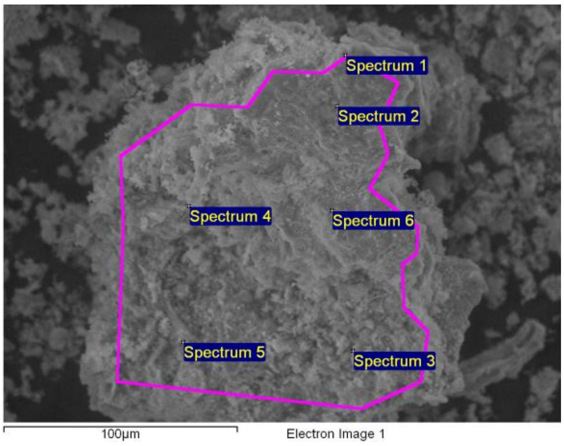
DDGS fly ash:

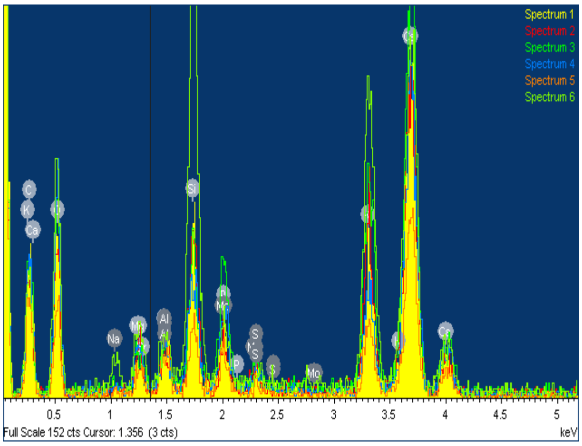




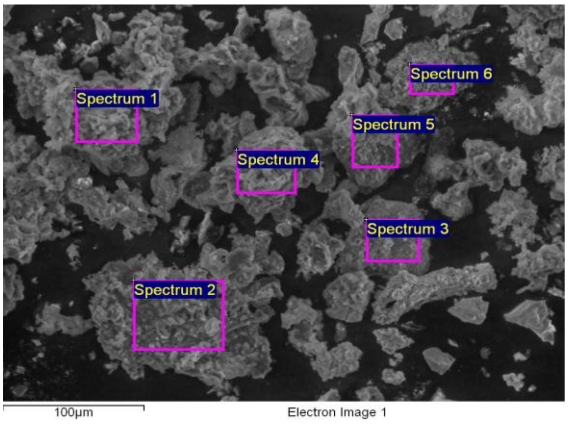
B.2. Gasification ash

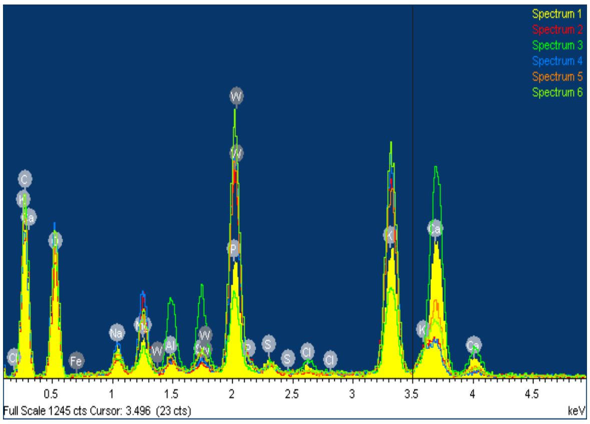
Miscanthus bottom ash:



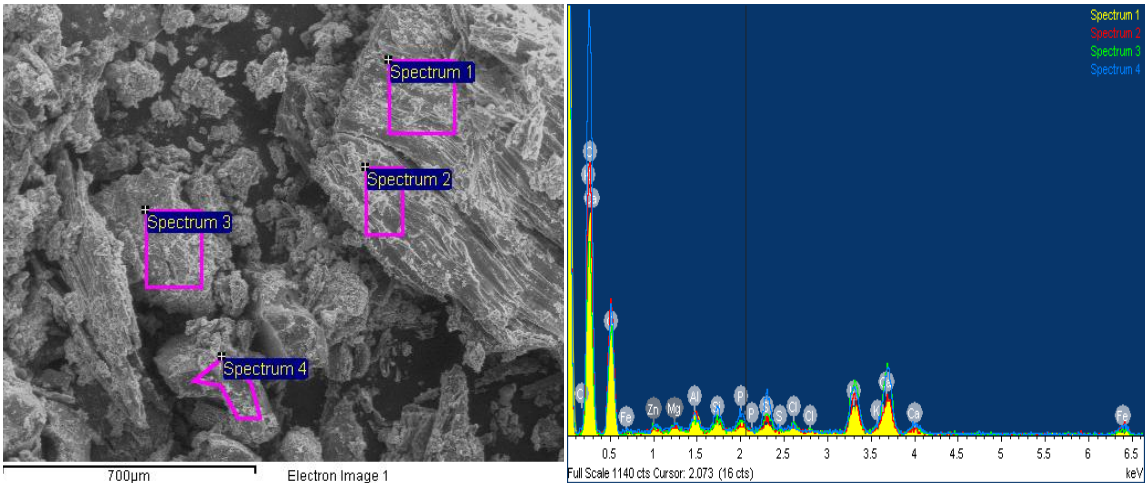


DDGS bottom ash:

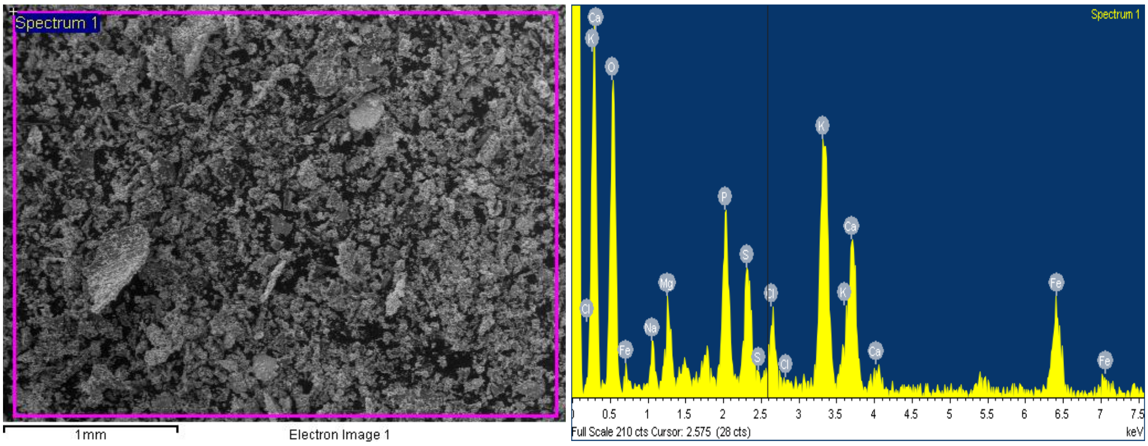




Miscanthus fly ash:



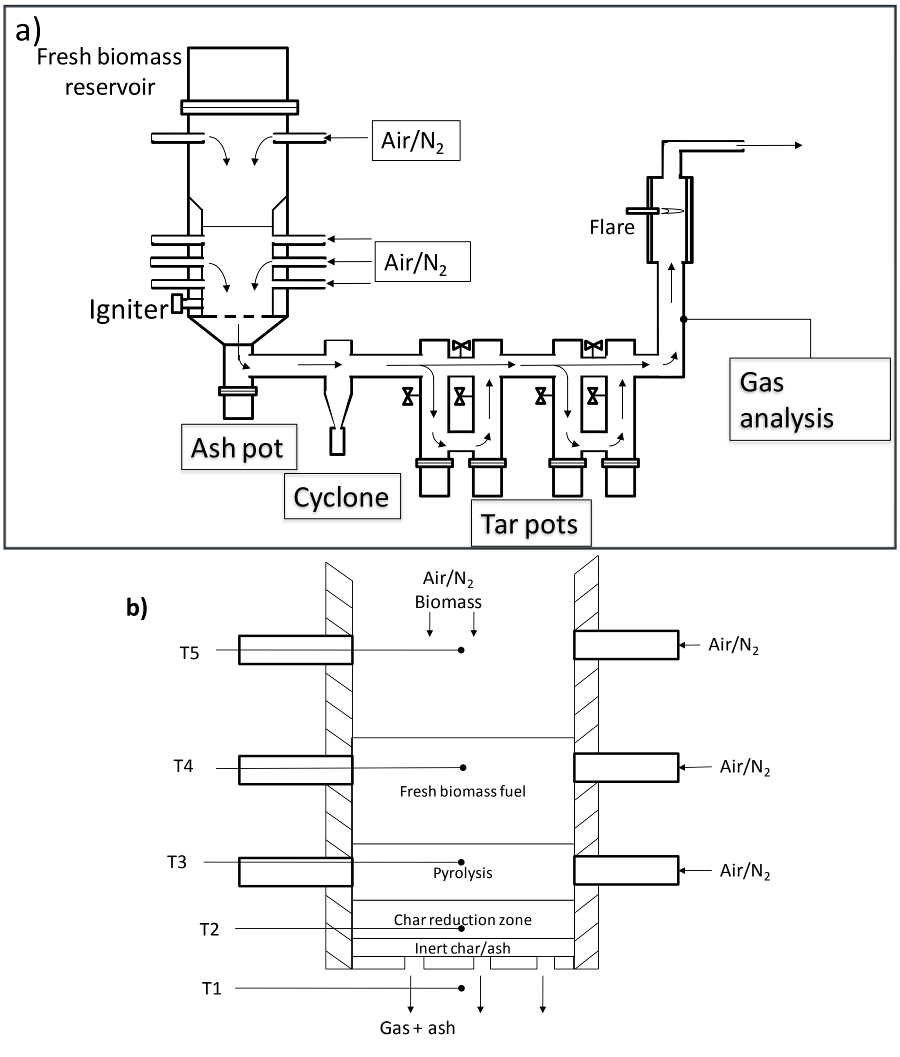
DDGS fly ash:



APPENDIX C: DOWNDRAFT GASIFICATION RIG DESCRIPTION

C.1. Rig description

A schematic representation of the combustion rig is showed in Figure 38a, whereas Figure **38**b is a cross section of the bed representing the reacting layers of gasifying biomass during the process. As it can be seen in Figure 38b, the rig is equipped with 4 nozzles from which either air or N_2 can be fed. Hence, this system allowed feed air or N_2 at different bed height or from above the bed. By using this system, the both temperature and equivalence ratio can be controlled, however in the present work only air was used at all times.



T5=20 ºC, T4=20 ºC, T3=850 ºC, T2=800 ºC, T1=700 ºC

Figure 38. a) Schematic representation of the pilot-scale downdraft gasifier.
b) Cross section of the fixed bed.

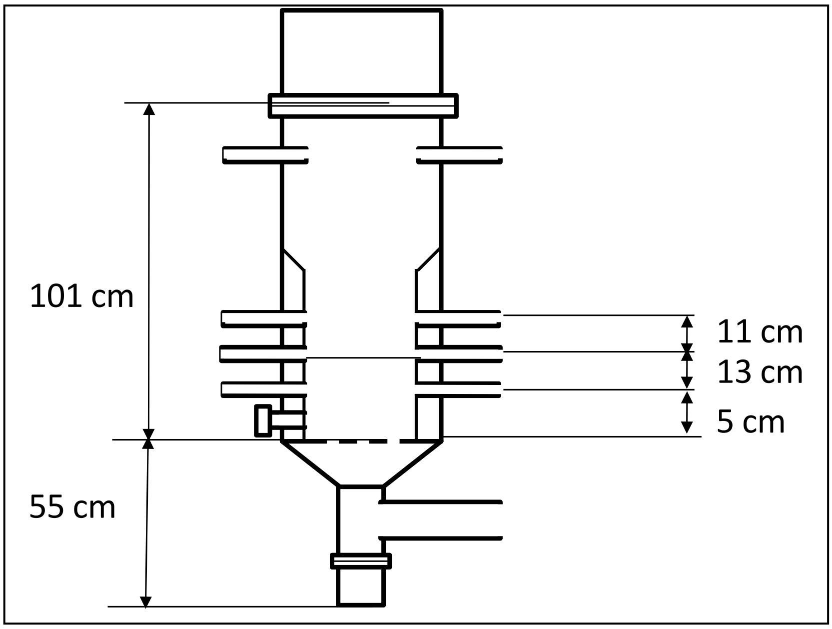


Figure 39. Dimensions of the downdraft gasifier

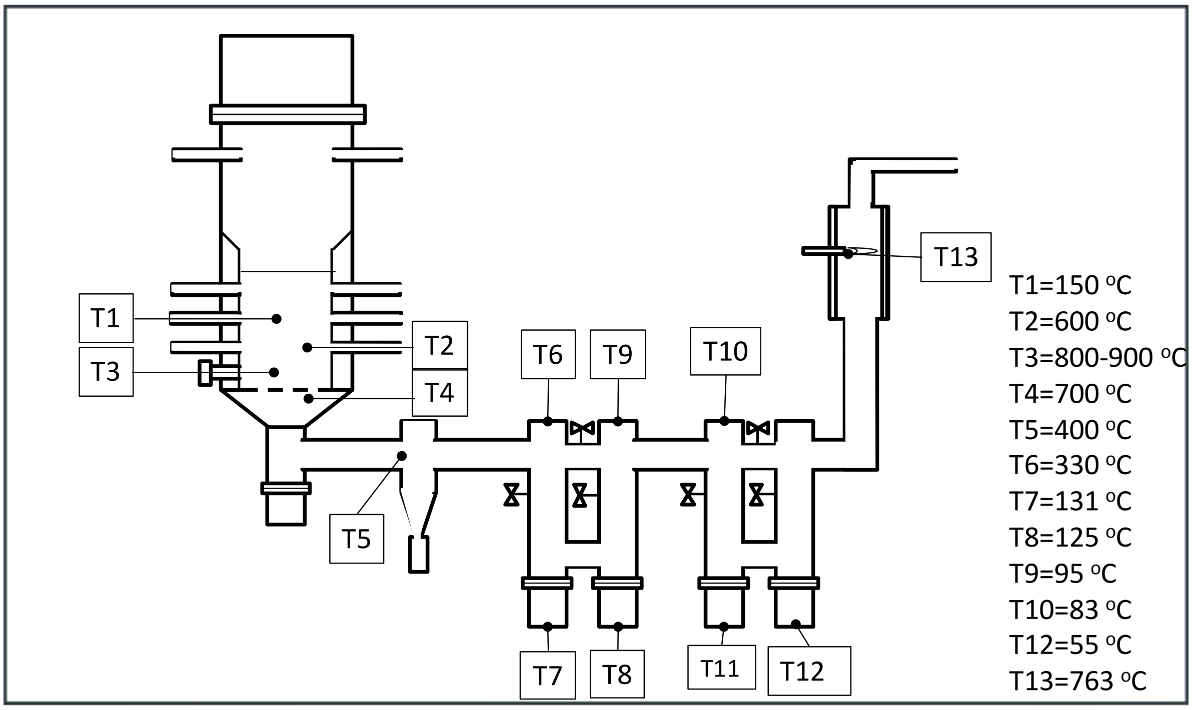
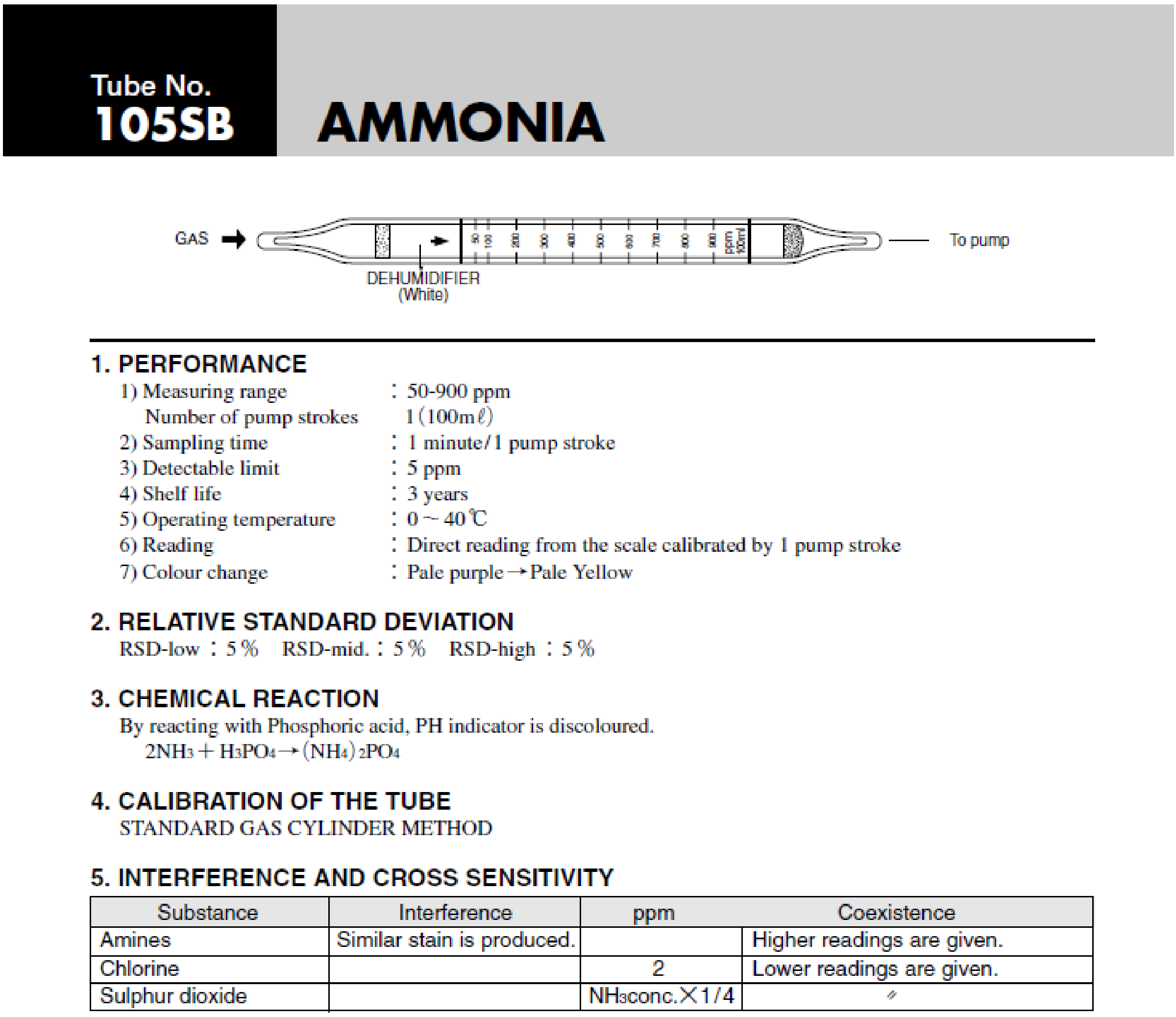


Figure 40. Averaged temperature of the thermocouples in the downdraft gasifier during a gasification test

C.3. Nitrogen species analysis

The concentration of NH_3 and NO_x was measured using Dräger tubes (ammonia 5/b 81 01 941 5 to 100 ppm, ammonia 0.5% to 10 Vol%, nitrous Fumes 2/a 5 to 100 ppm, nitrous fumes 20/a to 500 ppm, nitrous fumes 50/a 250 to 2000 ppm). The datasheets of the tubes used are reported below.



Tube No.
105SB

AMMONIA

1. PERFORMANCE

1) Measuring range : 50-900 ppm
Number of pump strokes 1 (100mℓ)
2) Sampling time : 1 minute/1 pump stroke
3) Detectable limit : 5 ppm
4) Shelf life : 3 years
5) Operating temperature : 0 ~ 40℃
6) Reading : Direct reading from the scale calibrated by 1 pump stroke
7) Colour change : Pale purple → Pale Yellow

2. RELATIVE STANDARD DEVIATION

RSD-low : 5 % RSD-mid. : 5 % RSD-high : 5 %

3. CHEMICAL REACTION

By reacting with Phosphoric acid, PH indicator is discoloured.

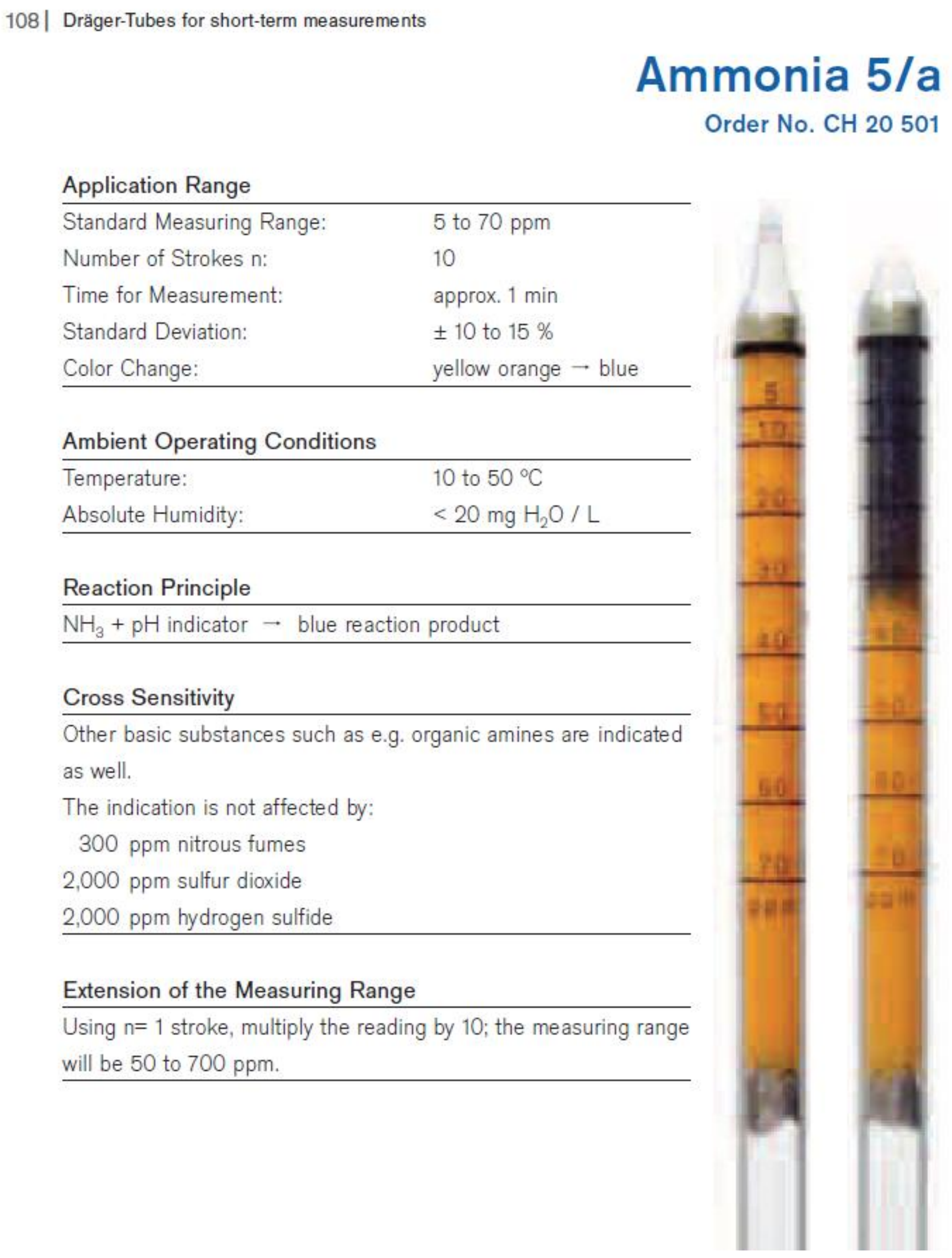
$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2PO_4$

4. CALIBRATION OF THE TUBE

STANDARD GAS CYLINDER METHOD

5. INTERFERENCE AND CROSS SENSITIVITY

Substance	Interference	ppm	Coexistence
Amines	Similar stain is produced.		Higher readings are given.
Chlorine		2	Lower readings are given.
Sulphur dioxide		NH_3conc.×1/4	〃



108 | Dräger-Tubes for short-term measurements

Ammonia 5/a

Order No. CH 20 501

Application Range

Standard Measuring Range:	5 to 70 ppm
Number of Strokes n:	10
Time for Measurement:	approx. 1 min
Standard Deviation:	± 10 to 15 %
Color Change:	yellow orange → blue

Ambient Operating Conditions

Temperature:	10 to 50 °C
Absolute Humidity:	< 20 mg H_2O / L

Reaction Principle

NH_3 + pH indicator → blue reaction product

Cross Sensitivity

Other basic substances such as e.g. organic amines are indicated as well.

The indication is not affected by:

300 ppm nitrous fumes
2,000 ppm sulfur dioxide
2,000 ppm hydrogen sulfide

Extension of the Measuring Range

Using n= 1 stroke, multiply the reading by 10; the measuring range will be 50 to 700 ppm.

Cyanide 2/a

Order No. 67 28 791

Application Range

Standard Measuring Range:	2 to 15 mg/m³
Number of Strokes n:	10
Time for Measurement:	approx. 2.5 min
Standard Deviation:	± 20 to 30 %
Color Change:	yellow → red

Ambient Operating Conditions

Temperature:	0 to 30 °C
Absolute Humidity:	< 20 mg H_2O / L

Reaction Principle

a) $2\ KCN + H_2SO_4 \rightarrow 2\ HCN + K_2SO_4$

b) $2\ HCN + HgCl_2 \rightarrow 2\ HCl + Hg(CN)_2$

c) HCl + methyl red → red reaction product

Cross Sensitivity

Free hydrogen cyanide is indicated already before breaking the ampoule.

Acid gases are indicated with different sensitivities.

A certain portion of the cyanide can have reacted with the CO_2 in the air through hydrolysis.

It is impossible to measure cyanide in the presence of phosphine.

Additional Information

After carrying out the 10 strokes the reagent ampoule must be broken, the liquid transferred onto the white separating layer and carefully drawn through with two strokes in cyanide free air using the pump. The indicating layer must not become moist.

Appendix D. Definitions and calculations

This section gives the formulas for the calculations done.

1. Calculation of the concentration of a gas component assuming 6% O_2

To normalise the concentration of a gas component to 6% of oxygen, first the volume (in Nm^3) of flue gas has to be calculated as follows:

$$V_{FG} = \frac{Nm^3\ dry\ FG}{Kg\ fuel\ (daf)} = \frac{100 \cdot X_c V_{mole}}{M_c \cdot CO_2}$$

Where:

X_c is the volume fraction of C in the fuel daf (dry ash free);

V_{mole} is the volume of 1 mole of ideal gas at STP (Standard Temperature and Pressure: 273.15 K, 101325 Pa);

M_c is the molecular weight of C;

CO_2 is the %vol of CO_2 in the gas;

Then, the volume (in Nm^3)of the flue gas at 6% oxygen is calculated as follows:

$$V_{FG(6\%O2)} = \frac{Y_{O2,air} - Y_{O2,dryFG}}{Y_{O2,air} - Y_{O2(6\%O2),dryFG}}$$

Where:

Y_{O2} is the molar fraction of oxygen.

Finally, the concentration (in mg/Nm^3) of the gas component is calculated as follows:

$$C_{i(6\%O2)} = C_i \frac{V_{FG}}{V_{FG(6\%O2)}}$$

Where:

Ci is the concentration of the gas component.

2. Calculation of gasification gas yield (in Nm³/kg):

$$Gas\ yield = \frac{Gas\ volumetric\ flow\ (Nm^3/h)}{Fuel\ mass\ flow\ (kg/h)}$$

3. Calculation of gasification gas heating values:

$$HHV_{Gas} = HHV_{H2} \cdot Y_{H2} + HHV_{CO} \cdot Y_{H2} + HHV_{CH4}$$

$$LHV_{Gas} = LHV_{H2} \cdot Y_{H2} + LHV_{CO} \cdot Y_{H2} + LHV_{CH4}$$

Where:

LHV = low calorific value

HHV = high calorific value

4. Calculation of the cold gas efficiency:

$$Cold\ gas\ efficiency = \frac{Gas\ yield \cdot LHV_{Gas}}{LHV_{Fuel}}$$

5. Calculation of the carbon conversion:

$$Carbon\ conversion = \frac{\text{molar flow}_{CO2} + \text{molar flow}_{CO} + \text{molar flow}_{CH4}}{molar\ flow_C}$$

Where the molar flow is in kmol/h.