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SUMMARY

CONCLUSIONS
1. INTRODUCTION

In this document, a short description of the current state of knowledge on the characteristics of the mineral matter and ash materials associated with biomass materials and the behaviour of these materials in combustion and co-combustion, gasification and pyrolysis systems at all relevant scales of operation is presented. The experience, to date, of biomass utilisation at domestic, industrial and utility scale is predominantly of combustion systems, and the great majority of the relevant technical literature is with the ash-related issues associated with combustion and co-combustion processes. This is reflected in the contents of the report. The majority of the report is concerned with the issues associated with combustion systems, and the behaviour of biomass mineral materials in gasification and pyrolysis systems is described in Sections 8 and 9.

A wide variety of different solid and liquid biomass materials, and biomass materials as components of mixed wastes, are combusted in a very wide range of combustion devices, for heating and power generation purposes. The general types of installations can be listed under the following broad categories, depending on the scale of operation:

- The very small stoves, fires and boilers employed for domestic cooking and heating,
- The small and medium scale boilers employed for commercial, process and district heat supply,
- The small and medium scale boilers employed for combined heat and power, or power-only applications,
- The co-firing of biomass materials in very large quantities with coal in large industrial and utility boilers.

As is the case with practically all solid fuels, biomass materials contain non-combustible constituents, and the nature and behaviour of these constituents have a significant bearing on the design, operation and performance of the combustor and the boiler.

For the gasification of biomass, the key interest has been at relatively small scale, up to around 100 MWth, and with the co-utilisation of biomass materials in small quantities in large coal gasifiers. It should be noted, however, that a relatively small number of these plants have been in commercial operation over the past 20 years or so, and the industrial experience with biomass gasification systems is limited. There is no significant industrial experience with biomass pyrolysis systems, which are currently in the development and demonstration phase. For both gasification and pyrolysis processes, the range of biomass materials and of ash qualities for which there is plant experience is strictly limited.

The principal types of biomass and biomass-based waste materials utilised domestically and commercially in significant quantities are listed in Table 1. The majority are waste and residue materials from agricultural, forestry and other activities. In most cases, these materials were traditionally left in situ or sent for disposal to landfill. In recent years, however, their value as a renewable fuel has been increasingly recognised, and they are being collected, processed, if necessary,
and delivered as fuels for utilisation in combustion and other thermal processing plants. There has been a significant increase in the commercial utilisation of these materials for heat and power production, particularly in Europe and North America, but also elsewhere in the world. This can be for purely commercial reasons, or in response to the commitment to reduce greenhouse gas emissions, and the financial and other instruments that have been put in place in many countries to encourage renewable energy production and utilisation.

Compositional and other relevant data for a wide range of biomass, biomass ash and other relevant materials are available in a number of excellent databases of biomass properties, viz:

- Phyllis, named for the Greek goddess of trees and wisdom, which has been compiled by ECN in the Netherlands, www.ecn.nl/phyllis.
- Biobank, which is compiled by Bios Bioenergiesysteme GmbH, in Austria, is available on the IEA Bioenergy Task 32: Biomass Combustion and Co-firing website, www.ieabcc.nl
- BIOBIB, which is a database of biomass properties compiled and maintained by the Technical University of Vienna, Austria, available on www.vt.tuwien.ac.at.
- The USDOE, has also compiled a biomass feedstock composition and property database www.eere.energy.gov/biomass/feedstock_databases.html.

All of the biomass and biomass-based waste materials are characterised by having relatively low calorific values, high volatile matter contents and low bulk densities, compared to most other industrial solid fuels. Most of the biomass materials, in raw harvested form, also have very variable moisture contents and in some cases, it can be advantageous to dry and/or densify the biomass, prior to transportation handling and storage as a fuel.

Most biomass materials have significant inorganic matter contents and many of the problems encountered with the combustion of biomass materials, or the co-combustion of biomass with coal, are associated with the nature and the behaviour of the biomass ash components and the other inorganic constituents.

The key technical ash-related problems encountered by operators of biomass combustors and boilers have been associated with:

- The formation of fused or partly-fused agglomerates and slag deposits at high temperatures within furnaces and stoves,
- The formation of bonded ash deposits and accumulations of ash materials at lower temperatures on surfaces in the convective sections of boilers,
- The accelerated metal wastage of furnace and boiler components due to gas-side corrosion under ash deposits, and due to ash particle impact erosion or ash abrasion of boiler components and other equipment,
- The formation and emission of sub-micron aerosols and fumes,
- Biomass ash impacts on the performance of flue gas cleaning equipment, and
The handling and the utilisation/disposal of ash residues from biomass combustion plants, and of the mixed ash residues from the co-firing of biomass in coal-fired boilers.

For biomass gasification and pyrolysis systems, the ash-related issues are largely similar to those for combustion, i.e. the accumulation of ash material within the reactor and associated equipment, the impact of ash on the integrity of the process plant and heat exchangers and the ash-related environmental impact of the process.

In this document, a short description of the nature of the inorganic constituents of biomass materials, and the behaviour of these materials in combustion, gasification and pyrolysis processes, is presented. There has been a good deal of technical research and development work on the behaviour of biomass ashes and biomass-coal ash mixtures over the past 10-20 years, both at laboratory scale and in test rigs of various types. There is also increasing operating experience of the processing and co-processing of biomass materials, and of the behaviour of biomass ashes and biomass-coal ash mixtures, in thermal processing equipment and heat exchangers. An attempt is made in this document to present a short summary of the key findings of the relevant technical development work and of the operating experience.

2. BIOMASS ASH CHARACTERISTICS

2.1 Introduction

There is an extensive technical literature on the nature and behaviour of the inorganic materials present in all domestic, commercial and industrial solid fuels, going back more than a century. This work has been concerned principally with the characteristics and behaviour of the ash residues of the thermal processing of coals, lignites and peats, which have been most widely utilised as industrial solid fuels.

The more recent research on biomass ash materials has benefited from this fairly extensive body of work, principally from some of the mineral matter and ash characterisation techniques, from the use of the combustion and other test facilities, developed over the years for the study of fossil fuels, and from the detailed understanding of the reactions undergone by the inorganic constituents of solid fuels in high temperature processes.

In very general terms, the inorganic materials in most solid fuels, including biomass, can be divided into two broad fractions, viz:

- The **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. These organic functional groups can provide suitable sites for the inorganic species to be associated chemically in the form of cations or chelates. Biomass materials tend to be relatively rich in oxygen-containing functional groups, and a significant fraction of the inorganic material in some of the lower ash biomass fuels is commonly in this form. It is also possible for inorganic species to be present in very fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel.
• The **extraneous inorganic material**, which has been added to the fuel through geological processes, or during harvesting, handling and processing of the fuel. Biomass fuels, for instance, are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage.

A listing of the major inorganic species found in the higher plants, and hence in the inherent inorganic material in most biomass materials, is presented in Table 2 (Korbee et al. 2001, Marschner, 1997). The data in this table provide a roughly quantitative overview of the major inorganic element speciation in three useful categories, viz:

• Water soluble, i.e. in free ionic form,

• Organically associated, and

• Precipitated as relatively pure compounds, in crystalline or amorphous forms.

The data in this table indicate clearly that in the inherent inorganic material in biomass materials, the alkali metals, sulphur, phosphorus and chlorine tend to be present largely in soluble form, as simple inorganic salts. Silicon is present predominantly as silica, in precipitated form. The alkaline earth metals are more complex and can be present in a number of forms.

The extraneous inorganic material can also be present in many forms. In most cases, however, it takes the form of contamination with sand, soil or other mineral materials, tramp metal components, etc.

2.2 **Laboratory characterisation techniques for biomass ashes**

The most commonly applied technique for the determination of the ash content and ash composition of coals and other solid fuels in the laboratory involve heating the fuel slowly in air to constant mass at a temperature of 815°C, and subjecting the resultant ash residue to chemical elemental analysis. The ash residue is normally weighed to provide an estimate of the ash content of the fuel, and then analysed for the ten major elements present in coal ashes, i.e. Si, Al, Fe, Ca, Mg, Ti, Na, K, P and S. The elemental concentrations are conventionally expressed as oxides, in their highest oxidation states. The analysis of the laboratory-prepared ash for its trace element content is also fairly common practice. This is a perfectly reasonable and practical approach for most coals, and many other solid fuels, and has been applied for biomass ash analysis.

For many biomass materials, however, a significant portion of the inorganic material is volatile at the conventional ashing temperatures for coal, and an ashing temperature of 550°C has been adopted as standard for ash content determination, to avoid underestimation of the ash content of the fuel, due to loss of the volatile inorganic components (CEN/TS 14775:2004)

For elemental analysis of biomass materials, wet chemical digestion of the raw biomass rather than of the laboratory-prepared ash is preferred, prior to elemental analysis using ICP-AES techniques, again principally because of concerns about the potential for the loss of volatile inorganic components during the ashing process (CEN/TS 15290:2006).
Ash elemental analysis data for a number of clean biomass materials which are important as fuels for combustion processes, at domestic and industrial scale are given in Table 3. It is clear from the data presented in this table that the ash contents of the majority of the biomass materials listed, with the exception of the poultry litter, are around 5-7% on a dry basis, or lower.

The clean wood materials, either in chip or in pellet form, are utilised as a fuel for a wide range of thermal processing equipment at domestic, commercial/industrial and utility scale. They have relatively low ash contents, less than 2%, and this is largely dependent on the level of bark in the fuel. Clean white wood materials have very low ash contents, generally less than 1%.

The straw and grass materials, and the solid residues from the vegetable oil producing industries, are utilised in substantial quantities as fuels for industrial scale boilers and have ash contents in the 4-7% range. The poultry litter is utilised in significant quantities as an industrial boiler fuel in Britain and there are a number of new projects particularly in Northern Europe and North America. It has been included as an example of a high ash fuel, with particularly difficult ash behaviour.

It is also clear from the data presented in Table 3 that all of the biomass ashes tend to be rich in a fairly similar suite of inorganic species, i.e. the compounds of calcium, potassium, silicon, phosphorus and magnesium. The clean wood materials are particularly rich in Ca, Si and K. In some cases, particularly with waste wood materials, the ashes can have significant levels of some of the heavy metals, particularly lead and zinc. The ash chemistries of the other biomass materials vary significantly but all are dominated by Ca, K, Si or P compounds.

One of the key properties of fuel ash materials is their behaviour at elevated temperatures and, in particular, their fusion behaviour. In very general terms, three types of biomass ash system have been described by Bryers (1996), in terms of their general ash chemical composition and their fusion behaviour, viz:

- High silica/high potassium/low calcium ashes, with low fusion temperatures, including many agricultural residues,
- Low silica/low potassium/high calcium ashes, with high fusion temperatures, including most woody materials, and
- High calcium/high phosphorus ashes, with low fusion temperatures, including most manures, poultry litters and animal wastes.

The relevance of the ash fusion temperatures to the behaviour of the biomass fuels depends, to some extent on the type of thermal processor. For example, the sintering and fusion of the ash particles on the grates in stoker-fired combustors, and the sintering, fusion and agglomeration of the ash particles in fluidised bed-fired combustors and gasifiers, are important processes.

The fusion behaviour of the ashes is also an important factor in determining the propensities of the fuels to form fused or partly-fused slag deposits on the reactor wall surfaces in all thermal processors systems and, in some circumstances, may have an influence on the nature of the fouling deposits that can occur on the heat exchange and other surfaces.
The fusion behaviour of most fuel ashes is a fairly complex phenomenon, which is best described in terms of a melting curve, where the percentage of the ash, by mass, which is fused is plotted against the temperature. An example of such a curve is reproduced in Figure 1. In this example, the melting curves of a model biomass ash system, comprising a mixture of alkali metal salts, have been calculated using a procedure, which has been developed at Abo Akademi in Finland, and is based on experimental phase diagrams and thermodynamic data, (see, for instance Backman et al, 2005, and the references given therein).

On the ash melting curves, two key temperatures are commonly identified, and can be used to describe the behaviour of the ashes, viz:

- The $T_{15}$ temperature, at which 15% of the ash material by mass is molten. This is considered to be the temperature at which the surfaces of the ash particles or slag deposits begin to become sticky and receptive to the adhesion of incoming solid particles, and
- The $T_{70}$, temperature at which 70% of the ash material by mass is molten. This is the temperature at which the outer surface of an ash deposit on a vertical surface will begin to flow.

The standard Ash Fusion Test, which has been applied for the characterisation of the fusion behaviour of coal ashes for many decades, is based on the determination of three or four key temperatures on the melting curve. This procedure has been developed specifically for alumino-silicate, coal ash systems, which have very complex melting behaviour, commonly over a fairly wide range of temperatures from around 1000-1500ºC, and which tend to produce relatively viscous melts. The results of the application of this test procedure to biomass ashes, most of which are not alumino-silicate systems, and many of which melt at temperatures less than 1000ºC, should be treated with great caution.

The use of chemical fractionation techniques, which were developed originally for the characterisation of the inorganic components of coals, has also been applied to the characterisation of biomass materials. The procedure normally involves the treatment of a small sample of the fuel by a standardised leaching process, with a series of progressively more severe chemical reagents, under standardised test conditions. The leaching reagents employed for this purpose are commonly:

Water $\rightarrow$ ammonium acetate solution $\rightarrow$ hydrochloric acid solution

Four fractions are normally obtained, viz:

- The water-leachable components, principally the alkali metal salts, sulphur and chlorine compounds,
- The acetate-leachable components, which are generally associated with the organic fraction of the fuel as cations and chelates,
- The acid-leachable components, generally carbonates and sulphates, and
- The solid residue, principally silica, silicates and other mineral species insoluble in mineral acids.
It is generally considered that the water and acetate-leachable elements are those that are more readily released into the vapour phase, and form the very finest aerosol fraction of the ash generated from the biomass at elevated temperatures. The acid soluble and residue fractions are not considered to be released into the vapour phase during most thermal processes, and tend to report to the coarser fractions of the ash.

The results of chemical fractionation analysis of a number of fuels, including wood chips, forestry residues, bark wheat straw, peat and bituminous coal are presented in Figure 2. These results are interesting in that they illustrate the differences in the leaching behaviour of biomass materials and of a number of more conventional fuels, i.e. bituminous coal and peat. The results can be summarised as follows:

- For the bituminous coal, very little of the inorganic material in the fuel, and generally only the sodium chloride, was found in the water and acetate soluble fractions.
- For the peat, there was a higher level of water and acetate soluble material, with some of the calcium in the acetate soluble category,
- The biomass materials, in general, had significantly higher levels of water and acetate soluble material, with the majority of the potassium and chloride, and some of the calcium and magnesium, being in this category. In the case of the wheat straw and the forest residue 1, a significant part of the silica was water/acetate soluble.

For the purposes of making simple comparisons between different fuels, a simple summary of the results of the chemical fractionation testwork can be prepared, and an example from the same source is presented in Figure 3. In this case, the distribution of the ash forming material in the fuels, expressed in g kg\(^{-1}\), dry fuel basis, between the water/acetate soluble and the HCl/insoluble residue fractions, are presented. The differences between the fuels are clear. The peat and coal have the higher ash contents, but only a very small proportion of the mineral material is considered to contribute to formation of the fine ash/aerosol fraction. In the case of the biomass materials, the total mineral matter contents are lower, but a much higher proportion of the mineral material is considered to contribute to the formation of the fine ash/aerosol fraction. Clearly, the chemical fractionation techniques can provide useful information about the nature and potential behaviour of ashes in combustion and other thermal processing plants. It is also clear, however, that the procedure has a number of important limitations and the results should be interpreted very carefully.

Conventional mineralogical and microscopic analysis techniques are increasingly employed for the characterisation of mineral materials in fuels, and of fuel ashes and deposits. X-ray diffraction is commonly used for identification of the major crystalline phases in these materials. Optical microscopic examination of polished sections is widely used, and scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) is a particularly power analytical technique for the examination of the microstructure and chemistry of ashes and deposits. These techniques are most commonly employed for fundamental research on the characteristics of ashes and deposits, and can be very useful for investigative work in industrial plants, where appropriate samples of the ashes and deposits are available for examination.
A number of **Slagging and Fouling Indices** are available for the assessment of the propensity of fuel ashes to form deposits, principally in combustors or furnaces. A detailed description of the technical basis and use of these indices is presented in Raask (1985). These are based either on the fuel ash content and the ash chemical composition, or on the results of laboratory tests that can be performed on small samples of the fuel. In the main, these indices have been developed for the assessment of coals, and are applied, with appropriate modifications, to other solid fuels, including wastes and biomass materials, and to the mixed ashes produced by the co-processing of biomass materials with coal.

The majority of the coal **Slagging Indices** are concerned with the fusion behaviour of the ash, and the traditional indices are based either on the results of Ash Fusion Test or on the chemical composition of the ash, commonly the ratio of the acidic metal oxides, \((\text{SiO}_2 \text{ and Al}_2\text{O}_3)\) to the basic oxides \((\text{Fe}_2\text{O}_3, \text{CaO}, \text{MgO}, \text{Na}_2\text{O} \text{ and K}_2\text{O})\). These indices provide a general assessment of the ash fusion temperatures, which is then employed to rank the ash in terms of its propensity to form fused slag deposits. Despite the technical limitations of both of these approaches, these are still used widely in the industry for fuel specification, reactor and heat exchanger design and plant operational purposes.

A number of more sophisticated approaches to the assessment of the slagging propensity, for instance based on the use of phase diagrams of the appropriate alumino-silicate systems, or the use of mineralogical analysis data derived from characterisation of the fuel using scanning electron microscopes, have been developed, however these have enjoyed only limited use within the industry.

Since the majority of the coal ash slagging indices are based on the assessment of the fusion behaviour of alumino-silicate coal ashes, the application to biomass ash systems, which are chemically very different, can be problematic, and great care should be applied when interpreting the conventional Slagging Index values for biomass.

When considering the potential slagging behaviour of the mixed ashes from the co-processing of biomass with coal, it is clear that, apart from \(\text{SiO}_2\), all of the significant components of most biomass ashes, and principally the alkali and alkaline earth metals, are powerful fluxes for alumino-silicate systems. It is expected, therefore, that the co-processing of biomass will result in a reduction in the fusion temperatures, and hence an increase in the slagging potential. This will, of course, depend on the level of fluxing agents in the coal and on the co-firing ratio. The effect will be more dramatic when biomass is co-processed with coals with high fusion temperature ashes, i.e. the effect of adding fluxing elements to a coal ash with low levels of the fluxing elements is much greater than to a coal with lower ash fusion temperatures and higher levels of fluxing elements.

For the co-processing of biomass at relatively low levels, the mixed ash is still predominantly an alumino-silicate system and the normal coal slagging assessment methods can be applied, with some confidence.

The **Fouling Indices** for coal ashes are, in the main, based on the sodium content of the fuel. The deposition of the sodium compounds by a volatilisation/condensation mechanism is considered to be the principal driving force for convective pass fouling in coal plant. The potassium in coal ash is principally present as a constituent of the clay minerals, and is not considered to be available for release by volatilisation in the flame.
For most biomass materials, potassium tends to be the dominant alkali metal, and is generally in a form that is available for release by volatilisation. The fouling indices for biomass materials tend, therefore, to be based on the total alkali content of the fuel (Miles et al. 1995).

Overall, therefore, a suite of ash characterisation techniques and ranking methods are available for biomass materials. The majority of these techniques were originally developed and applied for the characterisation of coals and other conventional solid fuels and their behaviour in combustion systems. Because they are already familiar within the industry, many of these methods have been adapted for use with biomass materials, and for gasification and pyrolysis systems as well as combustors. As always, the application of methodologies to materials and processes for which they were not designed should be done with caution.

3. THE BEHAVIOUR OF THE INORGANIC CONSTITUENTS OF BIOMASS MATERIALS AT ELEVATED TEMPERATURES IN COMBUSTION SYSTEMS

A general schematic illustration of the processes undergone by the inorganic fraction of solid fuel particles at elevated temperatures in combustion systems is presented in Figure 4 (Baxter 1993). As stated above, the inorganic species are generally distributed within the fuel particles in three forms, viz:

- Atomically dispersed within the fuel organic matter,
- In grains within the fuel particles, and
- Extraneous to the fuel particles.

As described in Figure 4, there are biomass inorganic constituents that are volatile at combustion temperatures, particularly some of the alkali metal (K and Na) compounds, phosphorus compounds and some of the heavy metals species, and these can be released into the combustion gases in the form of a condensable vapour. Other inorganic species, principally silica and the alkaline earth compounds, can be released from the burning fuel particle as very finely divided, sub-micron particles. The balance of the inorganic fraction will undergo a number of chemical and physical transformations, depending on the chemical composition, and the combustion temperature and residence time, to form the larger ash particles.

The key mineral transformations and chemical reactions that may occur at elevated temperatures include:

- 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 alumino-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,
The coalescence of intra-particle mineral particles.

The specific details of the ‘release mechanisms’ and the ‘residual ash formation processes’ depend largely on the type of combustor, i.e. on the flame temperatures and the residence times at elevated temperatures.

For most solid fuels, there are three general types of combustion plant, that are industrially important, viz:

• Grate combustors, which are generally employed for the domestic and the small and medium sized industrial and commercial applications,

• Fluidised bed combustors, of the bubbling bed and circulating types, which are commonly employed for the medium to large industrial, commercial and utility applications, and

• Pulverised fuel combustors, which are employed, in the main, for large industrial and utility applications. These are rarely used for 100% biomass firing, and the principal interest, in the current context, is in the co-firing of biomass materials in large coal-fired boilers.

The type of combustion equipment is relevant to the ash behaviour, since the combustion conditions are significantly different. The majority of the laboratory and industrial scale experimental work on these processes have recognised this, and these have generally been aimed specifically at one or the other of these types of combustor.

3.1 Grate-fired combustors

In grate-fired systems, the fuel particles are distributed over a moving or static grate to form a fuel bed, with some of the combustion air being supplied from underneath. The normal intention is to retain the majority of the ash on the grate, to be removed either manually or mechanically, to an ash pit, although a significant quantity of the ash will be released from the bed as fly ash particles entrained in the combustion gases or in the form of vapours and fine fumes.

The results of important and recent experimental work on the formation of the aerosols, the coarser fly ash particles and the bed ashes from the fixed bed combustion of biomass materials can be summarised in the reaction schemes presented by Obernberger et al. (2001). This scheme is reproduced in Figure 5. This provides an informative overview of the principal ash and aerosol formation processes occurring with wood fuels, but the key features apply to the fixed bed combustion of most biomass materials. The general description of these processes applies particularly to domestic and small industrial biomass combustors, although the details of the grate design and the air supply arrangements may vary significantly.

The reaction scheme shows the fly ash and aerosol formation processes that are considered to occur on and above the fuel bed. The diagram shows the fuel bed on the grate, with the undergrate windbox. In this case, the fuel is introduced on the right hand side of the diagram, and is dried and then ignited, principally by radiative heat transfer, as it passes along the grate from right to left. The combustible volatile components of the dried fuel are then released, and a flame is generated above the fuel bed. When the fuel has released all of the combustible volatile material, the
flame dies down and the fuel char burns out. Because the biomass materials have very high volatile matter contents, the char combustion zone is relatively short. The bed depth decreases as the fuel is progressively combusted, leaving a bed of the coarser ash particles on the grate. The maximum fuel bed temperatures in fixed bed combustion of biomass materials are generally of the order of 1000-1200ºC, and the overall residence times in the bed are relatively long, of the order of several minutes, depending on the size of the grate and the bed depth.

Depending on the ash composition and the local bed temperatures, a degree of sintering or fusion of the bed ash may occur. This is often exacerbated by imperfect fuel distribution over the grate. If the degree of fusion of the ash is excessive, relatively large ash agglomerates may form, and this can interfere with the distribution of the combustion air through the fuel bed, and may affect burnout of the char and the quality of the gaseous and gas-borne emission levels.

The bed ash comprises partially fused and agglomerated material, and the larger extraneous ash particles. The bed ash composition is usually fairly similar to that of the fuel ash, although it can sometimes be depleted in the more volatile inorganic species, principally potassium.

The coarse fly ash particles are largely small ash particles of aerodynamic diameter up to 1 mm or so, which are entrained with the upward flow of combustion air and gases, and carried upwards through the furnace. The chemical composition of the coarse fly ash is normally similar to that of the bed ash, however there is commonly a degree of condensation of volatile inorganic species, particularly alkali metal sulphates and some heavy metal compounds, on the surfaces of the coarse fly ash particles.

The fine aerosols, which are generally sub-micron, are generated by the condensation from the vapour phase of the volatile inorganic species, i.e. the alkali metal and some heavy metal compounds, principally as chlorides and sulphates, as the flue gases cool in passing through the boiler. Calcium compounds are not considered to be volatile under these conditions, and it was found by Obernberger et al. (2001) that the calcium content of the fine particulate material tended to increase with increasing particle size, and calcium was only present in significant concentration at particle sizes above around 0.8 µm.

Obernberger et al. (2001) investigated three wood fuels in fixed bed combustion systems, viz:

- Chemically untreated wood chips, with a very low ash content (< 0.5%), and an ash composition dominated by K, Ca, and Mg, with very low heavy metals content,
- Wood bark, which had a much higher ash content, 5-7%, and very much higher Ca content, and
- Waste wood materials with an ash content of around 5-6 %, and significant zinc and lead contents.

They found that the aerosols generated by the fixed bed combustion of the bark had much higher calcium content, than those from the clean wood chips, even at low particle sizes. They suggested that this is due to the release of very finely divided CaO particles from the bark during the combustion process.
The aerosols generated by the combustion of the waste wood materials had significant zinc, and to a lesser extent, lead contents. Both lead and zinc are considered to be volatile at the temperatures that apply in the fuel bed of grate-fired systems.

The authors came to the following general conclusions about fly ash and aerosol generation from the fixed bed combustion of woody biomass materials:

- The particle size distributions of the fly ashes are commonly bimodal, with the main coarse fly ash peak in the size range larger than 1µm, with a maximum particle size up to 200-500µm, and the aerosol peak in the submicron range.

- The total fly ash concentration in the flue gases, is dominated by the generation of the coarse fly ashes by bed ash particle entrainment in the combustion gases. This is influenced by the ash content of the fuel, the boiler load and the grate operating parameters.

- The aerosol concentration in the flue gases, and the composition of the aerosol material, are influenced mainly by the chemical composition of the fuel, i.e. by the levels of volatile species, principally the alkali metals and volatile heavy metals, and of the very fine Ca-rich particulate material contained within the fuel.

The work of Obernberger et al. has provided a very good and detailed description of the key processes involved in the generation of ash materials, and particularly of the fly ashes and aerosol particles, from the grate firing of biomass materials.

As stated above, the sintering and fusion of the ash material within the fuel bed in stoker-fired plants can be a significant practical issue. This can occur fairly rapidly, and is often associated with poor fuel distribution, or with slag falls from the upper furnace surfaces. These can cause areas on the fuel bed which are too deep, have poor combustion air distribution and hence tend to run relatively hot. The formation of substantial ash agglomerates on the bed can further interfere with the air distribution and this can lead to the growth of the agglomerates to form significant ‘pancakes’ of fused ash. This can result in very poor combustion conditions, increased combustion air velocities through the unaffected sections of the grate, and hence increased levels of fly ash carryover. The formation of large, fused ash agglomerates can cause difficulties with the removal of the ash from the bed, and downstream problems in the ash handling system.

### 3.2 Fluidised bed combustors

The behaviour of biomass mineral material and ash in fluidised bed combustion systems has been fairly extensively studied, particularly in Scandinavia, where this type of combustor is very important industrially, principally for the recovery of energy from the waste products of the pulp and paper industries, see for instance Valmari (2000) and the references cited therein.

In fluidised bed combustion systems, the fuel particles are suspended in a fluidising air stream, along with a relatively coarse-grained bed material. The great majority of the ash leaves fluidised bed combustor furnaces in the form of fly ash particles, generally of up to around 50-100µm in diameter. This material will also contain fine particles of elutriated bed material, which is commonly quartz sand, or unreacted limestone, with lime and calcium sulphate/sulphite. A relatively small portion of the ash will be removed through bed drains, located underneath the fluidised bed.
The combustion temperatures in fluidised beds are somewhat lower than those that apply in fixed beds. The bed and freeboard temperatures when burning biomass materials tend to be less than 900°C, and the ash particles tend, in a number of ways, to resemble the ash produced by combustion of the fuel in a laboratory furnace at similar temperatures.

The levels of release of alkali metals by volatilisation, and the degree of fusion of the ash, tend to be significantly lower than those that apply at the much higher temperatures in grate and pulverised fuel combustors. These are, however, very important processes. The mineral material in biomass will also undergo thermal decomposition reactions. The thermal decomposition of calcium carbonate to calcium oxide, and the subsequent sulphation of the lime particles, for instance, is a very important process in many fluidised bed systems.

In most fluidised bed combustion systems, the tendency of the bed particles to sinter and form agglomerates is a key process, the avoidance of which is an important combustor design and operational issue. In bubbling fluidised bed systems, in particular, excessive agglomeration of the bed particles can lead to poor air distribution and eventually defluidisation of the bed. In extreme cases, it may be necessary for the operators to reduce the bed temperatures or to bring the combustor off-line to remove and replace the bed material.

The bed ash sintering process involves the formation of particle to particle bonds, commonly by a viscous flow sintering mechanism, involving the low melting temperature ash components, initially in the form of necks between the particles. If the conditions are favourable, fairly extensive three-dimensional agglomerates can form.

The key processes responsible for the formation of bonds between the bed particles in biomass-fired fluidised bed combustors are:

- Partial melting of the low melting point ash components to form a liquid phase of low viscosity, which, in turn, forms the necks between the bed particles. This type of sintering mechanism is of key importance for fuels with ashes rich in alkali metals and some of the heavy metals.

- In some cases, the solid particles, and particularly silicates and alumino-silicate species may be partially soluble in the liquid phase at the sintering temperature, and this can contribute to the strength of the particle-particle bonding. At higher bed temperatures, it is possible for a silicate melt of high viscosity to form, on the surfaces of the bed material. The viscous liquid phase can also flow to form necks between the ash and bed particles.

- It is also possible for chemical reactions to occur at the surfaces of the bed particles, which can increase the strength of inter-particle bonds. Skrifvars et al. (1996), for instance, concluded that the reaction of lime on the surfaces of the bed particles with SO\(_2\), to form calcium sulphate, was responsible for the sintering of bed particles in fluidised bed combustors firing high calcium biomass materials.

In operating fluidised bed combustion plants, the key issue is the control over the bed temperatures and the fuel distribution. The formation of agglomerates is often associated with the formation of fuel-rich hot spots in the bed. These can also be formed as a result of slag falls from the upper furnace surfaces or the detachment of pieces of furnace wall refractory material.
Although fluidised bed combustors firing biomass materials operate at relatively low bed temperatures, the release of volatile inorganic species, particularly the alkali metals and some of the heavy metals, into the flue gases does occur. This can give rise to the fouling of the surfaces of the boiler convective section, by a volatilisation/condensation mechanism, as described in Section 4 of this report.

The ash residues from fluidised bed combustors are generally of two basic types, viz:

- The fly ash materials carried over from the combustor, and which report to the particulate emission abatement equipment. These materials generally comprise the smaller fuel ash particles, and particles of quartz sand or of lime/limestone and calcium sulphate/sulphite, elutriated from the bed. The great majority of the ash discards from fluidised bed combustion systems are of this type.

- The larger ash particles retained in the furnace and which are removed periodically via the bed drains. These generally comprise agglomerated fuel ash and bed materials, and slag deposit material detached from the furnace surfaces.

### 3.3 Pulverised fuel combustion systems

Pulverised fuel combustion systems, which involve the injection of the milled fuel, along with the majority of the combustion air, through suspension burners located in the furnace walls, are generally associated with very large, solid fuel boilers for power generation. It is relatively rare for these boilers to be fuelled with biomass materials alone, although there are a small number of pulverised wood fired boilers in operation, principally in Scandinavia. It is, however, becoming increasingly common practice, for biomass materials to be co-fired in large coal-fired power station boilers. Biomass co-firing is currently practised mainly in Europe and North America, however it is likely that this will become common practice on a worldwide basis.

In pulverised fuel systems, the flame temperatures are relatively high, commonly around 1200-1600ºC, and the fuel particle residence times at these temperatures are relatively short, of the order of a few seconds. The principal concerns in this type of combustor are with the behaviour of the inorganic material associated with the biomass when subjected to very high temperatures and the conditions that apply in suspension flames, and with the impact of the co-firing of the biomass on the behaviour of the resultant ash, i.e. with the characteristics of the mixed biomass-coal ashes.

There is a very extensive technical literature on the characteristics of coal and coal mineral materials and their behaviour in pulverised coal combustion systems. The classic text is a monograph by Erich Raask entitled ‘Mineral Impurities in Coal Combustion’, which was published in 1985, and which presents an excellent summary of the state of knowledge on coal ash characteristics and behaviour in pulverised coal combustors and other systems at that time. The series of conferences on this subject which have been held triennially by the Engineering Foundation for a number of decades, also provides an excellent source of technical information.

Literature reports of the results of detailed testwork on pulverised fuel-fired combustion systems firing 100% biomass are relatively rare. One recent and important example, reported by Skrifvars et al. 2004, describes the results of a programme of trials on a relatively small, 80 MW<sub>e</sub> downshot fired boiler in Sweden, which was firing pulverised wood fuels. Some very interesting data on the fly ash
formation processes occurring in the biomass suspension flames, as well as information on the ash deposit formation processes, were reported.

In this case, detailed chemical analyses of the inorganic components of the wood fuels and of the ash materials collected in the electrostatic precipitator were carried out, and samples of the fine fly ash particles were taken using a Berner-type low pressure cascade impactors, inserted into the flue gas stream in the convective section of the boiler, at flue gas temperatures around 400ºC.

The results of chemical analysis of the fly ash size fractions, in the range up to 10 µm, indicated that the concentrations of the more volatile inorganic elements, i.e. the compounds of K, Na, S and Cl decreased with increasing particle size, indicating that the condensation of the more volatile species on the fine fly ash particle surfaces occurred as the flue gas temperatures decreased. The concentrations of the less volatile species, i.e. the compounds of Si, Al, Fe, Ca, Mg, Mn, and P tended to increase with increasing particle size.

The general descriptions in the literature of the flame-imprinted characteristics of biomass fly ash particles generated by the combustion of pre-milled biomass particles in suspension flames, and by the co-combustion of biomass with coal, have benefited from the extensive literature on coal mineral matter transformations in this type of combustion system. The principal inorganic constituents of the biomass materials, i.e. the simple inorganic compounds of Si, K, Ca, Mg, Na, P, S and Cl, are also present in coal mineral materials, as both major and minor components, although there are some important differences in the detailed mineralogy.

A generalised reaction scheme, which attempts to describe the principal processes that occur in pulverised fuel flames, is reproduced in Figure 4, (Baxter, 1993). In this case, the original solid fuel particles are illustrated in the left hand side of the diagram, and the product fly ash particles to the right hand side. As indicated above, the inorganic material in biomass fuels can be present in a number of inherent and extraneous forms, and this has a major impact on their behaviour in the flame.

In Figure 4, the principal transformation processes are considered to be of two general types, viz:

- **Release mechanisms**, including the vaporisation of volatile inorganic species, principally the alkali metals, the thermal or mechanical disintegration of the mineral particles, chemical decomposition reactions resulting in the release of compounds of sulphur and the halogens, and the convective release of fine particulate material during the very rapid devolatilisation of the fuel particles. These release mechanisms tend to be responsible for the production of the submicron fume particles and the inorganic vapours, and the very fine aerosol particles, present in the flue gases.

- The processes responsible for the generation of the residual fly ash particles include thermally or chemically induced fragmentation of the mineral particles, fusion or partial fusion and coalescence of intra-particle mineral inclusions, and chemical decomposition reactions. These processes tend to produce the larger fly ash particles.

In general terms, the products of combustion of biomass materials when co-fired with coal in large utility boilers tend to have a higher level of submicron fume and vapour...
and the fly ash particles tend to be significantly smaller than those formed by the combustion of the pulverised coal.

The key ash-related impacts of the co-firing of the biomass with the coal are potentially on the slagging and fouling deposit formation potential of the mixed biomass-coal ash, and on the efficiency of the installed particulate collection equipment. As stated above, the biomass materials tend to have relatively low ash contents compared to most coals, however the biomass ash materials tend to be relatively rich in the alkali and alkaline earth metals and these are effective fluxes for the aluminosilicate coal ashes. In general terms, therefore, the co-firing of biomass with coal will tend to increase both the slagging and fouling propensity of the mixed fuel, depending on the chemistries of the coal and biomass ashes and the co-firing ratio. At low co-firing ratios, at less than about 10% on a mass basis, recent plant experience has indicated that these effects tend to be modest. These issues will be discussed in more detail in Section 4 of this report.

3.4 General comment

Overall, therefore, it is clear that there are reasonably detailed reaction schemes, presented in the technical literature, which describe the generation of ash particles from biomass materials in grate-fired, fluidised bed-fired and pulverised fuel-fired combustors, and from the co-combustion of biomass with coal. These reaction schemes are based largely on knowledge of the chemistry and mineralogy of the mineral matter constituents of the fuels, and on the results of extensive experimental work at laboratory scale, combustion rig scale and in industrial scale combustion plants, involving the sampling and characterisation of the fuels, and of the resultant bottom ash and fly ash materials. The current reaction schemes are soundly based and are reasonably powerful, and form the basis of the current understanding of the nature of the products of combustion and the impacts on the key downstream ash-related processes within boilers and environmental control equipment.

4. THE FORMATION AND NATURE OF ASH DEPOSITS ON THE SURFACES OF COMBUSTORS AND BOILERS FIRING OR CO-FIRING BIOMASS MATERIALS

Operational problems associated with the deposition and retention of ash materials can and do occur on all of the major gas-side components of combustors and boilers firing or co-firing biomass materials.

The more important occurrences that occur at high temperatures in the combustion system are associated with:

- The partial fusion and agglomeration of ash particles in the fuel beds of stoker-fired and fluidised bed-fired combustion equipment, can lead to poor combustion conditions, de-fluidisation of fluidised beds, and problems with ash removal and downstream ash handling equipment,

- The deposition of fused or partly-fused ash materials on burner component and divergent quarl surfaces in large pulverised fuel furnaces can result in interference with burner light-up, operation and combustion performance,

- The build up of large accumulations of fused and partially-fused ashes can interfere with the operation of stokers and fluidised bed combustors and can block ash hopper throats in pulverised fuel-fired furnaces. This can result in the
requirement for load reduction or for significant unplanned outages for off-load cleaning.

- The deposition of fused or partially-fused slag deposits on furnace heat exchange surfaces reduces furnace heat absorption, and leads to increased gas temperatures both within the furnace and at the furnace exit. This can lead to increased ash deposition and high metal temperatures in the convective sections of boilers, and it may be necessary to reduce load or to come off load for manual cleaning.

- The accumulation and subsequent shedding of large ash deposits on upper furnace surfaces can lead to damage to grates and to furnace ash hoppers, and to the defluidisation of bubbling fluidised beds.

These are slag formation processes which occur at relatively high temperatures in excess of around 800-1000°C, on furnace refractory or water wall surfaces in direct receipt of radiation from the flame. They occur relatively rapidly, over a matter of hours, when conditions are favourable, and usually involve the sintering and fusion of fuel ash particles within the furnace.

The accumulation of ash deposits in the convective sections of boilers also occurs. These ash accumulations are normally termed fouling deposits, and the more common occurrences include:

- The formation of ash deposits on the surfaces of superheater, reheater and evaporator banks occurs at flue gas temperatures less than around 1000°C, and is generally a much slower process than slag formation, with the tendency for significant ash deposits to grow over a period of a number of days. The process involves the formation of deposits in which the ash particles are bonded by specific low melting point constituents, principally the alkali metal species. The gas temperatures are generally too low for significant sintering or fusion of the bulk of the ash particles. In general terms, as the gas temperatures decrease through the boiler convective section, the deposits tend to be less extensive and physically weaker. This is commonly reflected in the design of the boiler convective section, i.e. it is often possible to reduce the cross pitches of the tube banks progressively as the flue gas temperatures decrease.

Convective section fouling is one of the most troublesome ash-related problems associated with the combustion of biomass materials, because of the relatively high alkali metal content, and hence high fouling potential, of many biomass materials. Fouling reduces the heat absorption in the convective banks, and results in increased flue gas temperatures. Increased fouling also increases the gas-side pressure drop across the banks, and can eventually lead to ash bridging between the tubes. This further increases the gas side pressure drop, and can result in the channelling of the flue gas. This, in turn, can result in local overheating of the heat exchange tubes, and localised damage to boiler tubes and other components by particle impact erosion due to the increased flue gas velocities.

- Ash deposits on economiser surfaces at low flue gas temperatures tend to be relatively weakly bonded. They are commonly initiated by the physical accumulation of ash, often by the gravitational settling of ash material which has been dislodged from primary deposition sites upstream of the economiser by the action of sootblowers.
• Low temperature fouling and corrosion of airheater surfaces are also common occurrences. These are complex processes and tend to be very specific to the design and operation of the airheater. As such, they are outside the scope of a general discussion of this sort.

It is clear from the discussion presented above that the ash deposition processes that occur in biomass combustors and boilers, and when biomass is co-fired with coal, are fairly complex phenomena, occurring over a wide range of flue gas and surface temperatures, and are dependent both on the characteristics of the ash and on the design and operation of the combustor or boiler plant. It is instructive, therefore, to try to summarise the major findings, described in the technical literature and from practical plant experience, on the more important ash deposition processes.

4.1 Slag formation processes

Slag formation processes, as stated above, are principally associated with the sintering and fusion of ash particles on surfaces within the furnace, at temperatures in excess of 800-1000°C. There is a fairly extensive literature on coal ash slag formation mechanisms, much of which is equally applicable to biomass combustion and biomass co-firing.

The details of the slag formation mechanisms do depend significantly on the type of combustor and the furnace design, although the basic processes are similar. For slag formation, the dominant process responsible for mass transfer of ash material from the flue gas to the surface at the primary deposition site is inertial impaction. Other mass transfer processes do occur, but they are generally of little importance in most practical situations, except perhaps during the very initial stages, when the deposit is beginning to form on a clean metal surface, and when the deposition rate is relatively low.

The key issues, therefore, in determining the distribution of slag deposits within a furnace, the rate of slag formation and the nature of the deposit is the adhesion of ash material to, and the removal of material from, the surface. The adhesion of solid or liquid particulate material is clearly dependent on the physical state of both the particles and the surface. For effective particle adhesion to occur, either the particles themselves must be molten or partially molten, or the surface must be receptive, i.e. must be at least partially molten and ‘sticky’. As stated in Section 2.2, above, this is commonly associated with the $T_{15}$ temperature, at which around 15% of the ash particles or the deposit surface is fused, and the particle or deposit surface begin to be ‘sticky’.

In the initial stages of slag formation, when the metal surfaces are clean and relatively cold, only the molten or partly molten particles can adhere to the surface, and the deposition rate is low. The dominant deposition processes are often the condensation of volatile inorganic species and the adhesion of the portion of the fly ash particles arriving at the surface that are at temperatures above $T_{15}$. The chemical composition of the initial deposit may be very different from that of the bulk fuel ash, and the deposit consists of relatively loosely sintered fly ash particles, bonded together by low melting point constituents. This tends to occur when the boiler is brand new or after an outage during which the furnace surfaces have been thoroughly cleaned. It is a common observation that there may be a ‘period of grace’ of a few weeks in duration when little or no slag formation is apparent. This is also the situation that applies when cooled deposition probes are inserted into the
flue gas stream for short exposure periods, for investigative and test purposes. This is one of the key limitations of this type of investigative work.

As the deposition proceeds, and the deposit thickness increases, the temperature of the ash material at the outside surface of the deposit also increases. The ash deposit becomes progressively denser and more fused. The surface material becomes progressively more receptive to the incoming particulate material, and the deposition rate increases. The chemical composition of the deposit approaches that of the bulk fuel ash.

In some cases, particularly with low fusion temperature ashes and in high temperature regions of the furnace, the deposit grows to the point where the temperature at the outside of the deposit is in excess of the flow temperature (or $T_{70}$) of the bulk ash, and a fused, flowing slag is formed. In this condition, the surface is very receptive even to solid particles arriving at the deposition site, and the deposition rate is at a maximum.

In some cases, with relatively high fusion temperature ashes and in low temperature regions of the furnace, the deposit surface may never reach a temperature at which the ash material is fused, and a relatively porous, friable deposit, which is relatively easily controlled by the on-line cleaning systems, is formed. This is obviously the most desirable condition in most cases.

The extent to which slag represents an operational issue depends, therefore, on the fusion behaviour of the ash, and the local gas and surface temperatures. These factors generally determine the rate of growth and degree of fusion of the deposits, and whether or not they can be controlled by the on-line cleaning systems.

The general process description presented above goes some way to explain the distinctly layered structure observed in many furnace slag deposits. The ash material adjacent to the furnace tube surface is generally relatively weakly bonded and has high porosity. This is also the mechanically weakest material and most likely to fracture under the action of sootblowing or thermal stresses. Slag deposits commonly detach in large pieces. The process description also indicates that the deposition rate is often largely controlled by the condition of the deposit surface, and less so by the fly ash particle flux or the condition of the fly ash particles.

It is also a common observation that hot spots on the furnace surfaces, often associated with areas of refractory material, can act as slag initiation points from which slag can grow out into the furnace volume and across the furnace tubes. The refractory surface is not efficiently cooled, and the surface temperature of the refractory or of any ash deposit material attached to it is much higher than that of the adjacent furnace tubes. This means that, for the reasons described above, the surface of the deposit is more receptive than the ash deposits on adjacent furnace tubes. The deposition rate is higher and the nature of the deposit is commonly very different from that on the adjacent tubes. This can act as a point at which the slag can grow in all directions. It is a common observation that the walls of a combustion chamber can be relatively clean, except for areas around patches of refractory material on and around which a fused slag has grown.

It is clear from the description of the slag formation and growth processes presented above that the key fuel-related factor that controls the extent of slag formation and the nature of the slag is the fusion behaviour, both of the individual fly ash particles and of the surface of the slag. The ash fusion behaviour of biomass materials varies widely, depending on their chemical composition.
These properties will be reflected in the Slagging Index values for individual biomass materials, based either on the ash chemistry or the ash fusion temperatures, as described in Section 2 above. The fusion properties of the ash will have a key influence on the design of the combustion equipment and the furnace. Furnaces are generally designed with the formation of slag deposits in mind, i.e. the furnace geometry should be such that the flames are adequately contained and that the gas temperatures local to the walls are low enough to avoid excessive slag formation. In boilers with water wall furnaces, it is also important that adequate on-line cleaning is provided to help maintain the furnace heat absorption.

One of the key functions of the furnace in this regard is to reduce the flue gas temperatures to a level below that at which excessive slag can form, prior to entry of the flue gases into the convective section of the boiler. Failure to do this would result in the formation of fused or partly fused slags in the convective section tube banks, and this is highly undesirable.

4.2 Convective section fouling

Convective section ash fouling is a lower temperature process, largely driven by the deposition of volatile inorganic species in the ashes, principally the alkali metals, and in some cases phosphorus compounds, by a volatilisation-condensation mechanism. The volatile species will condense on any cooled surface, initiating deposit growth and acting as a bond between the non-volatile, non-fused ash particles which may adhere to the deposits.

On deposition, there is also a tendency for the alkali metal compounds and other inorganic species to sulphate, a reaction with the sulphur oxides in the flue gases. This can add significantly to the mass and volume of the deposits, and may alter the physical properties of the deposits, particularly on cooling. Because the deposition occurs principally by a condensation mechanism, involving principally the volatile components of the ash, the overall ash deposition rate tends to be much lower than those that apply in furnace slag formation processes.

The physical properties of the ash deposits depend largely on the ash chemistry and on the flue gas temperature at the deposition site. The deposits in the higher temperature regions of the boiler convective section, and particularly at the entry to the final superheater, which is commonly the first packed tube bank encountered by the flue gases, tend to be partly fused at normal flue gas temperatures. For most biomass materials, this will occur if the flue gas temperatures are in excess of around 700ºC, and this is commonly the case at the entry to the superheaters. The ash deposits tend to act as a receptive surface for the other non-volatile ash components, which are present in the flue gas in the form of solid particulate material, and with time, the resultant deposits can be tenacious and hard to remove. This is particularly the case if ash bridges have formed between closely-packed tubes. On cooling, the deposits can be hard and well anchored to the tube bank surfaces. On-line cleaning techniques tend to be relatively ineffective if the deposition is extensive, and off-line the deposits cool to a hard dense solid, which can be very difficult to remove.

The deposits formed on boiler surfaces in contact with flue gases at lower temperatures, i.e. below about 600-700ºC, depending on the chemistry, tend to be relatively weakly bonded. They are more friable in nature and are usually easier to remove both on and off-line.
For this reason, it is common practice, when designing boilers for the firing of high fouling fuels, e.g. municipal solid wastes and some biomass materials, to have a large radiant furnace section, which acts to reduce the flue gas temperatures at the entry to the first tube bank to temperatures below 700ºC. This helps to control the fouling, and specifically helps to avoid the formation of partly fused ash deposits at the entry to the first convective bank.

There are a number of common knock-on problems associated with the formation of excessive levels of ash fouling deposits in the convective sections of boilers. These apply to all boilers fired with both liquid and solid fuels, particularly if the extent of deposition is sufficient to cause ash bridging between tubes, viz:

- The generation of high velocities in the open gas pass channels through the bank, resulting in increased gas-side particle impact erosion wear of the tube surfaces,
- The overuse of sootblowers in an attempt to control the gas-side fouling is a further common cause of boiler tube erosion,
- When there is excessive convective pass fouling, with blockage of a significant number of the flue gas passes in a tube banks, there is a tendency for the generation of high metal temperatures in tubes in the flue gas passes that remain open. This can result in accelerated metal wastage, due to gas-side corrosive attack, and to other thermal damage to the tubes and uncooled components, and
- Increased metal wastage of boiler surfaces due to the increased incidence of boiler outages, and hence increased out-of-service corrosion, particularly if the water washing of boiler surfaces to remove the ash deposits is applied. The metal wastage rates from this type of aqueous salt solution corrosion can be fairly dramatic if the boiler can not be drained effectively, or lies wet for a prolonged period after washing.

With increased operating time, there is a tendency for these problems to get progressively worse, i.e. the time between forced outages for cleaning will tend to decrease, and the number of tube leaks and the requirement for significant repair work will tend to increase. This is a fairly common experience with boilers where the extent of convective pass fouling is such that operation on a campaign basis, i.e. with regular outages for manual cleaning, is required.

Fouling deposits on convective pass surfaces at flue gas temperatures lower than around 600ºC tend to be very much less strongly bonded, and it is possible to reduce progressively the heat exchange tube cross pitching with decreasing flue gas temperature and, in some instances, to employ extended surface tubing. Ash deposits can and do accumulate in cooler regions of the boiler and the economiser, however, in the main, these are readily controlled provided that the heat exchange bank design is suitable for the purpose and there is adequate on-line cleaning.

4.3 Deposit growth, shedding and on-line cleaning

In all practical situations, the long term accumulation pattern of deposits in furnaces and boilers involves competition between processes which tend to add to the deposit and those which remove material from deposits. These have been described by a number of authors in the technical literature for fossil fuel and biomass ashes (Raask, 1985, Baxter, 1993). The key deposit growth processes are:
• Ash particle inertial impaction is the dominant process in high temperature slag formation, and for larger ash particles. The rate of deposition by impaction is a function of the particle flux, and of the deposition efficiency which, in turn, is dependent on the degree of fusion of the particles and/or the deposit surface.

• The condensation of volatile inorganic species, in vapour or fume form in the flue gases, on cooled surfaces, which is the principal driving mechanism for convective pass fouling, and is of particular importance for biomass materials because of the relatively high levels of volatile species in these fuels.

• Chemical reactions occurring within the deposits, and particularly oxidation, sulphation and chlorination processes.

• Thermophoresis, the transport of small, gas borne, ash particles to cooled surfaces by the effects of the local gas temperature gradients, is only important for very small, sub-micron particles and particularly during deposit initiation when the local temperature gradients are at a maximum and when the rate of deposition by inertial impaction is low.

Uncontrolled ash deposition, with no shedding or deposit removal would, in most plants firing solid fuels, very quickly result in operational problems, and most solid fuel furnaces and boilers are fitted with on-line cleaning systems of various types. There are also natural ash deposit shedding mechanisms and other processes which are responsible for the reduction in the extent of deposition. The key processes are:

• The principal means of on-line control of deposition in most furnaces and boilers is the use of the installed sootblowers. These devices direct a high velocity jet of steam, water or compressed air at the deposits, and employ a combination of mechanical impact and thermal shock to break up and remove the deposits. Sonic sootblowers can also be deployed, particularly for the removal of relatively weak deposits in the cooler parts of the boiler convective section. In extreme circumstances, where very tenacious and troublesome ash deposits have formed, small explosive charges can be employed to break up the deposit material.

The deposit material removed in this way may be carried forward with the flue gases, but can also accumulate elsewhere in the furnace or in the convective pass of the boiler.

• The natural shedding or detachment of deposits also occurs. This can occur when deposits grow too large for the adhesive forces to support them, or due to the effect of thermal expansion differences between the ash deposit and the boiler tube, during shutdowns and boiler load changes. Rapid boiler/combustor load changes can be deliberately used for deposition control.

The detachment of large accumulations of slag in this way can, however, result in damage to components or in troublesome accumulations of ash lower in the furnace.

• Heavily fused deposits of low viscosity can drip on to surfaces lower down in the furnace or boiler.

• In the boiler convective section, fly ash particle impact erosion wear can result in the reduction of the thickness of fouling deposits, particularly on the sides of tubes.
It is clear, therefore, that ash deposition control in biomass combustors and boilers is a fairly complex issue, involving both boiler design and operation. The key factors are:

- The careful design of the furnace and boiler convective section, which recognises properly the characteristics and behaviour of the fuel ash, is of prime importance and the boilermaker obviously has the key role in this regard. The incorporation of specific furnace and boiler design features, where appropriate, to minimise ash deposition and to aid the removal of ash, and the avoidance of ash accumulation within the system is also of key importance.

- The correct design, operation and maintenance of the combustion equipment and of the on-line cleaning systems are important issues. It is also often preferable to maintain the plants at a relatively low level of deposition, rather than to deploy the on-line cleaning systems only when there is evidence of significant deposition. Intensive cleaning of the furnace and boiler surfaces during outages can be very effective in increasing the operating times between outages.

There are specialised on-line deposition monitoring and sootblowing control systems that are commercially available and that can assist significantly with the optimisation of the sootblower operations and the control of ash deposition.

5. THE IMPACT OF BIOMASS ASH ON THE FLUE GAS CLEANING EQUIPMENT IN BIOMASS FIRING AND CO-FIRING SYSTEMS

The cleaning of the flue gases to a particular standard, prior to exhaustion to the atmosphere, is a feature of most industrial biomass combustion systems, worldwide. The larger biomass combustors and boilers generally have fairly tight controls on emission levels, which may depend on whether the biomass fuel is regarded as being a relatively clean fuel or as a waste material. The smaller domestic or commercial/industrial systems tend to have less onerous emissions control requirements. Appropriate flue gas cleaning systems, designed to comply with the relevant operating standards for most industrial biomass materials and combustion systems, are available commercially from experienced vendors, and are relatively well proven. A detailed discussion of the regulatory and technical issues associated with the control of the emissions from dedicated biomass combustion systems is clearly outside the scope of this document.

The main focus in this section, therefore, is on the impacts of the firing of biomass materials on the flue gas cleaning systems for the larger scale combustion systems and the co-firing of biomass in boilers originally designed for the combustion of conventional fossil fuels. As stated above, the quantities of biomass co-fired in large coal-fired and other fossil fuel-fired power plant boilers have increased fairly dramatically over the past few years, particularly in Northern Europe but also elsewhere in the world, and the level of activity is likely to increase further over the next few years.

In modern coal-fired power plant boilers, the principal gaseous and gas-borne emissions control equipment is currently concerned with the control of the following species, viz:

- Total particulate emissions control, principally using dry electrostatic precipitators or fabric filters,
• NO\textsubscript{x} emissions control, by both primary and secondary measures, with Selective Catalytic Reduction (SCR) being the most commonly applied secondary measure, and

• The control of SO\textsubscript{x} emissions principally by wet Flue Gas Desulphurisation (FGD) techniques.

All of the flue gas clean-up technologies listed above are very well proven industrially for pulverised coal firing, over a wide range of coals. There are a number of experienced specialist vendors for all of the most commonly applied equipment, and generally speaking, the implementation of these emission control measures in large solid fuel-fired boilers has been very successful.

As stated above, the level of co-firing of biomass materials in large coal-fired boilers has increased markedly in many countries and it is interesting to examine the evidence to date on the ash-related impacts of biomass co-firing on the performance of the emissions control equipment.

5.1 The impact on of co-firing on electrostatic precipitators

When considering the effects of the co-firing of biomass materials on the performance of the electrostatic precipitators and on particulate emission levels, the principal technical concern is that the fly ash particles generated from biomass combustion tend to be different chemically from pulverised coal ash, are significantly smaller than those from coal firing, and that there is a greater tendency towards the generation of sub-micron fumes and vapours. There may, therefore, be a tendency for the particle capture efficiency in electrostatic precipitators to decrease with increasing co-firing ratio, and for the total particulate emission levels to increase accordingly.

In most countries, it is necessary to demonstrate to the environmental regulators that the co-firing of the biomass materials has no significant negative environmental impacts, and there is a growing body of evidence that, at relatively low biomass co-firing ratios, i.e. less than 10% on a heat input basis, that there has been very few incidents of significant increases in the total particulate emission levels due to the biomass co-firing activities. There are concerns, however, that this may not apply at higher co-firing ratios, and that modifications to the installed particulate collection equipment may be required.

5.2 The impact on of biomass firing and co-firing on SCR catalysts

The performance of SCR catalysts, and particularly the effective catalyst lifetime, can be influenced by a number of factors, many of which are fuel related (Bill et al, 2005), viz:

• Thermal degradation by pore sintering,

• Ammonia salt condensation inside catalyst pores due to low temperature operation,

• The surface blocking of catalyst pores by small ash particles,

• Poisoning of catalyst surfaces by volatile inorganic species, and

• Fly ash particle impact erosion of catalyst material.
Early experiences of the use of SCR catalysts in wood chip and peat-fired boilers in Scandinavia, and of boilers firing animal manures and sludges, indicated that deactivation of the catalysts by sodium and potassium salts, and by phosphorus and silica compounds was a significant issue, which can result in markedly reduced catalyst lifetimes and increased operating costs (Ahonen, 1996, Beck et al, 2005).

A number of laboratory and plant tests of the impact of biomass co-firing on the fouling and deactivation of catalysts have also been performed over the past few years. Baxter and Koppejan (2005), for instance, presented some of the results of experiments involving the exposure of SCR catalyst materials in a slip-stream reactor on a combustor firing alkali and alkaline earth metal rich fuel. These data have been reproduced in Figure 6. The data indicate clearly that there were significant increases in the concentrations of calcium, sulphur and sodium compounds on the surfaces of the catalyst material after prolonged exposure to the flue gas. The results of the testwork also indicated that there was significant deactivation of the catalyst.

At Studstrup power station in Denmark where, since 2002, cereal straws and other baled biomass materials have been co-fired, at up to 10% on a heat input basis, with coal in a 350 MW_\text{e} boiler, the impact of the co-firing on a side stream SCR catalyst block has been studied over a period of up to 5,000 hours (Overgaard et al, 2004). The results of this testwork have indicated that there was no significant difference in the performance of the catalyst between the straw co-firing test and coal firing alone. Further testwork with exposure of the catalysts over periods of time up to 20,000 hours are planned at the station.

The deactivation of SCR catalysts associated with the firing or co-firing of biomass materials is clearly of industrial importance, and this has been the subject of a major EC-funded R&D project, CATDEACT, which is co-ordinated by IVD at the University of Stuttgart. The details of the project partners and the work programme are given in the project website, www.eu-projects.de.

Bill et al (2005) have reported the results of a programme of testwork using a side stream, pilot scale catalyst block at Borssele power station in the Netherlands in 2004. The boiler (425 MW_\text{e}) was co-firing biomass materials with coal at up to around 10% on a mass basis. The initial exposure test was over a period of 1,000 hours, and no significant decrease in catalyst activity, compared to that of a baseline test firing coal and refinery off-gas only, was detected. No evidence of significant increases in the levels of deposition of arsenic, sodium or potassium was detected, although there was a 30-40% increase in the P_2O_5 concentration.

Overall, it would appear that the increased deactivation rates of SCR catalysts due to alkali metal and phosphorus fouling is a significant technical issue when firing or co-firing biomass materials with high levels of these species. At the biomass co-firing levels that currently apply in large power plants, i.e. generally lower than 10% on a heat input basis, there have not, as yet, been any significant operational problems, and the results of a number of side stream tests at low co-firing ratios on operating plants have been relatively encouraging in this regard.

In the event of significant catalyst deactivation, it is possible to water wash the catalyst blocks to remove alkali metal and other salts and recover the catalyst activity. Avedore power station in Denmark, where they are involved in the co-firing of wood pellets with HFO and natural gas, has had such a system in commercial operation for a number of years (Ottosen, 2005).
5.3 The impact of biomass co-firing on FGD plants

The great majority of clean biomass materials of industrial importance have sulphur contents that are significantly lower than those in most coals and, in the great majority of cases, they also have similar or lower chlorine levels. The impact of biomass co-firing, therefore, in the great majority of cases is to reduce the acid gas abatement duty of the installed FGD system, and hence reduce the limestone usage and plant operating costs.

The great majority of biomass materials also have significantly lower levels of most of the key trace element and heavy metal species than most coals, and the duties of the waste water treatment plants are reduced. This is not the case, of course, for a number of the biomass-based waste materials.

The evidence to date from coal-fired power plants which have been co-firing clean biomass materials, albeit at relatively low co-firing ratios, has been that co-firing has had no significant negative impacts on the operation and performance of the FGD plants.

6. THE IMPACT OF BIOMASS ASH ON BOILER TUBE CORROSION, AND ON THE EROSION AND ABRASIVE WEAR OF BOILER COMPONENTS AND OTHER EQUIPMENT.

6.1 Technical background to gas-side corrosion processes in boilers

The corrosion processes that occur on the gas-side surfaces of boiler tubes are very complex and, since they occur at high temperatures and in very aggressive conditions, they are very difficult to study. Nevertheless, because of their great importance to the designers and operators of boiler plants, these processes have been the subject of a great deal of technical work, at laboratory, test rig and plant scale, over many decades. There is a substantial technical literature on this subject, particularly for fossil fuel-fired boilers, (Raask, 1988), and increasingly for biomass boilers and for boilers co-firing biomass with fossil fuels, as the industrial importance of biomass utilisation for power generation and combined heat and power applications has increased. Gas-side corrosion processes have generally been of less importance for domestic and small commercial/industrial biomass boilers, which tend to operate at much lower steam temperatures.

In general terms, it has been found that the gas-side metal wastage rates of boiler tubes are controlled by a number of factors, viz:

- The tube material,
- The flue gas and metal temperatures,
- The chemical composition of the ash deposit material at the metal-deposit interface,
- The chemical composition of the flue gases, and
- The operating regime of the plant.
For most biomass boilers, it has been found that, provided that the combustion equipment and furnace are well-designed and operating reasonably well, the principal concern has been with the high temperature corrosion rates that apply in the superheater section of the boilers. The concerns are principally associated with the final stage superheaters, with the leading elements and steam outlet legs being subject to the most aggressive attack, principally because of the relatively high metal temperatures.

As stated previously, the majority of biomass materials of industrial interest have the following key chemical characteristics, which have an influence on the high temperature corrosion processes:

- The biomass ashes tend to be relatively rich in alkali metals, and particularly potassium compounds, which tend to form deposits on the surfaces of the superheater tubes, via a volatilisation/condensation mechanism,

- Most biomass materials have relatively low total sulphur contents, generally less than 0.5%, and

- The chlorine contents of biomass materials vary significantly, but can be up to 1% or so in some cases.

As described in Section 4 above, the ash deposits that form on the boiler surfaces, therefore, tend to be rich in potassium salts, principally sulphates and chlorides, depending on the fuel composition and the gas and metal temperatures. The chemistry of the biomass ash deposits tend, therefore, to be very different from that of most coal ash deposits, principally in terms of the relatively high potassium contents and the relatively high chloride to sulphate ratios. This can have a significant impact on the corrosion behaviour, particularly at high metal temperatures on superheater surfaces. In general, therefore, it is necessary to design dedicated biomass boilers with final steam temperatures that are significantly lower than those that apply in large coal-fired boilers.

A number of very good technical reviews of the chemistry of biomass ash deposits and the corrosion processes in biomass boilers have been published in recent years; see for instance Neilsen et al (2000), and Henriksen et al (2002), and the references cited therein. There has also been increasing interest over the past few years in the impact of co-firing biomass materials on boiler corrosion processes, see, for instance Baxter et al (2003), for a very useful, recent overview.

### 6.2 Corrosion mechanisms

It is fairly common industrial experience that significant corrosion rates of the conventional superheater materials have occurred when firing most biomass materials at metal temperatures in excess of 450°C. A number of potential corrosion mechanisms are considered to be possible under the relevant conditions, and have been described, including:

- Corrosion processes involving the reactions between the metal/metal oxides and gaseous chlorine-containing species, i.e. Cl₂ and HCl,

- Solid phase reactions involving alkali metal chlorides, and

- Corrosion reactions involving molten alkali metal and other chlorides.
The experience from biomass boilers, particularly in Scandinavia, is that the most severe corrosion is associated with ash deposits containing alkali metal chlorides on high temperature superheater surfaces, which cause significant metal loss rates at temperatures below the melting temperature of KCl, and this is considered to be associated with the presence of low melting eutectic mixtures.

The melting and eutectic temperatures of the relevant inorganic salt species are listed in Table 4. It is clear from the data presented in the table that a number of the key binary mixtures, particularly the KCl-FeCl$_2$ and NaCl-FeCl$_2$ systems have low temperature eutectics, in the range 340-390ºC, i.e. local liquid phases can form within the deposits, as the KCl or NaCl in the deposited material react with the metal or the oxide scale.

Another reaction considered to be responsible for enhanced corrosion processes in biomass boilers involves the sulphation of the deposited alkali chlorides in contact with SO$_2$/SO$_3$ in the flue gases, with the release of HCl local to the metal surface/scale/ash deposit interface, according to the following reaction scheme:

$$2\text{KCl}(s) + \text{SO}_2(g) + 0.5\text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g)$$

The gaseous HCl can then diffuse to the metal/scale surface and react to form metal chlorides. These mechanisms are considered to apply when firing biomass fuels with low sulphur contents and significant chlorine contents, i.e. where the ash deposits are chloride dominated.

Riedl et al. (1999) described a further potential corrosion mechanism, which they called ‘active oxidation’, and that they considered may be responsible for the accelerated corrosion observed in small, hot water, fire tube boilers firing bark, woodchips and sawdusts in Austria. They described the enrichment of alkali metal chlorides on the heat exchange surfaces, by a condensation mechanism, as described in Section 4 above. They further suggested that the chlorides can react with the SO$_2$/SO$_3$ in the flue gases to form sulphates, and the subsequent release of gaseous chlorine, according to the following reaction schemes:

$$2\text{NaCl} + \text{SO}_2 + \text{O}_2 = \text{Na}_2\text{SO}_4 + \text{Cl}_2$$

$$2\text{KCl} + \text{SO}_2 = \text{K}_2\text{SO}_4 + \text{Cl}_2$$

One of the results of the sulphation reaction is the release of gaseous Cl$_2$ within the deposit and local to the metal surface, and this can react with the low alloy steel to form FeCl$_2$. The FeCl$_2$ has significant vapour pressure under the relevant conditions, and can diffuse through the corrosion product/deposit layer and react with the excess oxygen in the flue gases, according to the following reactions:

$$3\text{FeCl}_2 + 2\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{Cl}_2$$

$$2\text{FeCl}_2 + 1.5\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{Cl}_2$$

$$\text{FeCl}_2 + \text{O}_2 + \text{Fe}_2\text{O}_4 = 2\text{Fe}_2\text{O}_3 + \text{Cl}_2$$

The authors considered that these reactions are responsible for the regeneration of the gaseous chlorine local to the metal surface, and the resultant severe corrosion. The basic principles of the ‘active oxidation’ mechanisms are described graphically in Figure 7. This provides an illustration of the key chemical reactions that are
considered to be occurring within the tube metal/corrosion scale/ash deposit layers of the interactions with the flue gases.

Overall, it is clear that a number of potential corrosion mechanisms that may be responsible for the metal wastage observed on the surfaces of boiler tubes in biomass-fired boilers. The actual mechanisms which apply in particular circumstances will be determined by the local conditions, i.e. the chemistry of the flue gas and ash deposit, and the local gas and metal temperatures.

6.3 Plant experience and boiler probing trials with biomass firing and biomass-coal co-firing

A number of important plant-based corrosion probing trials in biomass boilers have been carried out over the past few years. These trials involved the exposure of small coupons of the test materials to the flue gases from biomass combustion at controlled temperatures and over relatively long periods of time. This type of trial is relatively expensive to perform however, along with carefully recorded plant experience of corrosion processes, they represent probably the best means of obtaining corrosion rate data under reasonably realistic conditions.

Montgomery et al (2002) and Henriksen et al (2002) have reported the results of a very important programme of plant-based corrosion testwork involving the insertion of corrosion probes into the flue gas streams of three small straw-fired power plants at Masnedo, Rudkobing and Ensted, in Denmark. The stations were firing cereal straws with ash levels typically around 5-7%, chlorine levels typically around 0.3-0.5%, sulphur contents less than 0.2% and potassium contents up to around 2% on a dry basis.

Three types of metal test piece exposure trials were performed, viz:

- The exposure of test metal rings on water/air-cooled probes,
- The exposure of candidate tube materials in a test superheater, and
- The exposure of test tube sections inserted into an existing superheater.

Both ferritic and austenitic superheater alloys were exposed to the flue gas atmospheres at metal temperatures in the range 450-620ºC. It was found that the measured corrosion rates for the test materials increased with increasing metal temperature, from less than 50 nm h\(^{-1}\) at 470ºC, to values in excess of 1,000 nm h\(^{-1}\) at temperatures in excess of 600ºC.

The basic findings on the corrosion processes and deposit morphologies were summarised in a table, and this has been reproduced in Table 5. These results indicate that there were significant differences in the deposit morphologies and corrosion chemistry at different temperatures. At relatively low temperatures, up to around 520ºC, there was the formation of the normal, stable protective oxide layer. At the higher temperatures, no stable protective oxide layer was formed, and rapid metal wastage by selective corrosion and grain boundary attack was observed. All of the alloys tested gave fairly similar corrosion rates, although there appeared to be a shallow optimum in corrosion resistance for alloys with chromium contents in the range 15-18%.
It is clear, therefore, that the enrichment of alkali metal chlorides at the metal/oxide/ash deposit interface can lead to increased rates of metal wastage due to gas-side corrosion, particularly on high temperature surfaces in the superheater sections of the boiler at temperatures in excess of around 480-500°C. In a number of cases, rapid metal loss, leading to significant corrosion-related operational problems has resulted.

Also in Denmark, there has been particular interest in the co-firing of cereal straws with coal in large power boilers for some time (see, for instance, Montgomery and Larsen, 2002, and the references cited therein, Henriksen and Larsen, 1997). This is of particular technical interest because of the high final steam temperatures, and hence high superheater metal temperatures, in coal-fired utility boilers, and the understandable concerns about the risks of accelerated metal wastage associated with biomass co-firing.

Important information on these processes has been derived from plant experience and testwork on the 80MWth CFB boiler at Grenaa in Jutland, which was designed for the firing of up to a 50:50 mixture of straw with coal, on a heat input basis. This experience has indicated that the corrosion rates of superheater tubes when co-firing straw were of the order of 5-25 times greater than those measured when the boiler was firing coal alone.

The history of the superheater fouling and corrosion at Grenaa is very interesting and the findings may be instructive in helping to identify the key plant operational and other factors that can affect the corrosion processes. For the first six months of operation, the unit was never run above around 80% load, and no particular problems with the formation of superheater fouling deposits were reported. Increasing the load to 100% resulted in significant increases in the flue gas temperatures in the cyclone from around 850°C to around 900-1000°C.

Serious problems with excessive fouling on the surfaces in the superheaters were reported. After 18 months operation, it was found that corrosive damage to the superheater elements, which were operating at a final steam temperature of 505°C, was so serious that replacement of the final superheater elements was necessary. Selective chloride corrosion was considered to be responsible for the accelerated metal loss. Examination of the superheater tubes and of test specimens suggested that the chromium had been selectively removed from the metal surface and along grain boundaries. The protective oxide layers on the metal surface were irregular, porous, cracked and partly exfoliated. In many cases, significant enrichment of chloride was detected at the corrosion front in the degraded metal zone.

Considerable efforts were made to provide a description of the key factors responsible for the accelerated superheater tube wastage. One of the most important observations was that the great majority of the potassium in the superheater tube fouling deposits, and particularly at the metal/oxide/ash deposit interface, was in the form of potassium chloride, and it was considered that this was the principal agent of the selective chloride corrosion.

A number of corrosion mechanisms have been suggested to describe the corrosion process at Grenaa in detail. The mechanism offered by Hansen et al, (2000) involves sulphation of the solid phase KCl followed by the release of chlorine gas, or possibly HCl, adjacent to the metal surface. The evidence for this type of mechanism lies in the results of the detailed microstructural examination and chemical analysis of the corroded metal specimens. The chlorine selective
corrosion involves the removal of chromium and to some extent iron from the metal grains and particularly at the grain boundaries. The chromium and iron formed oxides which were found at the degraded metal surface and between the degraded metal grains. In many cases, the degraded metal layers were porous, with no included metal oxides. No solid or liquid ash or flue gas components were found between the grains in the degraded metal except for chloride, which is associated with the chromium and iron. Hansen et al. were of the view that this makes a liquid phase corrosion mechanism involving fused ash components unlikely, and that a mechanism involving a gas phase corroden, probably chlorine gas or hydrogen chloride, is more plausible.

Significant modifications were made in response to the experiences of accelerated superheater corrosion and the other operational problems at Grenaa. These included:

- The installation of additional heat transfer surface to reduce furnace temperatures,
- A switch to a coal of lower sulphur content, and
- A switch to a limestone of higher quality.

These modifications had the effect of providing significant reductions in the extent of fouling deposition in the boiler convective section and in the rate of superheater metal wastage.

The results of the corrosion testwork performed during the straw/coal co-firing trials, at up to 20% straw on a heat input basis, in a 150 MWe pulverised coal boiler, Unit 1 at Studstrup power station, are also relevant in this context. The results were very different from those obtained from the circulating fluidised bed (CFB) boiler at Grenaa. At Studstrup, the impacts of co-firing straw, at a co-firing ratio of 10%, on the measured corrosion rates were modest, and the evidence indicated a very different corrosion mechanism from that observed at Grenaa (Montgomery and Larsen, 2002).

Examination of the fly ash material indicated that the great majority of the potassium was associated with the alumino-silicates in the coal ash. It was considered that the potassium species released into the vapour phase in the flame reacted with the other ash constituents, and that little or no free KCl was present at the metal/oxide ash deposit interface. The chlorine released from combustion of the straw was present in the flue gases in the form of HCl, and possibly Cl₂. It was found that the dominant corrosion mechanism relevant to the superheater tubes, at straw co-firing levels up to 10%, was oxidation with perhaps some alkali sulphate melt corrosion, i.e. the normal corrosion mechanisms associated with coal firing.

It was considered that the key difference between CFB at Grenaa and the pulverised fuel combustion at Studstrup is that the flame temperatures in pulverised fuel systems are considerably higher, and that this permits significant interaction between the released potassium species and the other ash components to occur. Furnace gas temperatures in CFB systems are too low for substantial interaction of this type. It should also be noted that the straw/coal co-firing ratio at Grenaa was significantly higher than at Studstrup, and that the differences observed in the behaviour of the potassium, the chlorine and the alumino-silicate fly ash particles may also be related to the co-firing ratio.
It is clear, therefore, that the co-firing of biomass materials with coal introduces a risk of accelerated corrosion rates of high temperature boiler tubes, and that the risk is associated with the increased levels of available alkali metal species and chlorine released into the boiler flue gases. Under unfavourable circumstances, as for instance at Grenaa, the impact of the accelerated metal wastage can be dramatic and there can be significant impacts on the operation and integrity of the plant. These risks appear to be significantly lower in pulverised fuel-fired boilers with biomass fuels with lower ash, potassium and chlorine contents, and at low co-firing ratios.

6.4 Preventive and remedial measures for fireside corrosion

The general experience with the operation of boiler plants firing a wide range of clean biomass materials has been that, at final steam temperatures in excess of 500ºC, unacceptably high rates of metal wastage of superheater elements can occur. In boilers firing contaminated biomass materials and a wide variety of waste materials, with high alkali metal contents, significant chlorine contents and low sulphur contents, significant corrosion of the superheater tubes can occur at even lower final steam temperatures.

There are a number of potential remedial approaches to the observed corrosion problems, viz:

- Control of the final steam temperatures, at the boiler design stage, to levels at which the corrosion rates are acceptable, for the fuel being fired and the superheater materials employed.
- The use of fireside additives to modify the flue gas and ash deposit chemistries, and
- The selection of more resistant alloys for construction of the final superheaters.

The conventional approach to the control of superheater corrosion is by selection of the appropriate combination of tube materials and final steam temperatures for the fuel being fired. For instance, in modern incineration plants for municipal solid wastes, where the flue gases and ash deposits are extremely aggressive, it is common practice to limit the final steam temperatures to around 400ºC, and to protect leading tubes in the final superheater against corrosion and erosion processes with SiC sleeving. Modern biomass-fired boiler plants commonly have final steam temperatures in the range 450-540ºC, depending principally on the characteristics of the fuel and the materials selected for the construction of the final superheater elements. These are design decisions taken by the boiler supplier, based on previous experience with the fuel and the best technical information available.

A number of plant-based studies, which involve the exposure of test coupons prepared from the candidate superheater materials to the flue gases from biomass combustion at controlled metal temperatures and for prolonged periods of time, have been carried out. The work of Montgomery et al (2002), who reported the results of a significant programme of plant-based corrosion testwork in small straw-fired power plants, i.e. Masnedo, Rudkobing and Ensted, in Denmark, has been described in Section 6.3, above.
The power stations were firing cereal straws and both ferritic and austenitic superheater alloys were exposed to the flue gas atmosphere at metal temperatures in the range 450-620ºC. It was found that the measured corrosion rates for the test materials increased with increasing metal temperature, from around <0.05 mm/1000h at 470ºC to values in excess of 1 mm/1000h at temperatures in excess of 600ºC. Clearly, one of the key parameter controlling the corrosion rate is the tube metal temperature.

They also found that all of the alloys tested gave fairly similar corrosion rates at any given temperature, although there appeared to be a shallow optimum in corrosion resistance for alloys with chromium contents in the range 15-18%. These results are not untypical for boilers firing biomass materials, where the corrosion process is driven by the presence of alkali metal chlorides at the metal/corrosion product/deposit interface.

The use of fireside additives to modify the chemistry of the ash deposits may be of some benefit. This is common practice, for instance, in oil-fired boilers, where magnesia-based additives are fairly commonly employed to reduce the rates of metal wastage associated with the relatively aggressive vanadium oxides and sulphates in the oil ash deposits.

Vattenfall has recently developed a fireside additive, which has been of some value in reducing the active chloride concentration in biomass-fired boilers or possibly waste incineration plants, and which may have wider application (Henderson et al. 2006). They reported the use of a proprietary liquid fireside additive, ChlorOut, which was effective in removing KCl from the flue gases, but had only a small effect on the SO\textsubscript{2} concentration and on the pH of the flue gas condensate. The results of 1,000 hour corrosion tests in a 100 MW\texttextsubscript{th} bubbling fluidised bed boiler firing demolition wood, forestry residues and coal in Sweden indicated that there was a significant reduction in the measured corrosion rates when the additive was applied. Vattenfall are currently applying the ChlorOut system, comprising the liquid additive and delivery system, with an in-furnace alkali chloride measurement system, for use in biomass boilers and waste incineration plants.

As stated above, the conventional responses to the excessive metal wastage of boiler tubes due to high temperature corrosion include replacement of the affected tubing with a more resistant material or to protect the tubing with a more corrosion-resistant coating or sleeving, or a weld overlay. The selection of the appropriate materials for these applications is obviously a key issue and this has been the subject of significant laboratory experimentation and boiler probing work.

Montgomery et al (2002) and Henriksen et al (2002) reported the results of an important programme of work which involved the insertion of corrosion probes, with a range of relevant conventional superheater materials into the flue gas stream of a straw-fired boiler, and the measurement of the metal wastage rates. The key results are summarised in Figure 8 (Henriksen et al. 2002). This shows the measured corrosion rates in mm/1000h as a function of the metal temperature. The major trend is clear, with the corrosion rates increasing sharply with increasing metal temperature, as expected. All of the superheater materials tested, which had chromium contents in the range 11.7-18.4%, showed the same trends with temperature. In very general terms, the authors were of the view that the corrosion resistance of the materials tested, with chromium contents in the range quoted above, were fairly similar.
Looking at the absolute corrosion rate values measured during these tests, it is clear that at metal temperatures around 460ºC the measured corrosion rates for all of the materials were less than 0.05 mm/1000h, the equivalent of around 0.4 mm p.a. This is a relatively high corrosion rate, and is probably a result of the relatively short exposure times for the probing trials. At metal temperatures above about 500ºC, the measured corrosion rates for all of the test materials were in the range 0.1-0.3 mm/1000h, or of the order of 0.8-2.4 mm p.a. These are very high corrosion rates, which would result in rapid failure if they were to apply to the boiler tubes.

Overall, therefore, it is clear from both laboratory and plants testwork, and from plant experience, that the high temperature corrosion of superheater tubes is a significant concern in biomass boilers, and particularly in boilers firing fuels with significant chlorine contents. The key to the avoidance of excessive rates of metal wastage is the selection, at the design stage, of the correct combination of the final steam temperature and the tube material for the particular application. It is also clear that the use of fuel additives can be of value in some cases, where problems arise on operating plants.

6.5 The erosion and abrasion of boiler components and other equipment

The erosion and abrasion of boiler components and other equipment in solid fuel-fired plants, at all scales of operation, is associated predominantly with the presence in the fuels and ashes of hard mineral particles, and particularly those that are harder than the steels and refractory materials employed for the construction of the interior surfaces in the boiler. The only mineral species that is commonly found in clean biomass materials in significant levels, and which is in this category, is quartz. Only high quartz biomass materials, or those contaminated with significant levels of tramp materials, are expected to present significant problems with erosion and abrasion of metallic components of the fuel handling and firing equipment.

The fly ashes from biomass combustion on grates and in fluidised beds tend, in the main, to be in fine particulate form and are relatively soft, and are not considered to be particularly abrasive or erosive in nature to boiler tubes and components of the ash handling systems.

In general terms, the majority of the biomass materials under consideration have relatively low ash contents and, for this reason, erosion and abrasion processes tend, on the whole, to be less important than they are in coal-fired plants. There are, however, one or two specific areas where erosion and abrasion can be significant issues, viz:

- The utilisation of some biomass materials, such as rice husks, which have particularly high quartz contents can give rise to abrasion problems in the fuel and ash handling systems and the erosive wear of boiler components,

- The formation of fused ash material, particularly the bottom ashes from grate-fired systems, can cause erosion and abrasion damage to the components of both mechanical and pneumatic ash handling systems,

- In biomass boiler systems which suffer severe convective section fouling problems, excessive rates of particle impact erosive wear of boiler tubes and erosive wear associated with the regular use of convective pass sootblowers, in an attempt to control the impact of the fouling, are common occurrences.
In general terms, however, the experience has been that the ash abrasion and erosion problems associated with the utilisation of the great majority of biomass materials are significantly less important than those experienced when firing more conventional solid fuels.

7. BIOMASS ASH UTILISATION AND DISPOSAL

With the increase in the industrial utilisation of biomass materials for the production of heat and power, and for co-firing with fossil fuels in large power plants, the optimisation of biomass ash utilisation for beneficial purposes and the minimisation of any negative impacts of ash disposal are becoming of increasing importance. For the sustainable utilisation of biomass in dedicated combustion plants, the most beneficial approach involves the return of the ash discards to the field or the forest as a relatively low grade fertiliser, based principally on the lime, potassium and phosphorus contents of the ash.

For clean, untreated biomass materials, this is fairly widely practised worldwide. In the more industrialised countries, where the biomass may contain significant levels of inorganic pollutants, and for ashes from combustion plants burning treated biomass materials, there may be restrictions on the quantities of ash that can be utilised in this way, or specific limits on the concentrations of particular trace element/heavy metal species in ashes that can be returned to the soil. The levels of the inorganic pollutants in the ashes are dependent entirely on the composition of the fuel being fired.

There are also some concerns about the potential for ashes to contain significant levels of organic pollutant species, i.e. polychlorinated dibenzodioxins/furans (PCDD/F) and polyaromatic hydrocarbons (PAH). The concerns are particularly with the fly ashes and boiler deposit materials from grate and fluidised bed boilers, and particularly in cases where the combustion conditions are relatively poor, and the unburned levels in the fly ashes are high. There are generally fewer concerns with the bottom ashes. Since the organic pollutants are principally a product of poor combustion conditions, the preferred means of controlling the levels of organic pollutants in the ashes, in most cases, is to specify a maximum unburned carbon level in the ashes to be utilised for a particular purpose.

If the ash cannot be recycled to the place of origin of the biomass, or utilised as a fertiliser, there are a number of other potential beneficial uses, (Pels et al. 2005), viz:

- The utilisation of bottom ashes from grate-fired and fluidised bed combustors as road construction or landscaping materials,
- The utilisation of fly ashes as a component of cement blends and mortars,
- The utilisation of fly ashes as a component of lightweight aggregates.

The main technical and commercial barriers to biomass ash utilisation for these purposes are that they tend to be available in relatively small quantities compared to other competitive materials, and that there is a perception by the end users that the quality of the fly ashes from biomass combustion processes tends to be relatively inconsistent.
When co-firing biomass materials with coal in large coal-fired boilers, mixed biomass ash/coal ash discard streams are generated, and the technical and commercial issues associated with ash utilisation/disposal are somewhat different from those for dedicated biomass combustion plants. A number of the more important environmental impacts of the operation of large coal-fired power plants are associated with the very large quantities of solid materials discarded from these processes. These are, principally:

- coal ash residues, and
- the solid residues of flue gas desulphurisation processes.

In the main, these materials are produced and handled separately. There are, however, a small number of plants that produce a mixed coal ash/FGD residue discard material.

Very large quantities of these materials are produced. Annual statistics on this are collected by the European Association for Use of the By-products of Coal-fired Power Stations (ECOBA), in Essen, Germany, by the American Coal Ash Association (ACAA) in North America, and by other national organisations.

Ash discards are produced from a number of outlets, including:

- fly ashes from the electrostatic precipitator or bag filter, and boiler ashes from the ash hoppers, commonly located under the boiler economiser and air preheater, and
- bottom ashes and slags from the furnace ash hoppers and slag taps.

On average, around 80% of the total ash discard material from large pulverised fuel-fired boiler plants is in the form of fly ashes from the particle collection equipment, and from the economiser and air preheater hoppers. This is, in the main, a fine, free flowing, dry powder with the great majority of the particles being less than 50 microns in diameter.

The overall level of utilisation of fly ashes in Europe is around 50%, however the rate in different countries varies markedly. In Holland, Germany, Belgium, Italy and Denmark utilisation rates are in excess of 80%, and significant advances have been made in the reclamation of old fly ash dumps. In other countries, utilisation rates are much lower. In Britain, for instance, which produces around 10 million tonnes p.a., the utilisation level is less than 50%. Overall, there is a trend towards the increased utilisation of fly ashes, particularly for higher value uses, as a constituent of construction materials.

For some of the higher value uses of boiler fly ashes, such as for cement and concrete applications, the quality of the fly ash is controlled by a standard specification or classification system. A very useful listing of the international standards and specifications of boiler ashes for different applications is given in www.iflyash.com.

These standards usually specify the weight loss on ignition, the $\text{SO}_3$ content, and the fineness, and sometimes include a specified level of pozzolanic behaviour for the ash, i.e. the tendency to set hard when mixed with lime and water and allowed to dry. In most countries, specialist commercial companies are involved in the treatment,
storage and sale of boiler ashes, principally to the manufacturers of construction materials and the civil engineering industry.

On average, around 20% or so of the total ash discards from pulverised coal-fired boilers is in the form of **bottom ashes and slags**, collected from the furnace ash hopper. In the main, this material comprises fused furnace slags and dislodged ash deposit material. It is very variable in nature, and can range in size from small particles less than 1 millimetre in diameter to large lumps of fused slag up to 1 metre or so in size. Chemically, the boiler bottom ashes are similar to the fly ashes, however they tend to have relatively low unburnt carbon contents and low SO$_3$ contents.

The co-firing of biomass materials with coal will result in the production of mixed ashes, i.e. the fly ashes, and the bottom ashes will comprise components of both the coal and biomass ashes. The chemical and physical properties of the mixed ash discards will clearly depend on the ash contents and qualities of the coal and the biomass ashes, and on the co-firing ratio. The utilisation and disposal of these mixed ash discards will require careful consideration, particularly at elevated co-firing ratios.

For the higher value uses, particularly of the fly ashes, compliance with the standard specifications and classifications will be a requirement, and it should be noted that these standards were not prepared with biomass co-firing in mind. It is sometimes the case that the standards are poorly drafted, and they may be over-prescriptive. In some cases, the standards have been redrafted recently to permit the ashes from biomass co-firing to be utilised in concrete production (Splitsfeld et al. 2001, van Loo and Koppejan 2003).

8. **BIOMASS ASH BEHAVIOUR IN GASIFICATION SYSTEMS**

8.1 Introduction

Gasification processes involve the reaction, generally at temperatures in excess of 700-800°C, of solid or liquid carbonaceous materials with an oxidant, commonly air, oxygen, steam or CO$_2$, but at levels of oxidant well below those required for complete combustion of the material. Gasification reactions, therefore, take place under strongly reducing conditions, overall. The reactions generate sufficient energy to convert the fuel substantially to gaseous products, principally CO, H$_2$, CO$_2$, H$_2$O, a variety of light hydrocarbons and a range of volatile and condensable organic and inorganic species. The product gas can be combusted immediately, or can be cleaned for further processing as a fuel or as a chemical feedstock.

The gasification of coal and other fossil fuels has been the basis of significant, large scale, commercial processes for a long time. The gasification of biomass materials was initially used commercially in the 1940’s as a source of gaseous fuels for internal combustion engines and, over the next 30-40 years, a number of small and medium sized biomass gasification units were introduced for heat and power generation applications. With the increasing interest in the development of renewable energy technologies over the past 20 years or so, there has been a significant increase in the technical interest in biomass gasification processes, particularly in North America and in Europe, however it is fair to say that the more widespread commercialisation of these technologies has been relatively slow.
There are a number of different gasification reactor configurations, depending principally on the scale of operation and the product gas quality requirements, which operate under very different conditions, viz:

- Fixed bed and moving bed systems, which tend, for biomass, to be at the smaller end of the scale, from a few kW\textsubscript{th} up to around 10 MW\textsubscript{th}, principally for the production of heat, but also for small scale power generation.

- Fluidised bed gasifiers, generally operate in the MW range, and are generally of two types, i.e. bubbling fluidised bed (BFB) gasifiers and circulating fluidised bed (CFB) gasifiers. In the main, the CFB units tend to be towards the larger end of the scale, i.e. above around 15 MW\textsubscript{th}.

- Entrained flow gasifiers are generally larger units for power generation and operate at very high temperatures, in excess of 1200°C and for very short residence times. These are normally fired with fossil fuels, and are co-fired with biomass materials at relatively low co-firing ratios.

The nature and behaviour of the inorganic constituents of the biomass are of key importance, both for the designers and the operators of the biomass gasification plants. The more important ash-related issues and problems tend to be similar, in many important respects, to those that apply in biomass combustion systems, viz:

- The fusion or partial fusion of the ash components can result in the formation of ash agglomerates in fixed bed and fluidised bed reactors, leading to poor air distribution and difficulties with ash removal from the system,

- The formation of ash deposits on the furnace and heat exchanger surfaces,

- The potential for increased corrosion rates of gas-side surfaces,

- The carryover of particulate material and of nitrogen, sulphur and chlorine-containing species, along with condensable organic species, into the heat exchangers and gas clean-up systems, and

- The utilisation/disposal of the solid residues from the plant.

In this section, a short summary of the state of the art as regards biomass ash behaviour in gasification processes is presented, covering each of the issues listed above.

### 8.2 Biomass ash fusion behaviour and slag deposition in gasification systems

The fusion behaviour of fuel ashes, as most commonly expressed in melting curves or the results of the Ash Fusion Test, as described in Section 2 above, is of key practical importance in gasification systems because of the tendency for fused or partly fused ash particles to form agglomerates and slag deposits in the gasification reactors. This can result in significant operational difficulties, and is a key concern for plant designers and operators.

In fixed bed gasifiers, the chemical reactions and temperature profiles are quite complex and, particularly in updraft gasifiers, the temperatures in the oxidation zone can be up to around 1200°C or so. There is potential for significant ash fusion to occur in these systems. The successful operation of fixed bed reactors depends to
a large extent on the maintenance of a good bed structure, good air and gas
distribution through the bed and the effective operation of the ash take-off system.
The tendency for ash to fuse and agglomerate, and to cause channelling within the
bed and difficulties with the ash removal system, are important factors in the design
and operation of these processes.

To date, the majority of small fixed bed gasifiers for biomass have been fuelled with
relatively high grade wood chips with very low ash contents, or biomass materials
with relatively high ash fusion temperatures, such as rice husks. Systems capable
of handling more difficult fuels, i.e. with higher ash contents and with more difficult
ashes are not well demonstrated. The ash content of the biomass and the ash
fusion temperatures are key components of the fuel specifications for gasifiers.
Fuels with significant ash contents and low ash fusion temperatures, i.e. with
deformation temperatures less than about 1200ºC, present particular problems and
commonly excluded from the ranges of acceptable fuels for fixed bed gasification
systems.

There is also a tendency for low fusion temperature ashes to form fused or partly-
fused slag deposits on the walls of the reactor. Excessive slag formation can result
in significant interference with the performance of fixed bed reactors and the
gasification process.

Air blown, atmospheric pressure, fluidised bed gasifiers for biomass are most
commonly applied commercially for medium-large scale applications, for the
generation of heat and power. Oxygen or steam-blown fluidised beds, and
pressurised systems, have been developed, but these are more complex and
expensive, and have tended to be less popular.

The fouling of furnace and heat exchanger surfaces, and the formation of ash
agglomerates and the subsequent defluidisation of the bed, are key process issues,
and these have been fairly extensively studied at laboratory, pilot plant and industrial
scale.

One of the key processes in fluidised bed gasifiers is the formation of agglomerates
within the bed by interaction between the inorganic compounds released from the
fuel and the bed material particles. As in fluidised bed combustion systems, the
principal ash components involved in these reactions are the alkali metals. The
interactions involved are relatively complex, and have been extensively studied over
the past twenty years or so (Ergudenler, 1992, Zevenhoven-Onderwater et al, 2001,
Visser et al. 2001).

Ergudenler et al (1992) carried out a series of laboratory scale tests in a muffle
furnace and a model fluidised bed reactor. They found that the silica sand-straw ash
mixtures began to agglomerate at temperatures around 800ºC and that around
850ºC, significant fusion had occurred, with the formation of a hard brittle mass. The
relatively low bed material agglomeration and fusion temperatures were considered
to be due principally to the presence of high levels of K2O in the straw ash and the
low solidus temperatures of the potassium silicates.

The biomass ash bed material systems were studied in more detail by Zevenhoven
et al (2001). They looked at seven different biomass materials, with ash contents
varying in the range 1.5-8.5% on a dry basis, and including:
Reed canary grass, miscanthus and Arundo Donax, which have ash compositions dominated by SiO$_2$.

Lucerne, forest residue and eucalyptus, which have ashes with relatively low SiO$_2$ concentrations, and

Salix, which has intermediate ash composition with significant levels of SiO$_2$, CaO and K$_2$O.

Thermodynamic multi-phase multi-component equilibrium (TPCE) calculations were carried out, and predictions were made of the distribution of potassium-containing phases, i.e. solid silicate, solid salt, silicate melt, salt melt and gas phase, at 700 and 900ºC, for both the ashes alone and in contact with silica, calcium carbonate and dolomite bed materials.

Calculations were also made of the initial melting temperature ($T_0$) of the ashes and of the ashes with the different bed materials. The data are reproduced in Table 6, in which the ashes have been reorganised in order of increasing SiO$_2$ content. The compositions of the condensed phases, i.e. solid and liquid silicates, solid and liquid salts and other phases, for the full range of ashes and bed materials were also calculated.

The authors made the following conclusions, based on the results of the TPCE calculations:

- For the biomass ashes rich in silica or using a silica bed material, the risks of bed agglomeration were high, with significant melting of the ash at temperatures around 800ºC, i.e. at normal bed temperatures for fluidised bed gasification systems for biomass materials,

- For the biomass ashes rich in CaO or when processes using a CaO-rich bed material, the risks of bed agglomeration at normal bed temperatures were significantly lower.

The results of laboratory testwork in a small 20 kW$_{th}$ fluidised bed test rig, were also presented. The results confirmed the basic agglomeration mechanism, i.e. that the formation of molten phases acted as a ‘glue’ for the bed material particles. The presence of a silica bed material promoted the formation of low melting temperature alkali metal silicates which played a key role in bed particle agglomeration at bed temperatures around 800ºC, which is reasonably consistent with industrial plant experience.

Overall, it is fairly clear that the bed agglomeration processes that occur in fluidised bed gasification plants are similar to those in combustors and involve the formation of low melting phases rich alkali metal silicates that form coatings around the bed material particles, at temperatures in excess of around 750-800ºC. These processes are not greatly affected by the reducing conditions that apply in gasification systems.

The alkali metal-rich coatings can be formed either from the vapour phase or by the fusion of alkali metal-rich ash particles. The agglomerates are then formed by a viscous flow sintering process with neck growth between the more refractory bed particles. At industrial scale, the agglomeration process is exacerbated by imperfect fuel and air distributions, which can give rise to hot spots in the bed. These tend to
act as locations where initiation of more extensive bed agglomeration can occur. When agglomerates form they can act to disturb the local air distribution and act as sites for further agglomeration to occur. In more extreme circumstances, the agglomerates can grow to the point where defluidisation of significant regions of the bed can occur, and it may be necessary to take the unit off-line to replace the bed material.

In practice, the key to avoiding bed agglomeration is the establishment of good fuel and air distributions, and operation at a bed temperature that is appropriate for the chemistry and fusion behaviour of the fuel ash, and bed material. It is also apparent that circulating fluidised beds, which operate at significantly higher fluidisation velocities, are generally less prone to bed agglomeration problems than are bubbling beds.

There can be a tendency for the low melting components of the biomass ash to sinter and form fused or partly-fused slag deposits on the walls of the furnace, very similar to those that can occur within fluidised bed combustors. This can result in significant interference with the operation of the gasification process. Large ash deposits can detach from the furnace walls, and contribute to bed agglomeration and defluidisation processes.

**Entrained flow gasifiers** are generally relevant to medium-large scale applications, and dedicated entrained flow units are relatively rare for biomass materials. In some cases, cyclone burners have been applied for the combustion of pre-milled biomass materials, and the cyclone chamber essentially operates as a gasifier. The cyclone chambers are generally refractory-lined and operate at gas temperatures around 800-900ºC. These are sensitive to ash deposition and accumulation within the cyclone chamber, and have been applied principally for low ash materials.

More commonly, biomass and waste materials have been co-fired in large coal-fired integrated gasification combined cycle (IGCC) plants and significant technical work has been done on the ash-related impacts. Coda et al (2004), for instance, reported the results of an extensive programme of experimental and modelling work, associated with the ash-related effects of the co-firing of sewage sludges and other biomass materials at the 253 MWe Willem Alexander IGCC plant at Buggenum in the Netherlands. The results of this work will be described in Section 8.3 below.

The majority of the entrained flow gasification systems for coal fire dry milled fuel or aqueous slurries, and are designed to operate at very high temperatures and for short residence times. The pre-milled biomass materials are normally mixed with the fossil fuel feed material. A portion of the ash is retained within the reactor and is drawn off at a slag tap at the bottom. The fly ash carried over from the reactor normally comprises small molten ash particles entrained in the syngas.

Overall, it is clear that the relatively low fusion temperatures of some of the components of the inorganic fraction of biomass materials can cause problems in all types of gasifier. In the main, the responses have been to restrict the range of biomass materials that can be fired in particular systems and to introduce specific design features for particularly troublesome fuels. In general terms, the appropriate fuel characterisation techniques and predictive methods are available, however industrial experience, particularly with the more difficult biomass fuels, is limited.
8.3 The fouling of heat exchangers and other components in biomass gasification plants

As with biomass combustion systems, the fouling of heat exchangers and other plant components has been one of the most common problem areas with gasification systems for biomass at industrial scale. The syngas produced from the gasification of biomass materials can have significant levels of both inorganic and organic volatile species, which can condense on cooled surfaces in the syngas coolers and gas cleaning systems. This has been a significant issue in industrial plants, both in dedicated biomass gasification systems and in the co-gasification of biomass with coal in large gasifiers, and has been the subject of intensive study over the past few years, see, for instance, Kiel (2002). The following industrial cases, where the fouling of syngas cooling equipment has caused significant operational problems, illustrate the importance of this issue:

- The Amer-9 project involved the installation of an 85 MW th wood-fired CFB gasification plant in the Netherlands, where the cleaned syngas is co-fired in a large 600 MW e coal-fired boiler. Very rapid and serious fouling of the water tube syngas cooling unit was experienced during commissioning, and in response to these problems, major modifications were made to the syngas cooling and cleaning system.

  The original configuration involved cooling the raw syngas to around 200ºC, followed by particulate collection in a fairly conventional fabric filter and wet scrubbing to remove halogens, ammonia and tars. This system involves fairly extensive cleaning of the syngas, with a view to firing a wide range of biomass materials without causing emissions and ash-related problems in the large coal boiler. The fouling problems in the syngas cooling unit were associated principally with the deposition of the tars and chars, although the carryover of ashes and elutriated bed material does contribute to the deposition process.

  The modified system involves cooling the syngas to around 500ºC, i.e. at a temperature above the tar dewpoint, followed by particulate collection in a hot cyclone. The extent of cleaning of the syngas, therefore, is significantly reduced, and this has implications on the fuel flexibility of the system. The modified system has been in operation since December 2002, with reasonably satisfactory performance.

- The small (8 MW e) biomass-fired IGCC demonstration project in Yorkshire, England (Project ARBRE) had numerous problems, and was never properly commissioned. One of the most important technical problems was the very rapid blockage of the syngas cooler, principally with ashes and bed material from the gasifier and tar cracking units. It became apparent very quickly that the syngas cooler design was woefully unfit for purpose. Plans to replace this unit and complete the commissioning of the plant were never implemented, and the project went into liquidation.

The general requirements for syngas cooling in integrated biomass gasification systems is illustrated in the schematic diagram presented by van der Drift and Pels (2004), which is reproduced in Figure 9.

It is clear from the analysis presented by these authors and by Kiel (2002) that the technical issues associated with the quality of the syngas, the deposition mechanisms and the design of the syngas coolers had been seriously
underestimated by the plant designers, and that these issues should be the subjects of significant further study.

Based on the results of a fairly extensive programme of laboratory testwork and detailed examination of syngas cooler deposits from the Amer plant, van der Drift and Pels presented a description of the key deposition mechanisms. It was found that the deposits on the heat exchange surfaces in the syngas cooler comprise two distinct layers, viz;

- A relatively dense inner layer formed principally by the condensation of tars, at surface temperatures up to around 350°C, which is considered to be the maximum dew point temperatures of the tars from CFB gasifiers. The condensation of the tars is followed by further reactions within the tar deposits, which produce higher molecular weight compounds.

- A porous gas-side layer comprising loosely bound char particles can be formed on the outside of the layer of condensed tars, and this can be quite extensive and can have a dramatic impact on the heat transfer. The outer layer is mechanically weak and will only form when the syngas is non-erosive, i.e. at low gas velocities and low char particle loadings.

The ash components are present in the syngas in relatively low concentrations and play only a minor role in the fouling mechanism.

It is clear from the results of this work that the formation of syngas cooler deposits by tar condensation is a very difficult problem, and that effective remedial measures involve a fairly fundamental redesign of the syngas cooling and cleaning systems.

The problems at the Project ARBRE were associated principally with the relatively high levels of carryover of inorganic material from the gasifier and tar cracking unit in the syngas, and the inability of the syngas cooler to cope with the dust loading without physical blockage.

Problems with fouling of syngas cooling section have also been experienced when co-firing biomass and waste materials in large coal-fired IGCC plants. As stated above, a fairly wide range of biomass and waste materials have been co-fired in the Willem Alexander IGCC plant at Buggenum in the Netherlands, including principally sewage and paper sludges, wood, and poultry litter, at co-firing ratios up to around 30% on a mass basis. A number of other materials have been co-fired in small quantities.

In most cases, no significant operational problems have been experienced. It has been found, however that the co-firing of sewage sludges resulted in significant fouling deposit formation on the surfaces of the syngas cooler, particularly in the high temperature regions, and that this was related to a significant change in the ash chemistry. This has been the subject of a programme of experimental and modelling work, reported by Coda et al (2004), in an attempt to identify the deposition mechanisms and to determine the appropriate remedial measures.

The results of this work identified the importance of phosphorus-rich, low melting temperature phases in the alumino-silicate deposit materials, which can lead to enhanced deposit ‘stickiness’. The most promising remedial measures identified in the report are based on the increase of the calcium content of the ash and deposit materials to promote the formation of phosphorus-rich phases of higher melting
temperatures. The work also identified that there was a limited amount of basic chemical and thermodynamic data on the behaviour of the key biomass and waste ash components under the conditions that apply in large entrained flow gasifiers, i.e. very high temperatures and intense reducing conditions.

Overall, therefore, it is clear that the fouling of syngas coolers, by the condensation of tars and/or the deposition of ash materials, has been one of the more important technical issues associated with the gasification and the co-gasification of biomass materials. It is fair to say that the significance of a number of these problems had not been anticipated by the industry, and that there has been, in a number of instances, a requirement for major redesign of the syngas cooling and gas cleaning systems, and modification of the plant operations. It is also not clear that the technical issues are now fully understood and that the appropriate design features and mitigation/remedial measures are in place. Significant further research and development work in this technical subject area is required to help to reduce the risks of syngas cooler fouling deposit formation and the associated problems for future projects.

8.4 The removal of ash and other particulate material from the syngas

As stated above, the utilisation of the syngases from biomass gasification systems as fuels for boilers, gas engines and gas turbines, and as a feedstock for further processing, commonly requires significant clean-up of the syngas to remove both particulate material and the acid gas species. This is of increasing importance and technical difficulty, as the trend towards using cheaper, more difficult and higher ash biomass materials, driven by the requirement to improve the overall energy conversion process economics, has intensified over the past few years.

The major undesirable constituents of the syngases are:

- Particulate materials entrained in the syngas,
- Low and high molecular weight organic compounds (tars),
- H₂S, COS and other sulphur gases,
- NH₃, HCN and other nitrogen-containing species,
- Other impurities, including HCl, and volatilised alkali metals and heavy metals.

The nature and concentration of the particulate material depends on the fuel, the type of gasifier and the operating conditions. The general ranges of tar and particulate matter concentrations from different gasifier types are presented in Figure 10. It is clear from the data on this figure that the particulate carryover levels from fluidised bed and entrained flow gasifiers, which generate relatively small quantities of bottom ashes, tend to be much higher than those from fixed bed units, which are designed specifically to retain the ash within the reactor.

In general terms, the particulate materials from biomass gasifiers comprise the inorganic constituents of the fuel, partly converted fuel (char) and soot particles. In the case of fluidised bed gasifiers there may also be small particles of bed material or other inorganic materials carried over from the gasifier units.
The total syngas particulate concentrations in most systems are a function of the gasification process, the ash content of the fuel and the carbon conversion level. In most systems, the total particulate loadings are generally of the order of 1-10 g Nm$^{-3}$ of syngas. The carbon contents of the particulates are commonly in the range 10-50% by mass, with the balance being ash. The optimisation of the gasification process can result in higher carbon conversion rates, and a corresponding reduction in the total particulate levels and the carbon content of the particulates. However it is clear that the carbon conversion levels in most commercial gasification systems for biomass are of the order of 94-99%, and the scope for significant improvement in most systems is limited (Nieminen et al., 2004).

The most commonly applied particulate capture technologies and the levels of capture efficiency available are listed in Table 7. It is clear from the data on this table that the majority of these technologies are only suitable for pre-treatment of the syngases, and that only fabric and ceramic filters, and electrostatic precipitators, are capable of particulate collection efficiencies capable of particulate collection efficiencies appropriate to the utilisation of the syngases in gas engine and gas turbine applications (Kleinhappl, 2002). Some applications involving the co-firing of the gas with coal may have lower syngas quality requirements and lower efficiency particulate collection may be sufficient.

As stated above, the principal problems encountered when designing syngas cooling and cleaning systems for particular applications are associated with the presence of condensable organic species, and the impact of these species on the operation of the gas cooling and cleaning equipment. This is still a subject of significant development work and a complete description of the issues involved is outside the scope of this document.

### 8.4 The utilisation and disposal of the solid residues from biomass gasification systems

The success of the commercialisation of biomass gasification technologies for the production of heat and power will be dependent, at least partly, on the availability of suitable outlets for the solid residues from the plants. This is also the case for biomass combustion technologies, as described above, however the solid residues from gasification processes commonly present additional problems in this regard and may require significant treatment prior to utilisation and/or disposal (Nieminen et al., 2004).

The key technical issues are the relatively high levels of carbonaceous material, and the incomplete oxidation of the inorganic constituents of the solid residues of most gasification processes. These issues can represent barriers to both utilisation and disposal routes for the residues. For most applications, there may be a requirement for further treatment, and principally oxidation of the ashes to reduce the char content and the levels of adsorbed organic species, and to convert the ash constituents to oxides in their highest oxidation states. There is also some interest in the simple fractionation of the gasification ashes into different grades, based either on their particle size or carbon content, for different applications.

As with the ash residues from combustion processes, the preferred route for utilisation of the gasifier residues is to recycle them directly to the land on which the fuel was produced, or to utilise the residues as a low grade fertiliser (van loo and Koppejan, 2003). The quality standards for this utilisation route are high since the residue materials are being used to replace natural raw materials, and it is clear that
in many cases, the gasification residues may require significant and relatively expensive upgrading before use.

The alternative is landfill disposal of the gasifier residues, however it is also clear that the increasing environmental standards associated with the landfill disposal of solid residues and other wastes will increase disposal costs, and may present barriers to the disposal of untreated residues.

The potential problems with the utilisation and disposal of ash residues from biomass gasifiers have been recognised, and this was the subject of an EU 5th framework project entitled GASASH. It was clear from the results of the work done under this project that the ash residues from biomass gasification processes tend to be significantly less attractive for most ash utilisation and disposal routes for the reasons given above.

In most cases, further oxidation of the gasification residues will be required. There is the possibility that the residues may have some value as a low grade fuel for combustion processes, when the combustible matter content is greater than about 35-40%. There is also the possibility of further treatment of the solid residues by leaching/washing to reduce pollutant levels, mechanical separation into fractions and immobilisation/pelletisation. The economics of these residue treatments are clearly open to question, and the key factors in residue disposal in future are likely to be the quality requirements and the gate fees for landfill disposal.

The experience of the biomass/waste gasification unit at Kymijarvi power station in Lahti, Finland, is also relevant in this context. One of the areas of concern in the initial stages of the project was associated with the ash behaviour and in particular with the utilisation/disposal of the gasifier bottom ashes and with the mixed ashes from the coal boiler when co-firing the uncleaned syngas (Wilén et al, 2004).

The Kymijarvi power plant was originally an oil-fired boiler (125 kg s⁻¹ of steam at 540°C and 170 bar), commissioned in 1976, which was converted to pulverised coal firing in 1982. The maximum electricity production is 167 MWe and the maximum district heat production is 240 MWth. A 50 MWth gasifier for biomass/secondary recovered fuel (SRF) was installed in 1997. The syngas from the gasification unit is fired directly into the boiler furnace with no prior clean-up. The gasification system has been operation, with high availability since installation, firing a variety of fuels including a variety of both wet and dry wood materials, the SRF, and shredded tyres. Only the shredded tyres had a significant impact on the operation of the gasifier. Significant accumulation of the wire occurred leading to blockage of the gasifier ash extraction system, and the gasifier had to be shut down. The introduction of the low calorific value syngas, at up to around 15% heat input, has had very little negative impact on the operation and environmental performance of the pulverised fuel boiler.

The biomass/waste gasifier and boiler system generates three major solid discard streams, viz:

- The biomass/waste gasifier bottom ash,
- The coal boiler bottom ash, and
- The boiler filter ash.
The gasifier bottom ash comprises principally the sand and limestone bed materials, with small quantities of tramp inorganic materials from the fuel, i.e. small pieces of metal, stone glass, concrete, etc. The unburned carbon content is generally less than 0.5%. In general terms, the gasifier bottom ashes were clean with low levels of the trace elements. Only when processing the shredded tyres were there significant increases in the trace elements levels and, in particular, zinc. The results of standard tests on the bottom ashes indicated low levels of the key organic pollutants and low trace element leachability, and the disposal of the ashes has not presented specific difficulties.

The solid discards from the coal boiler comprise principally coal ash mixed with up to 3-5% of the biomass/SRF ash materials. In general terms, the results of extensive analysis and testwork has indicated that the levels of unburnt carbon and of the key organic and inorganic pollutant species when co-firing the syngas were within the ranges normally found when firing coal alone. The results of the ash leaching tests also indicated similar behaviour, and the Finnish authorities have continued to permit the use of the ashes from co-firing as a constituent of construction materials, although new permissions have to be sought if there is a significant change in the biomass/waste fuels fired in the gasification system.

It should also be noted that the results of a programme of boiler deposition monitoring, inspection and probing work has indicated that there was no detectable changes in the ash deposition behaviour when co-firing the syngas compared to that for 100% coal firing.

Overall, therefore, the results of the demonstration project at the Kymijarvi power station in Lahti, Finland have indicated that the co-firing, at up to 10-15% on a heat input basis, of the untreated syngas from the gasification of biomass and SRF materials can be achieved successfully and with no significant additional environmental impacts compared to 100% coal firing.

9. BIOMASS ASH BEHAVIOUR IN PYROLYSIS PROCESSES

Pyrolysis processes involve the thermal treatment of the biomass at modest temperatures, generally in the range 400-1000°C and at oxygen partial pressures below those necessary for appreciable gasification reactions to occur. Three products are formed, viz:

- A pyrolysis vapour,
- A liquid phase, and
- The solid residues, comprising both char and inorganic materials.

The proportions of each of these products depend on the characteristics of the fuel and the pyrolysis conditions, although it is fair to say that the current interest in biomass pyrolysis is focussed largely on the production of the pyrolysis liquids or bio-oils, which may in the future command relatively high prices.

There are a number of general types of pyrolysis systems, depending on the desired products, and these are listed in Table 8. In general terms, the slower, lower temperature processes generate higher levels of char and the faster, higher temperature processes generate higher levels of liquid and gaseous products.
A number of specific process technologies for the pyrolysis of biomass materials are under development, at up to demonstration scale, principally in Europe and North America. The basic characteristics of a number of the key test rigs and pilot plants are listed in Table 9.

It is fair to say that pyrolysis technologies for biomass materials have not, as yet, achieved full commercialisation and that there is no practical experience of the operation of industrial scale pyrolysis processes. The majority of the development work on the test rigs and pilot plants has been concerned with the basic performance of the reactors over relatively short operating campaigns, and with the quantification and characterisation of the principal pyrolysis products.

To date, much of this work has been with relatively clean biomass materials of modest ash content, and principally with clean wood materials, in which the ash is predominantly in inherent form. It is considered that the utilisation of biomass feedstocks with higher ash contents, such as straws and other agricultural residue materials, and waste materials, which have significant levels of extraneous mineral materials, may present ash-related problems in the design and operation of industrial scale plant, and potentially with the quality of the products and residues from the process. This subject area, however, has not been extensively studied to date and there is no relevant industrial experience.

In most pyrolysis systems, the operating temperatures are fairly modest. It is commonly found at laboratory and rig scale that the inherent mineral material in the biomass tends to be retained within the char, and is not released into the gas or vapour phase in sufficient quantities to cause ash deposition or other operational problems within the reactor or in the gas collection equipment.

There is relatively little information available in the technical literature about the more practical ash-related aspects such as ash deposition, corrosion and erosion/abrasion. These tend to be relatively long term operational issues and are not always suitable for study in small test rigs and pilot plants.

One ash-related issue that has been studied at laboratory and test rig scale is the effect of the presence of inherent mineral material, and particularly the alkali and alkaline earth metals, in the catalysis of the pyrolysis process (Coulson et al 2004). The catalytic influence of ash components in pyrolysis processes tends to increase the reaction rate of the larger organic molecules producing higher levels of smaller, highly oxygenated organic compounds, CO and water. This can result in a significant reduction in the measured yields of bio-oils, and in the production of bio-oils with higher water contents, which may be unstable or in multiple, immiscible liquid phases.

The effect of the mineral material on the pyrolysis process was demonstrated by the results of testwork in a small fluidised bed pyrolysis test rig operating at temperatures in the range 425-550ºC. The fuels included a number of energy crop materials with a range of ash contents. It was found that the Arundo and Cardoon materials which have relatively high ash contents provided relatively low yields of liquid products, generally less than 50%, and this was accompanied by high levels of water in the liquid products. Reduction of the ash content, and particularly the levels of alkali metals, by water washing prior to pyrolysis, resulted in increased yields of liquid products, up to around 60% and closer to the levels expected for low ash, wood biomass materials.
There is also some concern about the potential for the biomass ash material to cause bed particle agglomeration in fluidised bed pyrolysis reactors. The concerns are very similar to those described for combustion and gasification systems in Sections 3.2 and 8.2 above. As stated above, the fusion temperatures of the biomass ash materials, and particularly those rich in alkali metal compounds, can be relatively low and this may have an impact on the design bed temperatures of fluidised bed pyrolysis reactors. In some cases, it is proposed that the chars generated in biomass pyrolysis reactors will be burned in fluidised bed char combustor units, for the generation of process heat. Since the great majority of the mineral material within the biomass will be associated with the char, the ash content of the chars will be concentrated by a factor of five or more, compared to that in the biomass, depending on the char yield. There are, therefore, significant concerns about potential problems with bed agglomeration in these units, as described above, more generally, for fluidised bed combustors.

10. REFERENCES

American Coal Ash Association (ACAA) [www.acaa-usa.org](http://www.acaa-usa.org) provides up-to-date statistics on coal ash production and utilisation in the USA.

Ahonen M, Long-time experience in catalytic flue gas cleaning and catalytic NOx reduction in biofuelded boilers, VTT Symp. 163, (1996)


Biobank, a database of biomass properties which is compiled by Bios Bioenergiesysteme GmbH, in Austria, is available on the IEA Biomass Combustion and Co-firing website, [www.ieabcc.nl](http://www.ieabcc.nl)

BIOBIB is a database of biomass properties, available on [www.vt.tuwien.ac.at](http://www.vt.tuwien.ac.at)

CATDEACT website at www.eu-projects.de


prCEN/TS 15289 Solid biofuels. Determination of total content of sulphur and chlorine.


European Coal Combustion Products Association (ECOBA) publishes useful information on the solid discards from coal plants. www.ecoba.com


Korbee R, Keil J H A, Zevenhoven M, Skrifvars B-J, Jensen P A and Frandsen F J. Investigation of biomass inorganic matter by advanced fuel analysis and


Obernberger I, Brunner T and Joller M, Characterisation and formation of aerosols and fly ashes from fixed-bed biomass combustion. Aerosols from Biomass Combustion, Zurich (2001)


Phyllis, a database of biomass properties, which has been compiled by ECN in the Netherlands. www.ecn.nl/phyllis.


USDOE, has compiled a database of biomass feedstock composition and property data. www.eere.energy.gov/biomass/feedstock_databases.html

Valmari T, Potassium behaviour during combustion of wood in circulating fluidised bed power plants. VTT Publication 414 (2000)


<table>
<thead>
<tr>
<th>Agricultural products</th>
<th>Forestry products</th>
<th>Domestic and municipal wastes</th>
<th>Energy crops</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harvesting Residues</td>
<td>Harvesting residues</td>
<td>Domestic/Industrial</td>
<td>Wood</td>
</tr>
<tr>
<td>Cereal straws</td>
<td>Forestry residues</td>
<td>Municipal solid waste (MSW)</td>
<td>Willow</td>
</tr>
<tr>
<td>Oil seed rape and linseed oil straws</td>
<td></td>
<td>Refuse-derived fuels</td>
<td>Poplar</td>
</tr>
<tr>
<td>Flax straw</td>
<td></td>
<td>Construction and demolition wood wastes</td>
<td>Cottonwood</td>
</tr>
<tr>
<td>Corn stalks</td>
<td></td>
<td>Scrap tyres</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waste pallets</td>
<td></td>
</tr>
<tr>
<td>Processing residues</td>
<td>Primary processing wastes</td>
<td>Urban green wastes</td>
<td>Grasses and other crops</td>
</tr>
<tr>
<td>Rice husks</td>
<td>Sawdusts</td>
<td>Leaves</td>
<td>Switchgrass</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>Bark</td>
<td>Grass and hedge cuttings</td>
<td>Reed canary grass</td>
</tr>
<tr>
<td>Olive residues</td>
<td>Offcuts</td>
<td></td>
<td>Miscanthus</td>
</tr>
<tr>
<td>Palm oil residues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citrus fruit residues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Animal wastes</td>
<td>Secondary processing wastes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poultry litter</td>
<td>Sawdusts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tallow</td>
<td>Offcuts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meat/bone meal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 The major biomass materials of industrial interest on a worldwide basis
<table>
<thead>
<tr>
<th>Element</th>
<th>Class 1 - water soluble (free ionic form)</th>
<th>Compound Formula</th>
<th>Share of total element (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Sodium nitrate, chloride</td>
<td>NaNO₃, NaCl</td>
<td>&gt;90</td>
</tr>
<tr>
<td>K</td>
<td>Potassium nitrate, chloride</td>
<td>KNO₃, KCl</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium nitrate, chloride, phosphate</td>
<td>Ca(NO₃)₂, CaCl₂, Ca₃(PO₄)₂</td>
<td>20-60</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium nitrate, chloride, phosphate</td>
<td>Mg(NO₃)₂, MgCl₂, Mg₃(PO₄)₂</td>
<td>60-90</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon hydroxide</td>
<td>Si(OH)₄</td>
<td>&lt;5</td>
</tr>
<tr>
<td>S</td>
<td>Sulphate ion</td>
<td>SO₄²⁻</td>
<td>&gt;90*</td>
</tr>
<tr>
<td>P</td>
<td>Phosphate ion</td>
<td>PO₄³⁻</td>
<td>&gt;80*</td>
</tr>
<tr>
<td>Cl</td>
<td>Chloride ion</td>
<td>Cl⁻</td>
<td>&gt;90%*</td>
</tr>
</tbody>
</table>

| Class 2 – organically associated (covalent or ionic bonding with tissue) |
|------------------------|------------------------|------------------------|
| Ca         | Calcium pectate        | macromolecule          | 0.8-2.6                  |
| Mg         | Chlorophyll, magnesium | C₅₅H₇₂MgN₄O₅,         | 8-35                     |
|            | pectate                | macromolecule-         |                          |
| Mn         | Various organic structures | Mn²⁺, Mn³⁺, Mn⁴⁺       | >90*                     |
| Fe         | Organic complex, organic | Fe³⁺, Fe²⁺             | >80*                     |
|            | sulphates              |                        |                          |
| S          | Sulpholipids, amino acids, | SO₄²⁻, S              | -                        |
|            | proteins               |                        |                          |
| P          | Nucleic acids          | PO₄³⁻                 | -                        |

| Class 3 – precipitated (pure compound, amorphous or crystalline) |
|------------------------|------------------------|------------------------|
| Ca         | Calcium oxalate        | CaC₂O₄ₙH₂O             | 30-85                    |
| Fe         | Phyt ferritin          | (FeO.OH)ₐₙ(FeO.OPO₃H₃) | Up to 50 in leaf tissue |
| P          | Phytates               | Ca-Mg(-K)-salt of C₆H₆[OPO(OH)]₂ₙ | Up to 50-86% in seeds |
| Si         | Phytolite              | SiO₂ₙH₂O               |                          |

Table 2 Speciation of inorganic materials in higher plants, according to the classes “water soluble”, organically associated” and “precipitated”. (after Korbee et al., Marschner, 1997). Note that for items marked * no quantities have been reported. The value quoted indicates that the speciation is the dominant one for that element.
<table>
<thead>
<tr>
<th>Biomass type</th>
<th>Coniferous forestry residue</th>
<th>SRC willow</th>
<th>Cereal straw</th>
<th>Oil seed rapeseed straw</th>
<th>Miscanthus</th>
<th>Reed canary grass</th>
<th>Olive residue</th>
<th>Palm Kernel</th>
<th>Poultry litter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur content (%; w/w, dry ash-free basis)</td>
<td>0.04</td>
<td>0.05</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Chlorine content (%; w/w, dry ash-free basis)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.4</td>
<td>0.5</td>
<td>0.2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Ash content (%; w/w, dry basis)</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>6</td>
<td>7</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>Elemental analysis (mg kg⁻¹; dry basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>1,500</td>
<td>750</td>
<td>600</td>
</tr>
<tr>
<td>Ca</td>
<td>5,000</td>
<td>5,000</td>
<td>4,000</td>
<td>15,000</td>
<td>2,000</td>
<td>3,500</td>
<td>6,000</td>
<td>3,000</td>
<td>20,000</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>900</td>
<td>2,500</td>
<td>900</td>
</tr>
<tr>
<td>K</td>
<td>2,000</td>
<td>3,000</td>
<td>10,000</td>
<td>10,000</td>
<td>7,000</td>
<td>12,000</td>
<td>23,000</td>
<td>3,000</td>
<td>21,000</td>
</tr>
<tr>
<td>Mg</td>
<td>800</td>
<td>500</td>
<td>700</td>
<td>700</td>
<td>600</td>
<td>1,300</td>
<td>2,000</td>
<td>3,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Na</td>
<td>200</td>
<td>-</td>
<td>500</td>
<td>500</td>
<td>-</td>
<td>200</td>
<td>100</td>
<td>200</td>
<td>3,000</td>
</tr>
<tr>
<td>P</td>
<td>500</td>
<td>800</td>
<td>1,000</td>
<td>1,000</td>
<td>700</td>
<td>1,700</td>
<td>1,500</td>
<td>7,000</td>
<td>14,000</td>
</tr>
<tr>
<td>Si</td>
<td>3,000</td>
<td>-</td>
<td>10,000</td>
<td>1,000</td>
<td>-</td>
<td>12,000</td>
<td>5,000</td>
<td>3,000</td>
<td>9,000</td>
</tr>
</tbody>
</table>

Table 3  Typical ash elemental analysis data (major elements) for a number of industrial important biomass materials. (These data are for relatively clean materials.)
<table>
<thead>
<tr>
<th>System</th>
<th>Melting/eutectic temperature (°C)</th>
<th>Composition at the eutectic point (mole % alkali)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>801</td>
<td>-</td>
</tr>
<tr>
<td>KCl</td>
<td>772</td>
<td>-</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>677</td>
<td>-</td>
</tr>
<tr>
<td>CrCl₂</td>
<td>845</td>
<td>-</td>
</tr>
<tr>
<td>NaCl-FeCl₂</td>
<td>370-374</td>
<td>c. 56</td>
</tr>
<tr>
<td>KCl-FeCl₂</td>
<td>340-393</td>
<td>45.8-91.8</td>
</tr>
<tr>
<td>NaCl-CrCl₂</td>
<td>437</td>
<td>53.7</td>
</tr>
<tr>
<td>KCl-CrCl₂</td>
<td>462-457</td>
<td>36-70</td>
</tr>
</tbody>
</table>

Table 4  Melting/eutectic temperatures for pure compounds and binary mixtures relevant to chloride rich, biomass ash deposits and the associated corrosion reactions (after Nielsen et al., 2000).
<table>
<thead>
<tr>
<th>Plant</th>
<th>Steam temperature (°C)</th>
<th>Metal surface temperature (°C)</th>
<th>Corrosion morphology</th>
<th>Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masnedo</td>
<td>520</td>
<td>450-570 460-615 Average 580</td>
<td>Protective oxide formation with grain boundary attack – oxide has a tendency to spallation. Selective corrosion and grain boundary attack at the higher temperatures. Protective oxide at the lower temperatures. Selective corrosion and grain boundary attack.</td>
<td>KCl with K2SO4 adjacent to the surface oxide. Iron oxide dendrites in both.</td>
</tr>
<tr>
<td>Rudkoping</td>
<td>450</td>
<td>520-650</td>
<td>Formation of a protective oxide</td>
<td>Predominantly KCl, minor amounts of sulphates and silicates or K2SO4 with some KCl. Iron oxide dendrites in both.</td>
</tr>
<tr>
<td>Ensted</td>
<td>470 447</td>
<td></td>
<td>Selective corrosion</td>
<td>K2SO4 with minor amounts of KCl. Iron oxide dendrites</td>
</tr>
</tbody>
</table>

Table 5 A summary of the findings on the corrosion and deposit morphologies on the superheater surfaces in straw-fired boilers (after Montgomery et al, 2002)
<table>
<thead>
<tr>
<th>Fuel</th>
<th>No bed material</th>
<th>Ca CO₃</th>
<th>CaCO₃-MgCO₃</th>
<th>SiO₂</th>
<th>0.6 MgO-0.4 SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eucalyptus</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>770 (silicate)</td>
<td>620 (salt)</td>
</tr>
<tr>
<td>Forest residue</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>770 (silicate)</td>
<td>885 (silicate)</td>
</tr>
<tr>
<td>Lucerne</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>770 (silicate)</td>
<td>620 (salt) 845 (silicate)</td>
</tr>
<tr>
<td>Salix</td>
<td>620 (salt) 825 (silicate)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>770 (silicate)</td>
<td>885 (silicate)</td>
</tr>
<tr>
<td>Arundo Donax</td>
<td>765 (salt) 765 (silicate)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>770 (silicate) 770 (silicate)</td>
<td>620 (salt)</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>770 (silicate)</td>
<td>620 (salt)</td>
<td>630 (salt)</td>
<td>770 (silicate)</td>
<td>620 (salt)</td>
</tr>
<tr>
<td>Reed canary grass</td>
<td>640 (silicate)</td>
<td>620 (salt)</td>
<td>620 (salt)</td>
<td>640 (silicate)</td>
<td>620 (salt) 880 (silicate)</td>
</tr>
</tbody>
</table>

Table 6 Calculated melting temperatures for the alkali salt and silicate melts for the different ashes and bed materials. (after Zevenhoven-Onderwater et al, 2001)

<table>
<thead>
<tr>
<th>Technology</th>
<th>Particulate collection efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone</td>
<td>50-90</td>
</tr>
<tr>
<td>Wash/spray towers</td>
<td>&lt;80</td>
</tr>
<tr>
<td>Mechanical scrubbers</td>
<td>50-85</td>
</tr>
<tr>
<td>Packed columns</td>
<td>80-99</td>
</tr>
<tr>
<td>Venturi scrubbers</td>
<td>90-98</td>
</tr>
<tr>
<td>Fabric filters</td>
<td>90-99</td>
</tr>
<tr>
<td>Bed filters</td>
<td>80-95</td>
</tr>
<tr>
<td>Ceramic filters</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Electrostatic precipitators</td>
<td>&gt;95</td>
</tr>
</tbody>
</table>

Table 7 The principal particulate collection technologies, and the general levels of collection efficiency achievable in biomass gasification systems.
<table>
<thead>
<tr>
<th>Technology</th>
<th>Residence time</th>
<th>Heating rate</th>
<th>Temperature (°C)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonation</td>
<td>days</td>
<td>very low</td>
<td>400</td>
<td>charcoal</td>
</tr>
<tr>
<td>Conventional</td>
<td>5-30 minutes</td>
<td>low</td>
<td>600</td>
<td>oil, gas, char</td>
</tr>
<tr>
<td>Fast</td>
<td>0.5-5 s</td>
<td>very high</td>
<td>650</td>
<td>bio-oil</td>
</tr>
<tr>
<td>Flash-liquid</td>
<td>&lt; 1 s</td>
<td>high</td>
<td>&lt; 650</td>
<td>bio-oil</td>
</tr>
<tr>
<td>Flash gas</td>
<td>&lt; 1 s</td>
<td>high</td>
<td>&lt; 650</td>
<td>chemicals, gas</td>
</tr>
<tr>
<td>Ultra</td>
<td>&lt; 0.5 s</td>
<td>very high</td>
<td>1000</td>
<td>chemicals, gas</td>
</tr>
<tr>
<td>Vacuum</td>
<td>2-30 s</td>
<td>medium</td>
<td>400</td>
<td>bio-oil</td>
</tr>
<tr>
<td>Hydro-pyro</td>
<td>&lt; 10 s</td>
<td>high</td>
<td>&lt; 500</td>
<td>bio-oil</td>
</tr>
<tr>
<td>Methano-pyro</td>
<td>&lt; 10 s</td>
<td>high</td>
<td>&gt; 700</td>
<td>chemicals</td>
</tr>
</tbody>
</table>

Table 8 General types of biomass pyrolysis processes
<table>
<thead>
<tr>
<th>Technology</th>
<th>Reactor type</th>
<th>Desired product</th>
<th>Capacity (kg h⁻¹)</th>
<th>Gas/liquid/char (weight %)</th>
<th>Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-alternative</td>
<td>Downdraft fixed bed</td>
<td>char</td>
<td>2,000</td>
<td>55/15/30</td>
<td>500-800</td>
</tr>
<tr>
<td>THEE</td>
<td>Fluidised bed</td>
<td>gas</td>
<td>500</td>
<td>80/10/10</td>
<td>650-1,000</td>
</tr>
<tr>
<td>Univ. Zaragosa</td>
<td>Radiation furnace</td>
<td>gas</td>
<td>100</td>
<td>90/8/2</td>
<td>1,000-2,000</td>
</tr>
<tr>
<td>Ensyn Eng.</td>
<td>CFB</td>
<td>liquids</td>
<td>30</td>
<td>25/65/10</td>
<td>450-800</td>
</tr>
<tr>
<td>Georgia Tech. Inst.</td>
<td>Entrained flow</td>
<td>liquids</td>
<td>50</td>
<td>30/60/10</td>
<td>400-550</td>
</tr>
<tr>
<td>Laval Univ.</td>
<td>Vacuum</td>
<td>liquids</td>
<td>30</td>
<td>15/65/20</td>
<td>250-450</td>
</tr>
<tr>
<td>Solar Energy</td>
<td>Vortex</td>
<td>liquids</td>
<td>30</td>
<td>35/55/10</td>
<td>475-725</td>
</tr>
<tr>
<td>Waterloo Univ.</td>
<td>Flash fluid bed</td>
<td>liquids</td>
<td>3</td>
<td>20/70/10</td>
<td>425-625</td>
</tr>
<tr>
<td>Twente Univ.</td>
<td>Rotating cone</td>
<td>liquids</td>
<td>10</td>
<td>20/70/10</td>
<td>500-700</td>
</tr>
</tbody>
</table>

Table 9 The basic characteristics of a number of the more important biomass pyrolysis test rigs and pilot plants
Figure 1  Calculated melting curves for salt mixtures with K/Na molar ratio 90/10, SO$_4$/CO$_3$ molar ratio 80/20 and Cl varying between 0 and 20% of the total alkali. (after Backman et al, 2005)
Figure 2  Examples of basic chemical fractionation data for a range of solid fuels (after Skrifvars et al.)
Figure 3  A summary of the chemical fractionation data for a range of solid fuels (after Skrifvars et al)

Figure 4  Schematic illustration of the fate of inorganic material in solid fuels during combustion processes. (after Baxter, 1993)
Figure 5  A schematic diagram of the key processes involved in fly ash and aerosol release from the combustion of wood on a grate. (after Obernberger et al, 2001)

Figure 6  The results of surface compositional analysis showing the concentrations of key elements (as oxides) in pre- and post exposure SCR catalyst from a slipstream reactor exposed to the flue gas from a combustor firing an alkali and alkaline earth metal-rich fuel (after Baxter and Koppejan)
Figure 7  The principles of the proposed ‘active oxidation’ corrosion mechanism (after Riedl et al, 1999).

Figure 8  The corrosion rates of boiler tube material specimens exposed to the flue gases from straw combustion, plotted against the metal temperature. (after Henricksen et al. 2002)
Figure 9  A schematic diagram of the syngas cooling requirements for integrated biomass gasification systems. (after van der Drift and Pels, 2004)