Biomass combustion in fluidized bed boilers: Potential problems and remedies

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ABSTRACT

Due to increasing environmental concerns especially related with the use of fossil fuels, new solutions to limit the greenhouse gas effect are continuously sought. Among the available alternative energy sources, including hydro, solar, wind etc. to mitigate greenhouse emissions, biomass is the only carbon-based sustainable option. On one hand, the versatile nature of biomass enables it to be utilized in all parts of the world, and on the other, this diversity makes biomass a complex and difficult fuel. Especially the high percentages of alkali (potassium) and chlorine, together with high ash content, in some brands of biomass prove to be a major source of concern. However, mechanisms leading to corrosion and high dust emissions problems have been identified and a range of possible solutions is already available. Among the technologies that can be used for biomass combustion, fluidized beds are emerging as the best due to their flexibility and high efficiency. Although agglomeration problems associated with fluidized bed combustors for certain herbaceous biofuels is still a major issue, however, but successful and applicable/implementable solutions have been reported. This review article presents the major issues concerned with biomass combustion with special reference to the small scale fluidized bed systems (small to pilot scale). Problems have been identified, mechanisms explained and solutions have been indicated. In conclusion, a range of concerns including environmental, economical and technical associated with biomass exist, but none of these issues represent an insurmountable obstacle for this sustainable energy source.

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1. Introduction

Today biomass is seen as the most promising energy source to mitigate greenhouse gas emissions [1–5]. Large scale introduction of biomass energy could contribute to sustainable development on several fronts namely, environmental, social, and economical [4–7]. World energy supplies have been dominated by fossil fuels for decades (approximately 80% of the total use of more than 400 EJ per year, see Fig. 1) [4,8]. Today biomass contributes about 10 to 15% (or 45 ± 10 EJ) of this demand. On average, in the industrialized countries biomass contributes some 9 to 14% to the total energy supplies, but in developing countries this is as high as one-fifth to one-third [1,6,9]. In quite a number of these countries, biomass covers even over 50 to 90% of the total energy demand. It should be noted, though, that a large part of this biomass use is non-commercial and used for cooking and space heating, generally by the poorer part of the population [9]. Modern production of
energy carriers from biomass (heat, electricity and fuels for transportation) or biofuels contributes a lower, but significant 7 EJ [4,6]. The utilization of biomass within the European Union (EU) has strongly increased over the last decades, and the ambitions of the EU for the use of biomass are high. Up to 6000 PJ in 2010 are targeted (tripling the use compared to 1999 levels), and possibly even more beyond the targets [10].

Over the past decade, substantial growth figures of bio-energy in the EU, particularly for the modern energy carriers, like electricity, and increasingly biofuels for the transport sector, are observed. Heat production increased by some 2% per year between 1990 and 2000, bio-electricity increased by some 9% per year and biofuels production increased about eight-folds (over 20% growth per year) in the same period. The 1999 contribution of biomass to the EU energy supply was little less than 2000 PJ, some two-thirds of the total renewable energy production in the EU or 4% of the total energy supply [9,11]. Fig. 1a shows the history and projection of world marketed energy consumption from 1980–2030 while Fig. 1b indicates a further renewable classified energy contribution for the year 1998 [12,13].

1.1. Bio-energy policy

Looking at the incentives that biomass offers, the governments in different countries are also committing more seriously for energy with least environmental impact. Every country in Europe has included bio-energy in its energy and climate policies. For the European Union (EU), targets have been set for bio-energy: in 2010 almost 10% of the energy supply of the EU is to come from biomass [11,14,15]. Few individual countries, especially in Scandinavia are setting up high goals for the future. For instance, Sweden formulated that 40% of its primary energy supply should be covered by biomass around 2020 [11,16]. Another example is a recent EC-directive on biofuels for the transport sector, which has set targets for the use of biomass for transport fuels [11,14]. Different global energy scenario studies indicate that in this century biomass may contribute much more: up to 30% of the 2100 energy supply from biomass [5,17], an average 50–250 EJ/yr in 2060. A global (technical) potential of primary biomass in 2050 of 33–1135 EJ/yr [8] is foreseen, depending on population growth and food demand (diet), economic development, food production efficiency, energy crop productivity on various land types, competing biomaterial products, and land use choices. This range may be narrowed down to 300–675 EJ or 40–60% of the energy demand in 2050, which could be produced on 4–10% of the terrestrial surface [5,8,18]. Such targets are in line with various global scenario studies for bio-energy which indicate that biomass may contribute 100 to over 400 EJ (or 25% to almost 100% of the current world’s energy use) to the world’s energy supply during this century [11,19,20].

1.2. Biomass availability and cost issues

The realization of all the above-mentioned target percentages will not be easy. Fuel availability over time, alternative applications, varying prices and sources of income are among the already foreseen problems. Dedicated production of biomass, the so-called ‘energy cropping’ or ‘energy farming’ is seen as the only measure to fulfill future renewable fuel needs with a variety of crops. In general, dedicated biomass
production is more expensive per unit of energy produced than the use of available residues and wastes. Typical cost ranges for perennial woody crops under North Western European conditions are 3–6 euro/GJ (compared to some 1–2 euro/GJ for imported coal) [5,11]. Biomass costs of dedicated production systems are especially dependent on the costs of land and labor and the (average) yield per hectare [7]. Using a crop only partially for energy and partially for material purposes may be a solution. This is because the material component of the crop may create (1) additional incomes and (2) additional GHG emissions reductions [21]. However, some studies have suggested that the large scale energy crop production including intercontinental trade of biofuels or bulk wood could be economically feasible and will not lead to dramatic energy losses [4,22]. The eventual costs of electricity may prove competitive with present day fossil electricity. Biofuels remain slightly more expensive than fossil automobile fuels, but the gap can probably be bridged when system scales are increased and bio-processing technology improves.

Biomass offers a number of advantages compared to fossil fuels. Biomass is regarded as a renewable energy source with zero to low CO₂ emissions if produced in a sustainable manner [23]. An evaluation of the CO₂ balance shows that compared with the combustion of hard coal, the CO₂ emissions can be reduced by 93% [24]. The thermal utilization of waste and residual material, as e.g., sewage sludge, along with reducing the CO₂ emissions helps to solve the waste disposal problem. Low SO₉ and possibly low NOₓ emissions are added benefits. The alkaline ash from biomass captures some of the SO₂ produced during combustion and therefore co-firing can also reduce the net SO₂ emissions. In addition, the fuel nitrogen content in biomass is in many cases much lower than in coals and may be converted to ammonia during the pyrolysis stage of combustion and thus can be utilized as reburning fuel. Hence, co-firing can also result in lower NOₓ levels. Blending can also result in the utilization of less expensive fuels with a reduction in fuel costs [25]. In addition, energy crops cultivated for sustainable biomass growth can be an employment generator, especially in rural areas. Furthermore, biomass can be an indigenous energy source for most countries, thus coal imports can be reduced [23].

However, apart from logistic and cost issues, there are certainly some big technical challenges associated with thermo-chemical biomass utilization. These include among others, NOₓ, N₂O and dust emissions, deposit and corrosion problems, agglomeration and ash related issues. High impact factors for life cycle assessment (LCA) have been assigned to wood combustion in comparison to natural gas and light fuel oil [26]. The major contributors to wood combustion LCA come from NOₓ and PM10 emissions.

This paper focuses on these issues with special reference to fluidized bed combustion technology (small to pilot scale). The objective has been to provide more information related to the effect of the physical and chemical properties of the biomass on the combustion process and emission characteristics. Four major areas are considered. In Section 1, biomass properties, densification process, and a short description of fluidized bed technology and co-firing are given. Section 2 discusses issues related with organic and inorganic gaseous pollutants. In Section 3, operational problems, deposits, corrosion and agglomeration are briefly discussed and finally in Section 4, dust and trace metal emissions are presented.

2. Biomass classification and properties

2.1. Biomass classification

Biomass is a biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material [14,27].

Biomass energy resources are diverse and therefore a great need exists for a comprehensive classification system. The motivation for such a system is to predict the behavior of biomass by identifying to which class it belongs. One approach could be on the basis of basic components namely, cellulose, hemicellulose, and lignin percentages and their behavior. However, such a system cannot account for possible interactions between the components and has been regarded unreliable [28,29]. However, some success in predicting biomass behavior during pyrolysis with this classification has been achieved with compensation of minerals’ effects taken into account [28].

Two classification approaches have been proposed based on the origin of the biomass and their properties [28,29]. Biomass fuels can be generally divided into four primary classes:

1. Primary residues: By-products of food crops and forest products (wood, straw, cereals, maize etc.).
2. Secondary residues: By-products of biomass processing for production of food products or biomass materials (saw and paper mills, food and beverage industries etc.).
3. Tertiary residues: By-products of used biomass derived commodities (waste and demolition wood etc.).

The classification based on properties can be categorized into:

1. Wood and woody fuel (hard and soft wood, demolition wood).
2. Herbaceous fuels (straw, grasses, stalks etc.).
3. Wastes (sewage sludge, refuse-derived fuel (RDF) etc.).
4. Derivates (waste from paper and food industries etc.).
5. Aquatic (Kelp etc.).

Because of the diverse nature of biomass fuel, properties in these categories vary in a wide range. For example, apart from energy crops, moisture content can easily vary with a factor 2 in all the categories.

An alternative approach based on the Van Krevelen diagram (plot of H/C versus O/C atomic ratios) has also been suggested [30]. The premise in this classification is that biomass from altogether different categories (waste, wood) fall in close proximity of each other but have very different properties.
Another, more recent, classification that can be used is the European standard for solid biofuels (CEN TC 335) [14]. This classification is based on the biofuel origin and source. In the hierarchical classification system, the main origin-based solid biofuel groups are:

1. Woody biomass (wood chips, pellets, log wood, saw dust etc.).
2. Herbaceous biomass
3. Fruit biomass
4. Blend and mixtures.

CEN/TC 335 is subdivided in 5 subgroups; WG1 (terminology, definitions and description), WG2 (fuel specification and classes), WG3 (sampling and sample reduction), WG4 (physical and mechanical test), and WG5 (chemical test methods).

Because of the diversity of the biomass fuels and therefore their effects during combustion, this article is limited to the biomass materials considered in the first classification approach provided above.

2.2. Biomass composition

The components of biomass include cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water, hydrocarbon, ash, and other compounds. The concentration of each class of compound varies depending on species, type of plant tissue, stage of growth, and growing conditions. Cellulose is a linear polysaccharide of β-D glucopyranose units linked with 1-4-glycosidic bonds. Hemicelluloses are polysaccharides of variable composition including both five and six carbon monosaccharide units. The lignin is an irregular polymer of phenylpropane units [29,31]. Due to the carbohydrate structure, biomass is highly oxygenated with respect to the conventional fossil fuels including hydrocarbon liquids and coals.

The bulk composition of biomass in terms of carbon, hydrogen, and oxygen (CHO) does not differ much among different biomass sources. Typical (dry) weight percentages for C, H, and O are 30 to 60%, 5 to 6%, and 30 to 45% respectively. C, H, O shares can be different for typical fuels (the higher C content is due to biological breakdown and plastic fraction) [9,32]. Nitrogen, sulfur and chlorine can also be found in quantities usually less than 1% dry matter, but occasionally well above this. Nitrogen is a micronutrient for plants, and critical to their growth. Certain inorganic elements can be found in high concentration as well. Relative to coal, biomass generally has less carbon, more oxygen, more silica, chlorine and potassium, less aluminum, iron, titanium and sulfur, and sometimes more calcium. Certain biomass types also contain contaminating species in trace amounts depending upon the source of the fuel. For example, heavy metals (cadmium, lead etc.) are commonly found in woody fuels (especially demolition wood) from paints and atmospheric deposition sources. These heavy metals make an important part of the emitted pollutants especially in sewage sludge combustion but are also important for contaminated wood operation and therefore have been treated separately in trace metal emission section.

2.3. Effects of certain elements in fuel

Certain elements in biomass deserve special attention. These include, chlorine, potassium, sulfur, nitrogen, and silicon. Perhaps the most important element, with regard to its behavior in different combustion related problems is chlorine. Chlorine, which is found in high quantities in certain biomass types, such as straw, may affect operation by corrosion. The high chlorine and alkali content of some biomass fuels can cause severe damage to the combustion units. The greatest concern focuses on high temperature corrosion of superheater tubes induced by chlorine on the surface. Chlorine facilitates the mobility of many inorganic compounds, in particular potassium. Potassium chloride is among the most stable high temperature, gas phase, alkali-containing species. Chlorine concentration often dictates the amount of alkali (potassium) vaporized during combustion as strongly as it dictates the transport of alkali from the fuel to surfaces, where the alkali often forms sulfates. In the absence of chlorine, alkali hydroxides are the major stable gas phase species in moist, oxidizing environments i.e., combustion gases [29]. Herbaceous fuels contain silicon and potassium in high percentages. High percentages of silicon together with potassium and chlorine also play their role in causing severe ash deposition problems at high or moderate combustion temperatures.

The primary sources of these problems are (1) the reaction of alkali with silica to form alkali silicates that melt or soften at low temperatures (can be lower than 700 °C, depending on composition), and (2) the reaction of alkali with sulfur to form alkali sulfates on combustor heat transfer surfaces [33]. Alkali compounds play a central role in both processes. Potassium is the dominant alkali source in most biomass fuels [29,34]. The high S content of coal leads without counter-acting measures to increased SOx emissions. Biomass is usually low in sulfur, but sulfur from coal during co-firing may or may not (especially for its part in corrosion issues) cause problems depending on the biomass composition. On the other hand, S contained in coal can be advantageous in preventing sticky deposits to some extend, as in the boiler chemistry KCl could be reduced in favor of K2SO4, which is somewhat less harmful. The high percentages of these elements (Cl, K, Si) also pose grave concerns for bed agglomeration problems in fluidized bed boilers.

A pretreatment process to remove potassium from straw fuel may be based on pyrolysis followed by char wash. The straw is pyrolyzed at moderate temperatures by which the potassium is retained in the char. Potassium and residual chlorine are extracted from the residual char by water [33–35]. Char and pyrolysis gases may then be used in a conventional boiler without problems due to the high straw potassium content. To evaluate this pretreatment process, knowledge about the char wash process is needed. Sulfur and chlorine together with nitrogen are also responsible for gaseous emissions including SOx, NOx, and HCl and to a certain extent dioxins and furans.

2.4. Combustion related physical properties

Physical property values vary greatly and properties such as density, porosity, friability, and internal surface area are related to biomass species whereas bulk density, particle
size, and shape distribution are related to fuel preparation methods. Depending on the combustion process technology chosen, various pretreatment steps such as sizing (shredding, crushing, and chipping) and drying are needed to meet process requirements. Storage, processing (e.g., densification) before transport, and pretreatment influence the moisture content, ash content (e.g., by means of sieving), particle size, and sometimes even the degree of contamination (an example being straw washing, which reduces the salt content (chlorine and alkali content)). Particle size, shape and specific gravity are all important properties for the pre-combustion (feeding, fuel preparation etc.) and combustion process. Preprocessing, separate feeding or a combination of both is usually applied. Inside the combustion chamber, these properties strongly affect among others combustion kinetics, dust emissions, entrainment and segregation issues especially in FBs.

Of all the physical properties, the bulk density of the fuel is of major importance because of economical and technical reasons. Most biofuels, especially from agricultural origin (e.g., straw, rice husk) have low bulk densities. For example, the bulk densities of chopped straw and rice husks are 50–120 and 100–125 kg/m³ [36], respectively. These are very low compared to the bulk densities of coals, which are in the range of 560–600 kg/m³ for brown coals and between 800 and 900 kg/m³ for bituminous coals. A number of disadvantages are attributed to the lower bulk density of biomass including relatively low heating values per unit volume, process control difficulties, feeding control, requirement of huge storage, expensive transportation, and limitation of technologies applied (e.g., fuel entrainment in fluidized beds). The energy density resulting from the bulk density and the net calorific values influences the necessary storage volume and the process control of the fuel supply system of the furnace.

Densification is a well known process utilized to overcome these disadvantages. In simple words, densification removes the inter and intra-particle voids. The three most commonly used densification techniques are baling, briquetting, and pelletization in the increasing order of equipment complexity, energy requirement, and costs. Table 1 shows the bulk densities and heating values achieved in these processes [37].

Almost similar results can be achieved from both pelletization and briquetting. Pelletization offers several advantages including higher press output and acceptance of materials with wider range of moisture contents. However, the raw materials for pelletization must be chopped and milled whereas for briquetting, chopping of straw may be sufficient. The design of a briquetting machinery is also simpler [36,38]. However, densification is an expensive process and cost addition to the fuel is significant. Even after pelletizing, feeding can become a significant issue. Fig. 2 shows greenhouse residue pellets and the pellets found at the end of screw feeder. Greenhouse residue contains a lot of plastic and during screw feeding, the pellets disintegrated and produced hair like structure which blocked the feeder. The solution in this case would be either another feeding system or use of a strong binder during pelletization or decreasing feed particle size and distribution.

<table>
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<th>Table 1 – Comparison of densification techniques for straw</th>
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<tr>
<td>Bulk density kg/m³</td>
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<tr>
<td>Baling</td>
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<tr>
<td>Briquetting and pelletization</td>
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</table>

Fuel properties often form the basis for the technology chosen for the combustion process. Depending on these properties, a biomass fuel can be excluded for specific combustion options, partially for technical and partially for environmental reasons. The characteristics of the biomass are influenced by the origin of the biomass, but also by the entire supply system preceding any conversion step.

2.5. Biomass fuel properties

Fig. 2 – Greenhouse residue pellets before and after screw feeding (a) before feeding (b) after feeding (found in the screw bunker). (Author’s own measurements).
gives precise elemental percentages of C, S, H, N, Cl, and O. Table 2 shows the proximate and ultimate analysis of some biofuels and bituminous coal [36,39]. The values vary in wide ranges. In comparison to coal, biomass generally contains less carbon, more oxygen, more potassium, less aluminum and iron, and has a lower heating value and a higher moisture content as shown in Tables 2–3 [40,41]. Biofuels show a high reactivity due to their high volatile content and highly reactive char but have a much lower carbon and high oxygen content which are responsible for their low heating values. Other important chemical and thermal properties include specific heat, thermal conductivity, chemical kinetics data, char and volatiles heating values, and emissivity. The most important characteristic properties of biomass are discussed below.

### 2.5.1. Heating value

The heating value, also called calorific value, of the biomass can be defined by the higher heating value (HHV), which is basically the energy content on a dry basis. The lower heating value (LHV) is calculated by subtracting the energy needed to evaporate the moisture content of the fuel. Biomass fuels have lower heating values compared to coal. C and H tend to raise the heating value while oxygen decreases it. The lignin content of the lignocellulosic fuel generally is strongly correlated with the heating value. The high heating values of lignin are reported to be higher than the cellulose and hemicellulose. The latter has a lower heating value due to its higher degree of oxidation [34].

### 2.5.2. Moisture content

The moisture content of biomass can vary in a wide range from 10–70%. The water content influences the combustion and the volume of flue gases produced per energy unit. The heating value of the fuel decreases with increasing moisture content. For biofuels, which have very high moisture contents, some problems may be encountered during firing. High moisture content can cause ignition issues and reduce the combustion temperature, which in turn hinders the combustion of the reaction products and consequently affects the quality of combustion [33]. Furthermore, a high moisture content leads to high fuel usage generating large flue gas amounts and therefore require large equipment dimensions. The presence of water in biomass influences its behavior during pyrolysis (the primary conversion stage during combustion) and affects the physical properties and quality of the pyrolysis gases [42].

### 2.5.3. Volatile matter

Biomass generally has a very high volatile content. Volatiles are further subdivided into gases such as light hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, moisture, and tars. The yields depend on the temperature and heating rate of pyrolysis. Due to their high volatile fraction, biofuels are easier to ignite even at low temperatures. The high volatile content of biomass affects the system in different ways [29,34]. The biomass combustion is expected to occur at a rapid rate and therefore has to be controlled accordingly. The amount of fuel devolutilized during the pyrolysis stage of combustion

| Table 2 – Analysis of some biofuels and bituminous coal (mass basis) |
|------------------|------------------|------------------|------------------|------------------|
| Fuel             | Proximate analysis | Ultimate analysis |                   |
|                  | Moisture % | Volatile % | FC % | Ash % | C % | H % | O % | N % | S % | Cl % |
| Wood pellets (pine) | 4.9      | 80.4      | 14.5 | 0.2   | 45.5 | 6.6 | 47.7 | LLD | LLD | LLD |
| Demolition wood pellets | 9.1      | 69.6      | 19.7 | 1.7   | 45.7 | 6.3 | 36.2 | 0.9 | LLD | LLD |
| Pepper plant residue | 6.5      | 60.5      | 19.5 | 13.5  | 33.8 | 4.0 | 39.1 | 2.5 | 0.5 | 0.1 |
| Greenhouse residue | 2.5      | 61.0      | 5.50 | 31.0  | 47.1 | 7.4 | 10.9 | 1.0 | LLD | LLD |
| Wheat strawa | 13.9      | 77.9      | 21.5 | 6.8   | 56.7 | 6.7 | 48.8 | 1.0 | 0.2 | N.R |
| Sunflower pellets | 11.2      | 65.2      | 19.5 | 4.1   | 44.1 | 5.17| 34.6 | 0.5 | 0.1 | 0.1 |
| Olive cake pellets | 11.9      | 64.2      | 15.7 | 8.2   | 42.1 | 4.99| 31.0 | 1.3 | 0.1 | 0.3 |
| Sewage sludge    | 6.9       | 44.6      | 7.0  | 41.5  | 52.0 | 6.3 | 32.1 | 6.3 | 3.1 | N.R |
| Bituminous coalb | 4.9       | 32.3      | 48.1 | 14.7  | 65.7 | 5.6 | 7.7  | 1.2 | 0.5 | LLD |

* * * Flowing at 815 °C by difference; LLD - below the lower detection limit; N.R - Not reported.

| Table 3 – Ash analysis of some biofuels and bituminous coal (mass basis % ash) |
|------------------|------------------|------------------|------------------|------------------|
| Fuel             | SiO₂ | Al₂O₃ | Fe₂O₃ | Mn | MgO | CaO | Na₂O | K₂O | TiO₂ | P₂O₅ | SO₃ |
| Wood pellets     | 4.3  | 1.3  | 1.5   | 5.9 | 8.5 | 55.9 | 0.6  | 16.8 | 0.1  | 3.9  | 1.3 |
| Demolition wood pellets | 20.4 | 3.5  | 2.2   | 0.3 | 7.5 | 27.5 | 4.8  | 10.5 | 2.5  | 11.1 | LLD |
| Pepper plant residue | 12.6 | 4.9  | 2.0   | 0.2 | 7.4 | 32.2 | 0.9  | 24.6 | 0.5  | 5.2  | LLD |
| Greenhouse residue | 28.5 | 3.9  | 18.4  | 0.3 | 5.7 | 25.8 | 0.8  | 9.7  | 0.8  | 3.8  | LLD |
| Sunflower pellets | 2.9  | 0.6  | 0.8   | 0.1 | 21.6 | 21.6 | 0.24 | 22.8 | 0.1  | 15.2 | 14.0|
| Olive cake pellets | 12.8 | 2.9  | 3.0   | 0.1 | 4.9 | 17.5 | 3.9  | 47.9 | 0.2  | 6.0  | 1.1 |
| Wheat strawa | 53.1  | 3.6  | 1.2   | N.R | 3.0 | 17.7 | 4.5  | 30.0 | N.R  | 4.1  | N.R |
| Sewage sludge    | 38.3 | 0.8  | 12.5  | N.R | 2.8 | 9.1  | 2.2  | 2.2  | 0.8  | 15.4 | 1.1 |
| Bituminous Coalb | 59.7 | 20.3 | 7.0   | <0.01 | 1.9 | 1.8  | 1.0  | 2.3  | 0.9  | 0.1  | 1.3 |

N.R not reported. * * * Ashing at 815 °C.
increases with increasing hydrogen to carbon ratio and, to a lesser extent, with increasing oxygen to carbon ratio. In comparison with coals (anthracite less than 10% and bituminous between 5 to 6%), biomass can lose up to 90% of their masses in this first stage of combustion. A typical volatile loss during early pyrolysis of biomass is about 75%.

The quick release of a large fraction of biofuels as volatiles makes it necessary to have longer high-temperature zones in order to achieve complete combustion at high efficiency and to ensure low pollutant emissions (CO and PAH). The implication of this is that the design and operation principles normally adopted for a coal combustion system, may not be applied for the combustion of biomass alone, however, co-firing units are not expected to experience such problems due to relatively low energy share of biomass in the system.

2.5.4. Ash
Ash is the inorganic uncombustible part of fuel which is left after complete combustion, containing the bulk of the mineral fraction of the original biomass. Inorganic material in biomass can be divided into two fractions, one of which is inherent in the fuel and the other of which is added to the fuel through processing steps. The latter, adventitious material originates from skidding and other operations whereby soil is incorporated into the fuel. This dirt often makes up a major fraction of the ash content of wood fuels. Its composition is typically different from that of the inherent materials, as is the mode of occurrence of the elements. Examples are crystalline silicates and alumina arising from the incorporation of sands, clays, and other soil particles, and potassium incorporated in feldspars with relatively little contribution to alkali reactions leading to fouling other than by inertial impaction and sticking of particles [29]. The major inherent ash forming elements in biomass include Si, Al, Ti, Fe, Ca, Mg, Na, K, S, and P. Table 3 shows the ash analysis of some selected biofuels and bituminous coal [36,39]. The ash content varies from one biofuel to another. It can be from <1% (wood, demolition wood) to up to 30–40% (green house residue). With high ash containing fuel, an efficient dust removal system becomes a must to handle particulate emissions. Also, high ash percentages lower the heating value of the fuel. The release of atomically dispersed inorganic material from a fuel particle is influenced both by its inherent volatility and the reactions of the organic portions of the fuel. Material that is inherently volatile at combustion temperatures includes derivatives of some of the alkali and alkaline earth metals, most notably potassium and sodium. Other, non-volatile material (Ca, Mg etc.) can be released by convective transport during rapid pyrolysis.

High alkali (potassium) and Si content typically gives low ash melting temperatures while Mg and Ca increase ash melting temperature [33,36,41]. Although a major fraction of low melting point alkali is released into the gas phase, the part left in the ash may deliver detrimental effects (bed agglomeration) during fluidized bed combustion. Ash sintering, softening, and melting temperatures can differ significantly among biofuels, and this characteristic is essential in determining temperature control to avoid sintering or slagging (resulting in deposits on, e.g., boiler tubes). Typically, grasses and straw have mineral fractions leading to low melting temperatures. Potential utilization of ash is also influenced by contaminants (such as heavy metals) and the extent to which the ash is sintered or melted. In case of clean

<table>
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<td>400 (&lt;2.5 MW&lt;sub&gt;th&lt;/sub&gt;)</td>
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Notes: (1): In case a filtrating separator can be applied. (2): The limit is 200 mg/nm<sup>3</sup> at 11% O<sub>2</sub>, though in practice the limit for animal waste (5 mg/ nm<sup>3</sup> at 11% O<sub>2</sub>) is often applied. (3): In case waste wood containing 80–90% particleboard is burned (4): Under preparation (5): Values under discussion. (6): The NO<sub>x</sub>-limit depends on the electricity-equivalent efficiency. This is defined as the sum of electric efficiency and electric-equivalent thermal efficiency (a conversion factor of 0.47 is assumed). The limit is 70 mg/nm<sup>3</sup> at 30% el. Efficiency and 133 mg/nm<sup>3</sup> at 57% efficiency. LCP: Large combustion plants; BEES — decided emissions requirement from combustion setups.
biomass, the ash contains much of the minerals and important trace elements, and therefore can be recycled to forest grounds. Certain biomass fuels (e.g., Demolition wood, wood bark etc.) also contain heavy metals including As, Cd, Cr, Cu, Pb, and Hg. Information regarding these trace metal is central to the utilization of ash waste products as well as to environmental monitoring and protection. Fortunately, these heavy metals typically concentrate in flyash, which itself presents the possibility of removing a smaller ash fraction with most of the pollutants [25,43]. However, smaller combustion units are not equipped with Electrostatic Precipitator (ESP) or FBH Bag House Filter (BHF) and in such cases these heavy metals can become an important environmental pollution hazard.

3. Emission limits

Table 4 provides an overview of the emission limits applied in the Netherlands. The decision which limit is enforced depends on the type of biomass and installation [44].

For all cases (besides combustion of own clean waste wood in an installation smaller than 5 MWth) where biomass is combusted for energy, NER or BEES A applies.

Table 4 also shows the European draft directive for Large Combustion Plants (LCP) exceeding 300 MWth, from which the national emission legislation has been derived. In the new national emission limits for biomass, a difference will be made between clean and contaminated biomass. For this purpose, the definition of clean biomass has been derived from the draft LCP directive. Clean waste wood can be regarded as clean biomass.

As can be seen from Table 4, small combustion installations for clean waste wood are particularly confronted with tightened emission limits for dust, NOx, and SOx. While an SOx level of 100 mg/m³ can be maintained without any measures because of the low sulfur content of clean wood, additional measures will be required to reduce dust and NOx emissions.

The NOx emission limit is dependent on the electricity-equivalent efficiency. As a result a trade-off may occur between higher overall efficiency and NOx emissions limits.

4. Combustion

A detailed description of biomass combustion is beyond the scope of this article. Only the shortest description can be provided here. Biomass combustion is a complex process consisting of consecutive homogeneous and heterogeneous reactions. The essential process steps include drying, devolatization, gasification, char combustion, and gas phase reactions. Fig. 3 shows a schematic description of these processes for wood. The biomass combustion process can also be briefly summarized as follows. When heating wood, its constituents start to hydrolyze, oxidize, dehydrate, and pyrolyze with increasing temperature forming combustible volatiles, tarry substances, and highly reactive carbonaceous char. At the ignition temperature of the volatiles and tarry substances, exothermic reactions known as combustion begin. Resinous compounds and decomposition products of cellulose, hemicelluloses, and lignin, together with water vapor are stripped off, and then undergo both partial to complete combustion in the flaming zone. During the smoldering process, enough heat is produced to propagate the charring process as well as the release of additional volatile wood decomposition products [45].

Composition and physico-chemical properties of the fuel are the determining factors for duration and rate of each of the above-mentioned steps. Influencing properties include the atomic structure and pathways for the movement of moisture, moisture content, specific gravity, hemicelluloses and lignin contents. In terms of process condition, heating rate (temperature) and excess air ratio are most important parameters.

5. Co-firing

Co-combustion refers to simultaneous combustion of two fuels. It is the practice of introducing biofuels as a supplementary energy source in high efficiency utility boilers, but combustion of two different biomasses is also not unknown, at least in smaller scale units (1–5 MWth). In this section, the focus will be on biomass-coal co-combustion. Coal is the most abundant of the fossil fuels and is responsible for about 27% of the world’s primary commercial energy use. It accounts for about 34% of all the electricity generated in the world [46].

As has been stated before that any contribution of biomass means reduction of net CO2 emissions. Initially, co-firing was seen as a means for reducing greenhouse gas emissions from fossil energy generation, when power plants voluntarily combusted some biomass fuel as an environment-friendly gesture. Today, co-combustion is an industrial practice. It is now an accepted fact that these savings come not only from displacement of coal, but also from displacement of materials being sent to landfill that ultimately decompose and form both CO2 and another, more powerful greenhouse gas, methane [47]. Therefore, governments in different developed countries are taking increasing interests and regulations and incentives have been put together to increase the biomass share in co-firing. Recent reviews of co-firing experience identify over 100 successful field demonstrations in 16 countries that use essentially every major type of biomass (herbaceous, woody, animal wastes, and anthropomorphic wastes) combined with every rank of coal and combusted in essentially every major type of boiler (tangential, wall, and cyclone fired). Comparing with other forms of renewable energy options in terms of costs and applicability, co-firing is among the lowest risk, least expensive, most efficient, and shortest term options for renewable-based electrical power generation [48]. Addition of biomass to a coal-fired boiler does not impact or at worst slightly decreases the overall generation efficiency of a coal-fired power plant [49]. Nevertheless, there remain substantial uncertainties associated with long-term implementation of this biomass technology.

Economics, as in all cases, has a major role to play in the success of biomass as a co-firing fuel. The costs involved are investment and working capital. Generally, capital costs
required are for the adaptation of the system for biomass combustion and therefore, both costs have to be taken into account. In some cases, capital costs can be avoided. The main issues that need to be concerned for co-combustion are discussed below with respect to costs, environmental impacts and boiler operation.

Fig. 3 – Schematic description of the combustion process of a wood chip.
5.1. Fuel availability, logistics, preparation, storage, and handling

In general, biomass in most cases is usually free or cheap but the cost involved for its transportation directly affects the total costs of biomass co-combustion. Furthermore, because of its low bulk energy density, together with the generally high moisture content, huge amounts of biomass need to be transported to form even a smaller share of the total heat input. Preparation, storage and handling (fuel pile or separate injection) also add significant costs to the total process. In case of fuel pile mixing, working capital increases while separate injection requires additional working capital and boiler retrofitting. In addition to that, fuel preparation involves bringing biomass fuel into the right fuel particle size to avoid segregation and entrainment. Therefore, biomass demands shipping, storage, and on-site fuel handling technologies disproportionately high compared to its heat contribution.

5.2. Fuel conversion and pollutant formation

Biofuels require comparatively longer residence times in the high temperature zone because of their high volatile content to avoid the escape of combustible fraction. The typical residence times in power plant boilers are high enough to handle these differences given the fact that the total heat input from biomass is generally not more than 10%. However, this may be a serious problem for a smaller unit. The high carbon content of coal and the high volatile content of the biomass can compensate each other during co-firing and may provide a better temperature profile for the combustion process than for the individual fuels [50]. However, biofuels also commonly contain more moisture than coal which results in decreasing the peak temperature. Pollutant formation and other gaseous emissions during biomass co-firing exhibit all the complexities as do the same issues for coal combustion [49,51]. SO₂ generally decreases during co-firing owing to the lower sulfur content of biomass, while NOₓ may increase, decrease, or remain the same, depending on fuel, firing conditions, and operating conditions. Biomass devolatilization appears to produce much higher NH₃ and lower HCN content in the pyrolysis product gas compared to coal [50,52]. In addition, since biomass has a high volatile content, it can also be used as a reburning fuel for NOₓ reduction in coal combustion, which gives a further potential for a significant decrease of the NOₓ emissions.

5.3. Ash deposition and corrosion

Ash deposition and corrosion is directly related to biomass composition. In general, herbaceous materials potentially produce high deposition rates while many forms of wood waste produce relatively less problematic deposit rates. The presence of potassium and chlorine in these deposits may lead to severe fouling and corrosion problems [53,54]. Also, the high percentage of alkali and alkaline earth metals in biomass ashes may deactivate the catalysts in the SCR (selective catalytic reduction) systems [55]. Furthermore, these alkali compounds, typically in herbaceous biomass can also lead to agglomeration problems in fluidized beds. In order to avoid biomass-ash agglomeration problems, fluidized beds may be forced to run at lower than optimal temperatures and thus decreasing the combustion efficiency. Treatment of the fuel by water leaching or other techniques impacts these results dramatically, consistent with the hypothesis that alkali (potassium) and chlorine play a major role in the process [56,57]. In addition, the high (heavy) metal content in some of the biomass fuel ash may also be a source of concern. Usually coal ash is used in cement kilns and the heavy metals addition from the biomass can affect the ash utilization [48].

Fig. 4 shows the superheater tube corrosion at a 100 MWth facility fired with high chlorine (>1%) biomass with bituminous coal (CFB boiler located in Germany). The biomass share was 6–10% on heat basis and the gas temperature in the superheater region varied between 450–900 °C.

In conclusion, the general observations presented above make it clear that co-firing biomass with coal introduces several significant issues into boiler operation that have the potential for deleterious effects but none of these issues represents an insurmountable obstacle for biomass.

6. Fluidized bed combustors

Bubbling fluidized bed boilers (BFBB) or circulating fluidized bed boilers (CFBB) are considered as mature technologies (for
small scale). Fluidized bed combustion has been indicated as one of the most promising techniques, because of its flexibility, high combustion efficiency and low environmental impact [25]. As this article mainly deals with the small scale FB units, the following paragraphs give a short description of such a FB unit.

In FB furnaces, an initially stationary bed of solid particles (usually silica sand), located in the bottom part of the furnace, is brought to a fluidized state by the primary air which is supplied through a nozzle distributor plate. In BFB, the bed particles are kept in suspension by the primary air at comparatively lower fluidization velocities (~1.0–3.0 m/s) while in CFBC, higher gas velocities (~3.0–6.0 m/s) are employed, more and more solids are carried out of the bed, the well defined surface of the bed (prominent in BFB) disappears, and the solids concentration decreases continuously with increasing height above the distributor plate.

The entrained particles, in CFB, are separated in an external cyclone and returned to the bottom of the fluidization vessel. For BFB, the entire size distribution of the feed should have a higher terminal velocity than the fluidization velocity, otherwise it will be elutriated out of the combustor and very large particle sizes will be segregated and therefore, will not fluidize properly. However, even this limitation leaves a very large window of feed particle size distribution. The particles collected in the cyclone of a BFB are (usually) not returned to the bed.

Secondary air, if employed, is introduced at the top of the bed (splashing zone) and further higher up (freeboard, also called tertiary air) through well distributed air inlets over the entire width of the boiler. The temperature normally varies between 800–900 °C and is controlled by the internal heat exchanger. CFBs generally have higher efficiencies than BFBs due to higher fluidization velocities. Fig. 5 shows the schematic of a simple BFB and CFB.

The fluidized bed is renowned for its flexibility in dealing with different feed sizes. The major advantages of fluidized bed combustors [58,59] are uniform temperature distribution, large solid–gas exchange area, high heat transfer coefficients between bed and heat exchanging surfaces, ability to handle a wide range of fuels having different sizes, shapes, moisture contents and heating values, stable combustion operation at low temperatures (ca. 850 °C) and no thermal/prompt NOx. The disadvantages include requirement of highly efficient gas–solid separation systems (Multi-cyclones and Electrostatic precipitators or Bag house filters (ESPs or BHFs)) especially for biomass, high erosion rate of boiler internals (erosion rate also strongly depends on the placement of the heat exchanger) due to high solid velocities (especially for CFB), high dust load in the fluegas and defluidization problems due to agglomeration of bed materials [60,61].

7. Pollutant emissions

Pollutants can be classified into two major classes:

1. Unburnt pollutants and
2. Pollutants that are produced by combustion.

The unburnt pollutant include CO, HC, tar, PAH, CxHy, and char particles. These pollutants are usually due to poor combustion which is a result of low combustion temperature, insufficient mixing of fuel with combustion air and too short residence time of the combustible gases in the combustion zone. They can be expected from all fuel categories depending on the furnace design and the operating conditions of the firing systems. Generally lower emissions of these pollutants can be realized by conducting the combustion at such conditions that higher burn-out efficiencies can be achieved.

![Fig. 5 – (a) Circulating fluidized bed boiler (CFBB) (b) bubbling fluidized bed boiler (BFBB).](image-url)
This requires efficient mixing of the combustion air with the combustibles (i.e. char and volatiles), high combustion temperature, and adequate residence time in the hot zone. Staged combustion has been found to be an effective way of ensuring high combustion efficiency [62,63] and consequently low emissions (higher residence time, attributed to the reduction of fixed carbon loss).

The second category includes ash, nitrogen, and sulphur related emissions as these are not the product of incomplete combustion. These pollutants are critically related to the properties of biomass and are generated during combustion. These are particulate matter (PM), oxides of nitrogen (NOx, principally NO and NO2 and N2O), and oxides of sulfur (SOx, principally as SO2). Acid gases, such as HCl, and heavy metals (condensed on fine ash fraction or in gaseous phase) may also be emitted. The formation of these species can be affected to a certain extent by air-fuel stoichiometry and other combustion parameters/techniques. Heavy metals can be present in high concentration in certain urban wood fuels and RDF, especially if treated or painted woods are present [29,64].

7.1. PAH emissions

7.1.1. Definition and sources
Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings. Some of them are known or suspected carcinogens. The simplest examples of PAHs are: phenanthrene (C13H10) and anthracene (C20H12) isomers of three fused rings (C4H6).

The US Environmental Protection Agency (EPA) has passed legislative restrictions regarding the release of PAHs into our environment, especially for 16 PAHs (carcinogens)[65].

PAHs may contain four-, five-, six-, or seven-member rings, but those with five or six are most common [45,65]. PAHs toxicity is very structure dependent, with isomers varying from being nontoxic to being extremely toxic. Thus, highly carcinogenic PAHs may be small or large. Following are a few examples of PAHs known for their carcinogenic, mutagenic, and teratogenic properties:

Benz(a)anthracene and chrysene (C18H12), Coronene, Dibenz(a,h)anthracene (C22H14); Indeno(1,2,3-cd)pyrene (C23H18).

7.1.2. Mechanisms and effects
Many organic materials, such as fossil fuels, have a chemical structure able to form polycyclic aromatic compounds (PAH) under pyrolysis and combustion conditions [66,67]. In fossil fuels, coals have the highest concentrations [68], whereas petroleum and their derived products have the least [69]. For example, in coal structure, the dominant component is considered to be a macromolecular three dimensional network composed of aromatic and hydroaromatic units connected by alkyl, ether, and thio-ether bridges [69]. Upon heating, the fuel structure undergoes important physical and chemical changes and a fraction is released into the atmosphere. As a consequence of the thermal process, both the released and the remaining fractions undergo cyclization reactions leading to polycyclic compounds which can exist in the gas as well as in the solid phase, depending on their molecular volume and on the environmental temperature. Biomass generally contains very low quantities of PAH structures [70].

The following PAH formation mechanisms have been suggested in the literature:

(1) Incomplete combustion: the fragments of the mainly aromatic structure of the fuel are emitted and escape unburned.

(2) Pyrolysis and pyrosynthesis: as a consequence of the chemical changes during combustion, reactions such as cyclization of alkyl chains and radical condensation can lead to polycyclic compounds through polymerization reactions, which are favored over oxidation in fuel-rich regions of the flame [69,71].

Considering the fact that biomass usually contains less aromatics, the main mechanism that holds for PAH emissions from biomass is pyrolysis and pyrosynthesis.

The mechanisms producing PAH in the combustion process are very complex, but it seems that the chemical reactions in flames proceed via the radicals released during the pyrolysis step which precedes combustion [66,71]. It is also strongly dependent on the type of biomass and the combustion operating conditions. Different synthesis mechanisms of PAHs have been suggested [69,72–74] and are being questioned by others [75] and these mechanisms are still in discussion.

For example, it has been shown that one way to produce PAH from smaller C3 species proceeds via the HACA mechanism. In this commonly called HACA mechanism (H-abstraction), PAHs are produced from the acetylene (ethylene) which forms benzene and multi-ringed PAH structures. The addition of acetylene to an aromatic ring, or the formation of an aromatic radical, like phenyl, leads to either bonding of an ethynyl (~C2H) group with the aromatic ring, or the formation of an additional condensed aromatic ring. Depending on the neighboring ring structure, the newly formed ring can either be a radical, which can grow readily with acetylene, or it may be a molecular species. The latter will have to be “activated” through the H-abstraction reaction to produce a PAH radical species before it can undergo the further growth reaction with acetylene. If the concentrations of aromatic species are sufficiently large, PAH growth through the direct ring–ring condensation is also possible. For example, benzene and phenyl can react to form biphenyl. Through the H-abstraction, a biphenyl radical forms and can react with acetylene to form the three-ring phenanthrene, or it can react with benzene to form a four ring aromatic species [72,74,76].

The simplest and earliest PAH formed can, depending on the flue gas conditions, undergo further pyrolytic reactions to form larger, highly condensed PAH by intermolecular reactions, such as condensation and cyclization. Therefore, the PAH can exist in the gas emitted or be supported on particulate matter (soot), or even give rise to particulate matter, depending on their association. Most three-ring PAHs are present in the gas phase emissions and compounds with four, five, and six or more ring PAHs are associated with flyash in biomass combustion emissions. PAHs are important precursors in the formation of PCDDs/Fs (polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxin). A simple formation scheme is given in Fig. 6.
At 800–950 °C during fluidized bed combustion (FBC), the destruction and chemical alteration of PAHs are possible in the presence of oxidants such as OH, O₃, HNO₃ etc. [77]. In practice, at typical FBC combustion temperatures, large molecules (if present) break up during pyrolysis, usually into smaller fragments, but small ones, e.g. of lower hydrocarbons, can yield higher molecular mass products. The PAHs produced in this step (~850 °C) may be mainly due to incomplete combustion. Above 850 °C, since the synthesis reactions of PAHs formation are endothermic (the enthalpy of formation (ΔH) of all the 16 PAHs is positive), more PAHs can be formed at higher temperatures [78]. As a consequence, the PAHs may be synthesized in the dense fluidized zone or freeboard region of the combustor at higher temperatures. The metals (Fe, Cu) in the particles may also act as catalysts for the synthesis reactions.

Excess air, residence time, and air staging are reported to affect PAHs significantly. Oxygen-rich environment helps in reducing PAHs. Air staging provides not only oxygen-rich conditions in the freeboard but also increases the residence time of fuel particles in the system. All these effects increase the efficiency of the system thus leading to lower PAHs [45,69].

Limestone added for SO₂ emission reduction in FBC system can also affect the PAH emissions. Increasing the Ca/S ratio causes an increase in PAH emissions due to a longer turnover rate of bed material and endothermic limestone decomposition [79,80].

It has also been reported that low percentages of excess oxygen favor the highest PAH deposition on particulate matter, while the highest percentages of excess air favor the sweep of PAHs to the gas phase. The highest percentages of excess oxygen seem to minimize possible interactions between PAHs inter-conversion, association and other condensation reactions, giving the lowest hydrocarbons emissions [69]. Perhaps, it is due to the formation of substituted PAHs and other oxygenated compounds, a consequence of the interaction between oxygen atoms and radicals. In this way, at the lowest percentages of excess oxygen, this interaction between oxygen and radicals should be less favored, and as a result, the PAH amount emitted would be higher. It can be concluded that once combustion efficiency is optimized, PAH emissions are a function of the interactions between radicals emitted by the devolatilization of the pyrolytic process and the combustion variables, combustion temperature, airflow, percentage of excess oxygen. The competition between oxidation and condensation reactions, retrogressive reactions, or the radicals conversion in CO, H, and O by oxidation reactions will determine the PAH formation [69,71].

7.1.3. Remedies
In order to avoid PAH formation, combustion efficiency should be kept as high as possible (close to 100%). A correlation between PAH and poor combustion conditions, particularly CO concentrations has been reported [81]. Some additives for the reduction in PAHs emissions with their limitations have also been proposed [82].

7.2. Dioxins and furans
7.2.1. Definition and sources
The term dioxins is popularly used to describe a class of halogenated organic compounds, the most common consisting

![Fig. 6–General formation scheme of PAHs, PCDDs, and PCDFs.](image-url)
of polychlorinated dibenzo-furans (PCDFs) and polychlorinated dibenzo-p-dioxin (PCDDs).

The basic structure of PCDD/Fs comprises of two benzene rings joined by either a single (furan) or a double (dioxin) oxygen bridge. Chlorine atoms are attached to the basic structure at any of the 8 different places on the molecule, numbered from 1 to 10 (see Fig. 7).

Different degrees and positions of chlorination on the aromatic ‘ring structures’ can occur leading to 75 PCDD and 135 PCDF isomers in total. In the environment, PCDDs and PCDFs are found in trace quantities as a mixture of the isomers. Some isomers of dioxin are known to be among the most toxic chemicals and may have carcinogenic and mutagenic effects.

Much of the environmental behavior of polychlorinated biphenyls (PCBs) can be related to their physical characteristics. Dioxins build up in living tissue (bioaccumulate) over time, so even small exposures may accumulate to dangerous levels.

Because of the non-polar nature of PCBs, they are strongly hydrophobic and thus strongly lipophilic. They readily climb the food chain because of their lipophilic nature. Dioxin enters the general population almost exclusively from ingestion of food, specifically through the consumption of fish, meat, and dairy products.

High level dioxin exposure to humans can cause severe diseases including chloracne, damage to immune systems, endometriosis, birth defects, diabetes, and liver and thyroid cancer [83].

7.2.2. Mechanisms and effects

The general hypothesis of dioxin formation can be stated as any situation where chlorine, carbon, hydrogen, and oxygen come into contact with heat; PCDD/Fs could be formed as trace by-products. Extensive research has been carried out to find the dioxin formation mechanisms [84–88]. The precise mechanisms about their formation have not been clarified yet [89,90], but a number of theories have been proposed [85,87,91–93]. In general, four sources of dioxin formation can be identified:

1. Dioxins entering with the feed.
2. Formation of dioxins through homogeneous gas phase reactions [93].
3. Formation of dioxins through heterogeneous reactions between organic precursor compounds (Phenols, PAH, acetylene) and flyash based metallic catalyst such as copper [88,92].
4. Formation through the De Novo synthesis involving flyash bound carbon, a chlorine source, and metallic catalysts [87,94].

A simple formation scheme of PCDDs/Fs is given in Fig. 6. All the above-mentioned four mechanisms are very sensitive to temperature. For the first two mechanisms, thermodynamic and kinetic studies suggest that these are only valid for temperatures between 500–700 °C and the dioxins in the feed or formed will essentially be destroyed at temperatures of 850 °C within 2 s or within 1 s at 1000 °C with good combustion practices. Good combustion practices for decreasing dioxins are based on oxygen availability, proper mixing, and uniform temperature [95]. Although even with good combustion practices, exceptionally high chlorine content feeds [96] or with high content of dioxins precursors (halogenated phenols or chlorinated aromatics) [86,97] or dioxins (as in pesticides, wood preservatives) could still lead to high dioxins emissions. Therefore, the research has been mainly focused on catalytic heterogeneous mechanisms.

Post-combustor dioxin formation may be due to reactions occurring on particles entrained in flue gas during the short time they pass through the low temperature zone (~ 300 °C), or from reactions on particles deposited on ductwork in the region where these temperatures prevail. The formation rate of PCDD/Fs from the precursors such as chlorophenols, chlorobenzenes, and polycyclic aromatic hydrocarbons, is reported to be 1 or 2 orders of magnitude higher than the De Novo synthesis. Lab scale experiments suggest that carbon is the primary source for dioxins in the De Novo synthesis [98]. Here, the PCDD/PCDFs form from a variety of carbon species, condensed to a polymeric network referred to as particulate carbon [81,84,86]. The precursor theory predicts PCDD/PCDFs formation from chemical similar species such as chlorobenzenes and chlorophenols. There is further evidence that carbon of different origins may serve as a source for the synthesis. The dioxin synthesis is catalysed by copper (II) and iron chloride; copper being about 20 times more effective than iron. The temperature once again is the most important factor and the reported temperature window for dioxin formation is between 250 and 450 °C [81,92,94,99]. The optimum temperature for the reaction of chlorophenol or other precursors showed a peak formation temperature of 400 °C, whereas for De Novo synthesis it is 300 °C. The dioxin concentration depends on reaction, time, concentration of particulate organic carbon, composition of the catalyst (chloride, copper) and of the atmosphere (oxygen, water). Recently, it has been demonstrated that polycyclic aromatic hydrocarbons also
chlorinate and decouple to form PCDD/Fs [100-102]. Since HCl is a combustion product of all organochlorine compounds, it follows that any of these compounds is a potential dioxin precursor during combustion.

It is a well established fact that dioxins can be formed in all combustion processes where organic carbon, oxygen and chlorine are present. Limited work has been reported on dioxin emissions from biomass combustion. It is well known that PCDD/Fs are always formed during wood combustion via precursors like phenols and lignin or via De Novo reactions in the presence of particulate carbon and chlorine [102]. However, the emissions in the flue gas are significantly lower in comparison to other sources. According to the European Emission Inventory [81,86], wood combustion (biomass) is at present one of the most important emission sources for dioxins (about 25% of the total emissions). However, it should be mentioned that the major share in these emissions is from residential burning, accidental fires, forest fires, and combustion and land filling of pentachlorophenol (PCP) treated wood. Data reported in literature indicates that emissions from controlled units equipped with efficient dust cleaning devices burning biomass, are well within limits [86,100].

7.2.3. Remedies

Operational parameters of fluidized bed combustion (air staging, excess air, etc.) can be effectively used to reduce PCDD/F emissions [103]. Good combustion practice, minimizing the flue gas residence time in the critical temperature zone (250–450 °C), and use of electrostatic precipitator/bag house filter are possible ways to reduce dioxins. In addition, a number of commonly used additives and inhibitors including urea, limestone, SO2, NH3, are also reported to be effective [104]. A number of comprehensive reviews about the formation and control techniques can be found in the literature [84,86,100].

7.3. CO emissions

7.3.1. Definition and sources
Carbon monoxide (CO) emissions are essentially the result of incomplete combustion and belong to the category of unburnt pollutants. They may be considered as a bench mark of combustion efficiency, although some studies reported higher combustion efficiencies with higher CO emission [105,106].

7.3.2. Mechanisms and effects
Reasons for the CO formation among others could be lower excess air, restricted residence time, temperature, and diffusion controlled reactions due to fuel composition (high ash content).

In comparison to coal combustion, the CO concentrations emitted from biomass fuels in BFB combustion can be higher when combusted in the small scale units designed for coal combustion and not modified for biomass or co-combustion. This is usually because of the high volatile content of biomass [60,107]. Significant methane formation has also been observed during devolatilization which subsequently converts into CO and CO2 later in the freeboard [107].

CO emissions are often a major concern for biomass (co)-combustion. Emissions of the order of volume percentages have also been reported [64,105,108,109]. The reasons differ from fuel composition to combustor design.

The most evident difference is because of the basic fuel composition difference between coal and biomass. Small scale units can produce high CO emissions due to shorter free-boards characterized by smaller residence times. Biomass has a comparatively higher volatile content and therefore needs more residence time in the freeboard to completely burn the volatiles. Another reason is also related to fuel composition. As biomass can have a higher ash content and such biomasses do not follow shrinking core model but rather a shrinking sphere model, which results in an ash layer surrounding the fuel particle and makes the oxygen diffusion difficult [109]. Also, heat exchangers located in the freeboard of common fluidized bed boilers decrease the temperature and therefore inhibit conversion of CO to CO2. Irregular or improper feeding could result in higher CO emissions as well [106].

Larger fuel particle size and high ash content have been reported to contribute to high CO levels. In terms of CO emissions, FBs possess formation and reduction zones of CO [110]. Limited work that has been reported on the influence of feed particle size distribution on CO emissions validate the fluidized bed capacity in handling a range of feed particle sizes [111]. These observations signify the role of heterogeneous reactions (on the char surface), of char-carbon with CO2 and water vapor, at typical FB temperatures [55]. These reactions are followed by fuel in-bed devolatilization and further oxidation of the carbon-based components, released from the fuel particles with volatiles, to CO [36]. In the reduction zone, the CO is basically oxidized in the chain termination reaction with OH radicals as well as by oxygen directly [112].

These observations suggest that the units (especially the small scale) designed for coal combustion may have problems while combusting biomass alone or higher share of biomass.

7.3.3. Remedies

In terms of design improvements, longer freeboards are recommended for biomass combustion in FBs, taking the high volatile content of biomass into account and increasing the total residence time. Also, an internal heat exchanger possibly presents in the freeboard and splashing zone in small scale FBs should be removed to keep these sections at higher temperature and therefore helping the conversion of CO to CO2. Regarding operating conditions, excess air is also reported as one of the very important factor for the burn out of the fuel. The system load and air staging can also be used as operating variables to increase the fuel residence time in the hot zone [64,105,110,111].

7.4. NOx emissions

7.4.1. Definition and sources
Nitrogen compounds include nitrogen oxide (NO) and nitrogen dioxide (NO2), which are commonly summarized as nitrogen oxides (NOx) and nitrous oxide (N2O). NOx emissions play an important role in the atmospheric reactions that create harmful particulate matter, ground-level ozone (smog), and acid rain. These emissions in combination with HC (hydrocarbons) photochemically lead to the formation of ozone, which is a lung and eye irritant and a major problem in urban environments.
NOx emissions are a part of a suite of year-round environmental problems, from acid rain in the mountain regions to eutrophication (the buildup of nutrients in coastal estuaries), leading to oxygen depletion that degrades water quality and harms fish. NOx emissions also contribute to haze air pollution in our national parks and wilderness areas.

7.4.2. Mechanisms and effects

NOx formation in combustion systems involves four main paths:

1. Formation of thermal NOx: requires sufficiently high temperatures for dissociation of the atmospheric diatomic species N2 and O2.
2. Formation of fuel NOx: the result of reactions involving fuel bound N.
3. Formation of prompt NOx due to fast reactions within the flame zone involving N2 and fuel bound hydrocarbon radicals, forming HCN as the most important intermediate reactant [105,113].
4. Nitrous oxide mechanism [114].

Thermal NOx is significant for firing of solid fuels in suspension systems with relatively low stoichiometric ratios (1.1-1.3) at high temperatures (typically >1500 °C) [25]. Specifically in fluidized bed systems, the temperature is usually below 900 °C and the formation of thermal NOx is very unlikely. The trends shown in the literature for NOx emissions suggest that much of the NOx originates from fuel nitrogen [33,115,116]. However, some investigators have also indicated a significant amount of prompt NOx formation [113,117]. The formation of fuel NOx is due to the oxidation of nitrogen in the fuel and it is of considerable greater significance in the combustion of solid fuels and wastes. Fluidized bed systems are typically operated at 815–925 °C and at such temperatures, the fuel nitrogen dominates [33,117].

The formation of NOx from fuel bound nitrogen takes place by the oxidation of the nitrogenous species released with the volatiles and the oxidation of the nitrogen retained in the char. NO is the dominant species with NO2 mostly being less than 5%. However, downstream of the flue gas path, at low temperature, NO is readily oxidized to NO2. Here, NO and NOx is interchangeable [118,119]. The distribution of the nitrogen between the volatiles and the remaining char is roughly proportional to the volatile matter in the fuel. During devolatilization of biofuels, as the char content is small, most of the nitrogen is believed to be in the volatile phase (66–75%). NOx is therefore formed via two different pathways, i.e. through gas phase oxidation of the nitrogenous group in the volatiles, and also through the heterogeneous catalysed oxidation of the char-bound nitrogen species [36,120,121]. A number of different fuel NOx conversion percentages have been reported for different biomass fuels [62,122,123].

Studies [124] suggest that the dominant nitrogenous volatile species are NH3 and HCN, and their concentrations depend on the devolatilization and combustion temperature. These reactions, resulting in the rapid formation of NOx, are most likely to proceed in the bottom region of the FBC with bottom air injection. Meanwhile, in the fuel-rich zones (i.e. the level of the fuel penetration into the combustor and above), the NH3 content is probably elevated due to the rapid formation of NH3 from HCN, as well as due to the emissions of NH3 released with the volatiles. This may lead to NO reduction in the upper combustor region through its reaction with NH3, followed by the formation of nitrogen gas and water vapor. At low temperature typical for fluidized bed combustion, the study showed that NH3 is the dominant species, a fact which has been supported by the measurements of others [125]. In the case of volatile nitrogen, the NH3 formed may decompose to NH2 and NH radicals that can either be oxidized by O2 to form NO or react with available NO and OH radicals to form N2. Thus, NH3 is both a source and a reducing agent of NO depending on the prevailing circumstances [123].

Measurements in laboratory units and large scale plants confirm that high NOx emissions (up to 1000 mg/m³) can be generated during the combustion of biofuels [36,62]. It seems that these high emissions are simply a reflection of the relatively high nitrogen content in these fuels. NOx from biomass is strongly dependent on fuel nitrogen and limitedly effected by operating conditions [115,126]. The formation of fuel NOx is not so temperature sensitive, it is largely a function of the percentage nitrogen in the fuel, reactivity of the fuel and the concentration of available oxygen during the primary pyrolysis and in the initial combustion sections of the furnace [127,128].

Different biomass derived NOx related studies show declining NO formation with increasing fuel N concentration but not as significantly as for coal [116,118,121,129]. The most likely explanation for this relatively low conversion is that the char, which is present in relatively high concentrations, is effective in reducing overall NOx emissions by catalyzing the reduction of NO by CO [126]. Char, for example, provides a catalytic surface for the gas phase NO reduction by CO, which is estimated to account for about 50% of the NO reduction, formed at primary stage during bituminous coal combustion [62,130]. However, for biomass, this effect is not that significant due to lower char content in biomass but is a valid reason for co-firing units.

The most tenable explanation for mostly low but sometimes high NOx emissions follows from the fact that biomass has high volatile content but low nitrogen content. This in turn means that the dominant source of NOx and N2O is originating from volatiles. NOx production from high nitrogen content biomass is usually very high because of the lower char content in bed and therefore oxidation of NH3 arising from the volatiles has little char available for reduction by CO. In this regard, as the NOx emissions are dependent on unburned carbon content in the flyash, the lower the NOx emissions, the higher the unburned carbon [131].

In the case of fluidized bed combustion, the presence of CaO, MgO, and Fe2O3 in the fuel can lead to the formation of an active bed which can catalyse the reduction of NO and N2O, especially under fuel-rich combustion conditions [123,132]. Fortunately, this reduction of NO is directly proportional to nitrogen rather than to N2O [133,134]. Another reason for this declining N to NO conversion is postulated to be due to the formation of a nitrogen containing species important for both the production and removal of NO. In addition, the relative NOx and N2O production for biomass appears to be less than that for coal, although this conclusion is only weakly
supported by the limited results for biomass [106]. Another possible explanation for low conversion (compared to the fuel N content) could be the presence of higher H and OH radicals concentration due to higher O/C and H/C ratios in biomass than coal. Reduced furnace temperatures for biomass compared to coal likely account for much of the difference [29]. Reported work also suggests that N₂O does not influence overall NO emissions [133,134]. A generalized fuel nitrogen conversion scheme is given in Fig. 8 [26].

7.4.3. Remedies
In order to reduce NOₓ formation, primary measures (air and fuel staging) have been comprehensively investigated for grate firing, BFB and CFB furnaces. Flue gas recirculation as a primary measure is of minor influence on NOₓ emissions [26]. Both staging options enable significant NOₓ reduction (30–80%) [25,26]. The results show that primary and secondary air should be injected in geometrically well separated furnace sections (BFB, CFB). Furthermore, the air fans should be frequency controlled to be able to ensure a primary air ratio of 0.6–0.8 in the furnace. Moreover, the excess oxygen amount, determined by the secondary air, should be as low as with the side constraint that a complete combustion has to be guaranteed. However, different specific conditions have to be met accurately to utilize this reduction potential including temperatures up to 1150 °C (at the injection point, for e.g., splashing zone) that have been recommended for staging [26] to deliver optimum results. The technology has been successfully applied at lower temperatures as well. For fuel staging, reduction can be achieved at lower temperatures (~850 °C) [108,109,121,135]. However, the furnace concept and operation is more complex due to the need of two independent fuel feeding systems [26]. For both types of staged combustion, accurate process control is needed to ensure an operation at the excess air ratio needed in the different zones.

If NOₓ reduction by primary measures is not efficient enough to meet the limiting values aimed at, secondary measures are also possible [61,119,136]. These are selective catalytic reduction (SCR) by injecting ammonia or urea over a catalyst at about 250–450 °C and selective non-catalytic reduction (SNCR) by injecting ammonia in a separate reduction chamber at 850–950 °C [25]. The reaction may be described as

\[
2\text{NO} + 4\text{NH}_3 + 2\text{O}_2 + 2\text{H}_2\text{O} = 3\text{N}_2 + 8\text{H}_2\text{O}
\]  

(R1)

The NOₓ conversion rate is mainly dependent on the reaction temperature, the NH₃/NOₓ molar ratio, and the number and location of ammonia injection nozzles. Fluidized bed combustors operate at temperatures found favorable for highest NOₓ conversion rates [137]. NH₃ injection rates are commonly adjusted to changing NOₓ concentrations in the gas stream. NH₃/NOₓ molar ratios well above the stoichiometric NH₃ to NOₓ equilibrium ratio promote high NOₓ reduction rates, but also result in increased and undesired NH₃ slip. NOₓ emissions for biomass fuels not containing any fuel N remain unknown.

Up to 95% reduction in NOₓ emissions for SCR and 90% for SNCR have been reported [137]. However, relevant HNCO, N₂O, NH₃, HCN, and other N-containing species can be formed in both types of secondary measures under unfavorable conditions. Hence, primary measures are preferable if they can achieve the sufficient emission reduction [26].

Reburning has also been suggested as a possible solution to high NOₓ emissions. It is a combustion modification technology that removes NOₓ from combustion products by using fuel as the reducing agent. The concept was originally based on the principle that hydrocarbon fragments (CH) can react with NOₓ. Reburning is accomplished by secondary fuel injection downstream of the fuel-lean primary combustion zone of a furnace [138]. The second stage or reburning zone is usually operated at overall fuel-rich conditions, allowing a significant fraction of the primary NOₓ to be reduced to N₂ and other nitrogenous species. In the third zone, additional air is introduced to establish overall fuel-lean conditions and allow for the burn out of remaining fuel fragments. This form of NOₓ abatement has been applied to full-scale units and appears to be attractive when natural gas is used as the reburning fuel to

Fig. 8 – Conversion of fuel nitrogen in biomass combustion.
destroy pollutants created in pulverized coal combustion. Reduction of NOx occurs primarily in the reburn zone by reaction of NO with hydrocarbon fragments (CH, CH₂). These reactions typically produce HCN, which decays in the reburning zone along the chemical pathway:

\[ \text{NO} + \text{CH}_4 \rightarrow \text{HCN} + \text{NCO} + \text{NH}_2 + \text{N}_2 \]  
\[ \text{(R2)} \]

The last step in this chemical pathway which converts N to N₂ is called the reverse Zeldovich reaction, which is accepted as the primary route of NO formation and destruction in the thermal NOx mechanism.

Low nitrogen content biomass because of its high volatile content can be used as a reburning fuel. The use of wood to reduce NOx is attractive for several reasons. First, wood contains little nitrogen compared to coal; this results in lower nitrogen oxide production from fuel nitrogen species for wood. In addition, wood contains virtually no sulfur, so SO₂ emissions are also reduced together with its CO₂ emission reduction effect. Finally, since the reburning fuel is normally 10–20% of the total heat input, large quantities of wood are not necessary as compared to firing 100% wood.

There is one additional benefit of wood compared to the case of reburning with natural gas. In large scale systems, it is difficult to mix natural gas into the products of the primary combustion zone since the gas must be injected from the wall, at relatively low flows. Wood particles, which must be transported to the furnace by a carrier medium (likely candidates are air or flue gas), would have a ballistic effect upon entering in a furnace that would enhance cross-stream mixing compared to the natural gas case.

The concept of reburning with wood is not without difficulties. Since wood is primarily comprised of cellulosic material, a large fraction of the volatiles that result from wood pyrolysis contain a carbon-to-oxygen bond. The large fraction of CO and CO₂ that results from the pyrolysis of wood suggests that there will be diminished reburning capabilities with wood compared to natural gas or coal since the CH-fractions necessary for reburning would be lower in the wood reburning case [139].

7.5. N₂O emissions

7.5.1. Definition and sources
N₂O belongs to the category of greenhouse gases because of its potential role in the depletion of the stratospheric ozone. N₂O is regarded to contribute to the greenhouse effect and ozone depletion. Although the atmospheric concentrations of N₂O are low (1100 times less than CO₂), the relative strength of N₂O as an infra-red absorber is reportedly 200 times more than CO₂. In addition, N₂O, being a stable compound, is transported to the stratosphere where it photochemically oxidizes to NO, the major contributor to catalytic ozone depletion [140].

7.5.2. Mechanisms and effects
HCN is considered as the precursor for N₂O [113,115]. HCN may react with an oxygen radical following the path such as

\[ \text{HCN} + \text{O} \rightarrow \text{O} + \text{HCN} + \text{NO} + \text{N}_2 \text{O} \]  
\[ \text{(R3)} \]

Bench scale studies suggest that cyano species produce more N₂O than NH₃ does, indicating that fuels that produce NH₃ rather than cyano species as intermediates will show lower N₂O emissions [140]. This reaction mechanism is believed to be the main formation route leading to N₂O formation in fluidized bed combustion [133]. It is known that HCN is the major nitrogen species evolving from the devolatilization of bituminous coals whereas for low rank coals and for biofuels the NH₃/HCN ratio increases. This means that less HCN is available to produce N₂O in biofuels. As for the distribution of nitrogen in the fuel, which is responsible for the formation of N₂O, it is almost the same as for NOx, so a major share comes from volatiles while char combustion contributes its fraction [120]. Contrary to NOx, N₂O emissions from fluidized bed combustors are not significantly affected by air staging but are a strong function of operating temperature and excess air level. Air staging and sorbent feed rate do not significantly affect N₂O emissions [140].

At temperatures higher than 900 °C N₂O decomposes to N₂. The net concentrations of NH₃, HCN, NO, and N₂O from the furnace are a function of the homogeneous gas phase reactions, the heterogeneously catalysed reactions, and the gas/solid phase reactions. Thus, increasing off-gas temperature is effective for N₂O reduction during fluidized bed combustion [141–143].

With excess air, N₂O increases due to a drop in temperature that reduces H and OH radicals and increases NO formation. With air staging, the temperature increases resulting in the formation of more O and OH radicals and thus destruction of N₂O. However, this destruction reaction must compete with other reactions like oxidation of OH by carbon in char, CH₄ and CO, which are more sensitive than the destruction of N₂O. Furthermore, due to decrease in NO as air staging increases, the formation of N₂O from NO may also decrease.

N₂O emissions have been found relevant only to fluidized bed combustion because of its low temperature operation [143]. However, N₂O emissions from FB units combusting biofuels are reported to be lower than from natural gas or coal [105,115,143]. N₂O is largely reduced in the flue gas stream of high temperature combustion systems, whereas, this reduction is less efficient in low temperature and fuel-lean combustion systems [113,143]. In fluidized beds, during the combustion of coals, it is usual to have, depending on the temperature and air excess conditions, a concentration between 20–200 ppm of N₂O in the combustion gases [144]. Reduction in NOx emissions for biomass combustion systems with reduced excess air levels and staged combustion techniques have been reported [115,143].

Analogous to the case of NOx reduction, char plays an important role for N₂O reduction as well. Char is very effective for the catalytic reduction of N₂O as well as for direct reduction of N₂O. Whereas the role of char in the formation and reduction mechanisms of NOx and N₂O applies to all types of combustion systems, under fluidized bed combustion conditions, other factors come into play. The presence of CaO, MgO, and Fe₂O₃ from the fuel can lead to the formation of a very active bed which can be very effective in catalyzing the reduction of NO as well as N₂O [132]. For example, brown coal is known to contain very finely dispersed calcium in its
structure which enriches the bed with CaO during combustion and forms a very active bed. Although as stated before, the char effect is not very significant for biomass due to low char content of biomass but is well effective for co-firing.

7.5.3. Remedies
Existing data indicate that several techniques exist to keep the N₂O emissions at low level including an increase in operating temperature and decrease in excess air levels. Other control methods include afterburning of gaseous fuel in the cyclone or freeboard of the combustor with natural gas or propane or reversed air staging. Afterburning can reduce N₂O emissions up to 90% but involves significant costs while reverse staging can reduce N₂O emission by a factor 4. However, the process is accompanied with the increase in CO emissions [119,136,140,142].

When alternating oxidizing and reducing conditions occur, NO formation from N₂O decomposition over sulphated limestone is possible and high percentage of this NO will then be reduced to nitrogen by the available char content and active catalytic bed [59]. Limestone has been reported to play an important role in the reduction of N₂O emissions from coal and other alternative fuels [143,145]. The effect of limestone is related to some threshold level and higher levels do not produce any benefits in terms of net reduction of N₂O [59]. For biomass, however, this is not of very much significance because biomass generally has lower S and N content. At first, due to lower nitrogen content, N₂O emissions are not expected to be a major concern. Secondly, due to lower sulfur content, limestone usage in biomass combustion is very limited and therefore reduction of N₂O by CO over CaO can also not be realized but may be significant for co-firing.

7.6. SO₂ emissions

7.6.1. Definition and sources
It is an established fact that SO₂ from combustion sources is one of the causes for acid rain. Also, sulfur together with chlorine may play an important role in corrosion of boiler components [146,147]. Sulfur exists in plants in both organic (amino acids and sulfolipids) and inorganic (sulfates) forms. The concentration of organic sulfur is reported to be usually constant but inorganic sulfur can vary by a factor 100 [105].

7.6.2. Mechanisms and effects
Fuel bound S forms the gaseous compounds SO₂, SO₃ and alkali sulfates during the combustion process. As a result, the biggest part of S (up to 75%) is released to the vapor phase [148,149]. In the boiler where the flue gas gets rapidly cooled, the sulfates condense on the flyash particles or at the tube surfaces. Furthermore, SO₂ can be bound to the flyash by sulfation reactions. Test runs and evaluations of the material balances have shown that 40–90% of the total S input by the biofuel is bound in the ash, the rest is emitted as SO₃ and to a minor extent as SO₂ with the flue gas [148]. The efficiency of S-fixation in the ash depends on the concentration of alkaline earths (especially Ca) in the ash as well as on the efficiency and technology used for dust precipitation. The importance of S in biomass combustion does not result from the SO₂ emissions but from the role S can play in corrosion processes [25,43].

Biomass addition in co-combustion with coal not only reduces the CO₂, but at the same time decreases the SO₂ emissions due to lower inherent sulfur content of biomass (0.02 to 1% on dry weight basis) [150]. Two reasons cause the decreasing SO₂ emissions. The first reason is that the sulphur content of the blends decreases with an increasing biomass share. The other reason is the change of the conversion rate. As the biomass ash contains often relatively high CaO and MgO, the SO₂ may be absorbed to a certain extent [151]. Higher alkaline earth content in the ash seems to result in higher SO₂ capture.

7.6.3. Remedies
In-situ use of limestone and dolomite is a common practice in fluidized bed combustion of coal to control sulfur dioxide emissions. At the combustion temperatures, usually in the range of 800–900 °C, the CaCO₃ calcines to CaO and CO₂. The CaO then reacts with SO₂ and O₂, or with SO₃, to form CaSO₄. Theoretically, the formation of CaSO₄ requires 1 mol of Ca for each mole of S released during combustion of the fuel. However, the Ca utilization of the solid sorbents is usually significantly lower, with efficiencies (moles S adsorbed divided by moles of Ca available) typically ranging from 25% to 45%. The low utilization of the sorbent is mainly due to relatively large particles used and blockage of pores by CaSO₄ formed. This sulfation pattern is commonly referred to as the unreacted-core model [152].

The Ca utilization of limestone is known to be highly dependent on the flue gas temperature and particle size. Several researchers have found that increasing particle size reduces the utilization significantly, and that the sulfur capture capacity passes through a maximum at temperatures between about 800 and 850 °C. Limited knowledge is available on the influence of the flue gas moisture content on the calcium utilization. There is some evidence that long-term exposure to relatively high temperatures, and/or high CO₂ and high H₂O concentration can “dead-burn” a partially sulfated limestone, making it inert to further SO₂ retention. The moisture content also shows some influence (utilization decreases with increasing moisture) on calcium utilization (0 to 70% moisture) [111].

Limestone sulfur retention can be significantly influenced by operating conditions [111,153,154]. An optimum 3:1 Ca/S ratio has been reported [111]. CaO utilization is greatest for smaller particles (larger surface area) and decreases for all temperatures with increasing particle size. However, at lower sulfation temperatures (675 and 725 °C), the particle size has a significant effect [155]. Limestone is reported to show some catalytic selectivity of HCN and NH₃ towards NO, thus increasing the total NOx emissions whereas SO₂ is termed as a homogeneous catalyst recombining free radicals (H, O, OH) and increasing CO emissions.

All the parameters mentioned above have little significance for biomass combustion. However, these parameters (CaO content, temperature etc.) become important for co-combustion operation as and effect of biomass share on flue
gas temperature can significantly affect the SO\textsubscript{x} capture depending on the fuel blend ratio.

8. Deposits and corrosion

8.1. Definition and sources

Deposits or fouling, in terms of combustion, are commonly known as the layers of materials (ash) collected on the surface of heat transfer equipment. Another important term, slagging, characterizes deposits on the furnace walls or other surfaces exposed to predominantly radiant heat. Corrosion is the deterioration of intrinsic properties of a material due to reaction with its environment. Corrosion can be caused either directly by gas phase species, by deposits or by a combination of both [156]. Slagging and fouling reduce heat transfer of combustor heat exchanger surfaces and causes corrosion and erosion problems, which reduce the lifetime of the equipment. The main contributions to fouling come from the inorganic fraction of the fuel which is known to cause severe deposition problems at moderate to high temperatures [157]. Alkali compounds, potassium and sodium, are known to play a major role in the deposition processes [158]. These alkali metals, in biomass, are primarily present as organic compounds or simply as salts and therefore are readily released to the gas phase during combustion [156]. They form alkali silicates that melt at low temperatures (can be lower than 700 °C), thus providing a sticky surface for enhanced deposition. The ash deposition rate from biomass can easily exceed that from coal simply due to high ash content of the fuel. Although the deposits decrease the heat transfer rate and thus boiler capacity, it should be mentioned here that deposits themselves are not harmful to the boiler. High alkali metals and Si content biofuels can easily exceed the deposition rates from coal. It is basically the complex chemistry involving Cl, S, Si, and alkali metals which can cause severe corrosion problems [158,159].

8.2. Mechanisms and effects

A general sketch of potassium, sulfur, and chlorine chemistry in a biomass fired boiler is given in Fig. 9 [156].

Chlorine plays a very important role in terms of the formation of alkali silicates. It increases the volatility (or mobility) of the alkali metals, releasing them as alkali chlorides and hydroxides in the gas phase. The chlorine concentration often dictates the amount of alkali vaporized during combustion more strongly than the alkali concentration itself. In most cases, chlorine appears to play a shuttle role, facilitating the transport of alkali from the fuel to the surface. In the absence of sulfur, chlorides often reside on the surface [149,158]. When the flue gases are subsequently cooled in the convective pass, these alkali compounds nucleate and then impact or directly condense on the heat exchanger tubes/superheater. A part of these compounds also condenses on the flyash which may subsequently impact on the heat exchanger. For both alkalis and chlorine, the deposition of the aerosols from the combustion gases onto the boiler walls and heat-exchange surfaces has been pointed out as the main source for their presence in deposits [160,161]. These alkali compounds then react with SO\textsubscript{2} and form sulfate compounds on the metal surface. In the absence of sulphur, they remain as chlorides on the surface. If chlorine is also absent, then alkali hydroxides are the dominant gas phase species. These alkali compounds on the metal surface lead to the creation of sticky coatings enhancing deposit buildup with inertial particle impaction [159].

The non-volatile compounds remaining in the charcoal, by coalescence or melting, form ash particles with a wide range of compositions, shapes, and sizes, related to the characteristics of the parent material. They consist mainly of inorganic refractory species such as Ca, Mg and Si as well as of smaller amounts of bound volatile compounds such as K, Na and Al. A substantial part of this ash usually remains in the bed and forms the bottom ash and cyclone ash in case of FB, while the rest gets entrained with the flue gas and forms the coarse part of flyash with particle sizes between few \textmu m to some 100 \textmu m. Coarse flyash particles can cause depositions on furnace walls and heat exchanger surfaces and contribute to particulate emissions [43]. Coarse ash particles impact on the heat exchanger surfaces with a high probability, but often they do not adhere to the surface. Their retention on the deposit is facilitated if the deposit surface or the surface of the impacting particle is formed of sticky material. The major deposition mechanisms for submicron particles are thermophoresis and Brownian diffusion for the finest particles [159,162].

This impaction of this coarse flyash on the superheater/heat exchanger basically defines the presence of Ca and other non-volatile species in the deposits [43]. In biomass, potassium is the major source of concern not only for deposits but also for agglomeration problems. Potassium, sometimes in combination with alkaline earth metals like Ca, reacts with silicates deposited as flyash to form molten glassy phases leading to hard sintered structures. The glass reactions lead to the formation of heavy slag deposits resembling fuel ash in composition but substantially depleted in sulfur [158]. Hard deposit formation due to sticky flyash particles can be accelerated by alkali and heavy metal salt mixtures (mixtures of alkali chlorides and sulphates with Zn and Pb chlorides) [43].

Fig. 9 – Principal pathways of potassium, sulfur and chlorine in a biomass fired boiler.
Biomass deposits usually have a high content of potassium, silicon, and calcium, but may also be rich in chlorine. Chlorine percentages of up to 38 wt.% have been found in deposits. Chlorine-based corrosion is affected by the temperature and concentrations of chlorine, sulfur, alkali metals, and oxygen [149,150,156,158].

In general, all the metal surfaces, which are alloys of different metals, are attacked either by gaseous components such as Cl₂, NaCl(g) etc. or by compounds such as sulphates, chlorides etc. releasing the metal from the alloy in different composition (metal chlorides, sulphides, Na-metal compounds etc.), thus making the alloy structure deficient in one of the essential metal components. The corrosion mechanisms in biomass fired boilers can be broadly classified into three classes [156]:

2. Solid phase corrosion.
3. Molten phase corrosion.

These classes are further classified into a number of different subclasses. Even the shortest description of these mechanisms is outside the scope of this article. Readers are referred to the available literature [146,148,163–165]. Although it is reported that most of the severe problems associated with Cl induced corrosion occur at metal temperatures higher than 500 °C and even the steam producing boilers operating the superheater below 450 °C have not experienced great problems, the fact is that the process is still ongoing but only at lower rate, so even the hot water boilers (tube temperature 100–150 °C) do experience problems but not in a short term and not as severe as at higher temperatures [148].

8.3. Remedies

Remedies available for the successful removal or at least hindering the effect of Cl in deposits and subsequently corrosion are basically focused on the capture of alkali compounds [166–168]. Studies suggest the use of different materials such as bauxite, kaolinite, limestone etc. to produce high melting point alkali compounds relative to alkali chlorides. These additives are meant to increase the melting point of the ash formed during combustion. With the use of most of these materials, Cl is released in gas phase, thus not totally eliminating the corrosion effect.

9. Agglomeration

9.1. Definition and sources

Ash from any combustion system can essentially be divided into four classes:

1. Bottom ash
2. Cyclone ash
3. Filter flyash
4. Flue dust.

The fraction of fuel ash in each class essentially depends upon the technology and solid emissions control devices installed with the system. Bubbling fluidized bed systems contain nearly no bottom ash as all ash is entrained out of the bed by the flue gases. The cyclone ash, filter flyash and flue dust are discussed under dust emissions in the following sections.

Although the bed in BFBs, in principle contains virtually no free ash, the ash released during combustion forms layers around inert particles (usually quartz sand). This is the main reason of agglomeration problems in fluidized beds.

Agglomeration is one of the few potential problems associated with fluidized bed combustion processes. In its extreme case, agglomeration leads to unscheduled shutdown of the plant. For these reasons, it is essential that this problem should be brought under control if not totally eliminated.

Agglomeration is not a new problem in FB plants. Work on agglomeration problems has been in progress for decades mainly with coal [169–172]. The ash characteristics of biomass are different from those of coals. Combustion processes with biomass, especially with herbaceous biomasses which have a high content of alkaline elements, are prone to experience severe agglomeration problems [150,156,173–175]. Silicon, calcium, potassium and aluminum are the agglomeration related components in biomass ash [174,176,177]. Potassium is dispersed in biomass in ionic and organometallic forms, while silicon occurs primarily as hydrated silica grains. The mechanism of potassium release has already been discussed under deposits and corrosion (Section 8) and will further be discussed under dust emissions (Section 10). Part of the potassium tends to stay in the bed by recapture of vapors by mineral components in the bottom ash under FBC conditions [178].

9.2. Mechanisms and effects

As mentioned before, a smaller part of ash remains in the bed. It is this remaining bed ash that is the main cause for bed agglomeration related problems. There are at least three different mechanisms identified for ash sintering:

- the presence of a liquid phase
- solid-state sintering
- chemical reactions.

The first mechanism, which is commonly called partial melting, can be further classified according to the type of melt in question. A highly viscous problematic melt also referred to as ‘viscous flow sintering’ may occur in the presence of silica. This kind of melt poses the greatest problem due to the formation of glassy phase which does not crystallize upon cooling [175,179].

In the case of low viscous melts, alkaline compounds can melt and act like a bonding agent. Sintering, in this case strongly depends upon the amount of the melt which in turn is a function of temperature and chemical composition. The amount of liquid phase controls the stickiness of the particles and the agglomeration of the particles [175,180]. Eutectics of low melting point are created by absorption and chemical interaction between silica (SiO₂) and potassium compounds, e.g. K₂O or KCl of the ash biomass [149,181]. In biomass fired FBC boilers, partial melting is considered as the main mechanism leading to bed agglomeration [174].

Fig. 10 shows the development of an ash layer rich in potassium after few hours of operation in a fluidized bed boiler.
which ultimately results in the formation of agglomerates. EDX analysis of the particles and agglomerates indicates that the initial concentration of potassium in the outside layer is usually low (1–2%) and it increases with the passage of operation time. Potassium percentages as high as 15–20% have been observed.

9.3. Remedies

Co-combustion, pre-processing of the risky fuel, use of additives, and use of alternative bed materials can be utilized individually or in combination to handle these risky biomass. The basic idea behind all these remedies is to increase the melting point of sintering compounds.

Co-combustion with clean fuels generally delays the time of occurrence for agglomeration and it also has a very limited window of operation.

A number of different additives including kaolin, dolomite limestone, lime, alumina etc. have already been proposed. However, efficiency, subsequent problems, and applicability of such materials have definitely limited their use.

The third remedy to agglomeration, i.e., use of alternative bed material, is the most attractive solution for plant owners and operators not only due to its ease of use but also because of relatively low costs. Different alternative bed materials including dolomite, magnesite, ferric oxide, alumina, feldspar, and aluminum rich minerals have been proposed and tested with a range of problems [182–184]. Problems associated with the proposed materials include high attrition and entrainment rates, chemical stability, and other problems (namely windbox and air nozzle plugging).

Recently, a new patented bed material called “Agglostop” has been reported to be successfully used in a number of plants without any operational problems [182]. The free quartz of the natural sand is said to be responsible for the formation of low melting point silicate compounds. It is claimed that the material can easily handle high alkali-induced agglomeration problems.

10. Dust emissions

10.1. Definition and sources

Biomass combustion leads to relatively high emissions of particulates, i.e., well above 50 mg/m³ at 11 vol.% O₂ [26]. The size distribution of the particles varies for different combustor setups. Particles in submicron (less than 1 μm) and supermicron (greater than 1 μm) range are usually emitted with size distribution differing with respect to technology used [43,148].

Fine particles propagate far away from the source and have a high probability of penetrating into the alveolar regions of lungs when inhaled [185]. Exposure to sulfate and fine particles (aerodynamic diameter less than 2.5 pm) has been found to correlate with cardiopulmonary and lung cancer mortality [186].

Particulate emissions from a combustion system can be classified into two broad classes:

(i) Particles from incomplete combustion (soot, condensable organic particles (tar), and char).
(ii) Particles from the inorganic material in the fuel ash.

The first category is not a major concern as these can easily be controlled by operating parameters. Inorganic particles are produced from two different mechanisms; large particles are produced from fusion (agglomeration of both regular and irregular shape particle through the outer layer) of non-volatile ash elements in the burning char particles and fine particles are produced from nucleation and condensation of volatile ash elements [187,188]. Inorganic solid emissions from biomass is one of the major environmental issues associated with biomass combustion. Respirable particles of 10 μm or smaller (PM 10) are breathing hazards, as they are retained deep in the alveoli of the lungs. Mechanically generated particulate matter including carry-over fuel fines and ash particles tend to be fairly large compared to combustion aerosols. Biogenic silica in some materials, such as rice straw, is partly released as fibrous particulate matter which has recently become the source of
10.2. Mechanisms and Effects

The inorganic particles emitted can be further classified on aerodynamic particle size class basis. The most common is the fine (submicron) and coarse flyash (larger than a micron). Most combustion generated particles are less than 1 µm aerodynamic particle size (fine particle class) [189]. The submicron particles are generally perfectly spherical due to the formation through a nucleation mechanism while the surface structure of coarse particles is irregular, indicating incomplete ash coalescence due to the relatively low temperature during ash formation [162,190].

Mass concentrations of particles downstream of the convective pass (upstream of dust separation devices) for different biomass fuels and boilers vary between 60 and 2100 mg/nm³ [162,190]. Contrary to other firing systems, mass size distributions of flyash in fluidized beds are generally bimodal containing one submicron and one supermicron maximum (Fig. 11). These distributions are dominated by supermicron particle, and fine particles are only a minor part of the particles mass downstream of the convective pass. A displacement of the maximum in number size distribution towards larger particle sizes when oxygen concentration decreases is observed [189,191]. As most biomass fired boilers are generally operated under favorable combustion conditions, particles originating from incomplete combustion are very few and organic content of the particles is negligible.

The supermicron particles generally contain refractory species such as calcium, magnesium, silicon, phosphorous, and aluminum [192,193] and essentially represent the mineral composition of the fuel, while submicron particles are mainly composed of alkali salts like potassium chloride and potassium sulfates [189]. Increased potassium, chlorine, and sulfur concentrations in the fuel lead to increased mass concentrations of particles in the flue gas. These trends suggest that the fuel composition is strongly related to the composition of the particles emitted [189].

In a manner similar, but not identical, to that for coal combustion, these fine particles have been shown to be generated by devolatilization of a part of the mineral matter (alkali compounds) in the fuel and subsequent nucleation/condensation of these vapors when the flue gases cool [194]. The release of alkali and chlorine has already been discussed under deposits and corrosion (Section 8) [195,196].

At higher temperatures, the alkali metal release is correlated with the chlorine content. A study of chlorine emissions during combustion of herbs and wood shows that flyash was mainly formed from evaporation of inorganic compounds, such as KCl, which may undergo subsequent chemical transformation, for example to K₂SO₄ in the presence of SO₂. The initial feedstock composition was the most important factor for the amount and species of alkali metals released during combustion [197]. As has already been discussed in Section 8, the dominant alkali species, which in the case of biomass is usually potassium, are released as potassium chloride. Combustion temperature, oxygen concentration in the emitted flue gas, and moisture content in the fuel seem to have small influence on the alkali release [189].

Either alkali chlorides, hydroxides, sulfates, or cyanide can be formed depending on the concentrations of chlorine, moisture, sulfur, and nitrogen content of the fuel [198,199]. This indicates that increasing the moisture content of the fuel or by adding steam, the formation of alkali chlorides can be avoided. The nucleation of these species to form submicron particles (aerosols) is a complex chemistry of KCl, K₂SO₄, K₂CO₃, and K₂SO₃ and depends on the availability of the component (sulfate, hydroxides, chlorides or cyanide) and temperature of the system. Nucleation can also take place at high temperature if some fraction of alkaline earth metals is also volatilized. These high temperature nuclei then provide surfaces for the condensation of alkali compounds and metal vapors. Some studies [148] suggest otherwise, but high percentages of calcium sometimes found in submicron classes are probably formed by this mechanism. Thus nucleation is usually limited to alkali chlorides and sulfate compounds while alkaline earth metals provide surfaces in coarse particle class and sometimes in fine class as well [189].

In a recent experimental study, it is found that the particles collected at 900 °C contained potassium and sulfate while those collected at 560 °C also contained chlorine thus suggesting K₂SO₄ nucleation and potassium chloride condensation at lower temperatures [161]. Alternative K₂SO₄ formation by heterogeneous transformation of KCl or other compounds has also been suggested [200].

It is relevant to note that both theory and experiments support the idea of a competition between sulfur and chlorine in the capture of potassium vapors at the exit of a combustion chamber. In this process, sulfur acts first, since the formation of K₂SO₄ occurs at higher temperatures, while chlorine proceeds as a sink for the remaining potassium which condenses as KCl [160].

Due to the high volatility of Cd, Zn, and Pb, amounts of these heavy metals can also be present in the aerosol fraction depending on the heavy metal concentration in the fuel [43]. Aerosols work as a sink to these metal vapors because of the large surface they provide. Metal emissions are dealt with in the next section separately.
10.3. Remedies

Primary measures to control dust emissions are either not yet economically feasible (leaching etc.) or simply conflicting with the desired combustion conditions, therefore secondary measures are necessary. Efficient aerosol precipitation and further treatment to control particulate and heavy metal emissions are recommended [201]. These solutions (bag house filters and electrostatic precipitators) are cost intensive and can only be economically feasible for medium to large combustion units (greater than 20 MWe). Even ESPs and BHF (Electrostatic precipitators and Bag house filters) show the lowest efficiency for submicron particles and therefore there is a strong need to further develop efficient dust cleaning devices for submicron particles. For coarse flyash (>5 micron), cyclone separators can be used. High ash containing or metal containing biomass fuels should not be combusted in units with no ESP or BHF.

11. Trace metal emissions

11.1. Definition and sources

Trace elements (As, Ba, Cd, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, Zn) present in some biomass fuels play an important role in the various practices of this renewable feedstock. These elements are of great biochemical, nutritional, and clinical importance and also of great environmental concern for heavy metal emissions [202]. Cd in agricultural products is potentially a public health problem, owing to its accumulation in the kidneys and its effects on skeletal density [203].

The presence of the trace elements in the fuel depends upon the source of biomass. For example, for agricultural biomass, age of plant, growing site, distance from the source of pollution generally determine the trace element fraction in the fuel while for others, past processing of the source is of great biochemical, nutritional, and clinical importance. Efficient aerosol precipitation and further treatment to control particulate and heavy metal emissions are recommended [201]. These solutions (bag house filters and electrostatic precipitators) are cost intensive and can only be economically feasible for medium to large combustion units (greater than 20 MWe). Even ESPs and BHF (Electrostatic precipitators and Bag house filters) show the lowest efficiency for submicron particles and therefore there is a strong need to further develop efficient dust cleaning devices for submicron particles. For coarse flyash (>5 micron), cyclone separators can be used. High ash containing or metal containing biomass fuels should not be combusted in units with no ESP or BHF.

11.2. Mechanisms and effects

Analogous to ash, the total metal flow with the feed is essentially divided into four fractions in FB combustors but are distributed differently in different fractions. Relatively small fraction stays in the bed with the bed material (usually quartz), a large fraction leaves with the entraining flyash (see Fig. 12) with major fraction of the volatile elements ending up in fine ash fraction (ESP or BHF ash) and non-volatiles in coarse ash (cyclone ash). Some fraction of volatile elements also escapes with stack gases in fine dust. The partitioning of heavy metals to different ash fractions is determined by many factors including temperatures in various combustion zones, combustion air distribution, and the physical and chemical form of compounds containing the metals. Besides the temperature, the particle size of the flyash and the gaseous atmosphere in the precipitation zone also play an important role [148].

In fluidized beds, volatile metals such as Cd, Pb, Ar, and Zn are volatilized as chlorides and oxides at combustor temperatures. Thermodynamic calculations suggest that cadmium and lead are preferentially converted into CdCl2/PbCl2 during combustion. Furthermore, not only the metal itself, but also chlorides and, to a limited extent, oxides of metal can be vaporized [204]. Zinc is comparatively less volatile than cadmium and lead, but the ZnCl2 and traces of metallic zinc are volatilized. However, the conversion into ZnCl2 is limited since a substantial amount of the zinc is already present in the ash in stable oxide form. Eventually, the bulk of the zinc is recovered in the cyclone ash. Other volatile metals including Ar and Sb somewhat show a similar behavior but their concentration in the fuel ash is generally very low. Thus chlorine, just as for alkali, acts as a carrier to transfer the sublimating metal from the fuel to the flyash [192,205].

In a similar fashion to alkali compounds, the low volatile metals at low temperature condense on the flyash and are present in comparatively high percentages in submicron the particle class due to their large surface area. Hg escapes almost completely with the flue gas due to its high vapor pressure but the concentrations of Hg in chemically untreated biofuels are very low (between 0.01 and 0.1 mg/kg d.b.) [148,206,207]. Lithophilic metals such as iron, copper, chromium, and aluminum end up in coarse flyash to a large extent not just because of their low volatility but also because they are present in oxide form and are very stable. Cyclone ash (bed ash) generally has average properties of plant nutrients and thus can be utilized potentially in agricultural fields.

11.3. Remedies

Filter ash enriched in metals is a point of concern. Primary measures to prevent metal enrichment have also been suggested [208]. Fuel bound heavy metals can be captured by adsorption and chemical reaction by adsorbent materials such as alumina, kaolinite, bauxite, and emathlite. Absorption and chemical reactions of the heavy metals cadmium and lead with absorbent particles have been studied. This may already happen inside the burning char particle and hence suppress volatilization of the heavy metals [192].
Several methods such as adsorption using activated carbon or other appropriate sorbents, post-precipitation, ion exchange, etc. have been applied in order to remove the greatest possible degree of the toxic metals residual concentrations. A secondary measure, which is also the most convenient, is to dispose the metal concentrated ash to a landfill.

12. Conclusion

With the growing concerns of greenhouse emissions, biomass is set to become an important contributor to the world energy need. Although present biomass economics are a bit more expensive than fossils fuels but trends show that with an efficient bio-cycle including cultivation, transportation and combustion, biomass can also compete economically.

Apart from small scale greenhouse or community boilers, the use of biomass as a sole energy source is unimaginable especially for electricity production. At least for now, the most feasible way of increasing the share of this sustainable energy fuel in world energy supply is through co-firing. Comparing with other available renewable energy sources, co-firing offers the lowest risk, most efficient and shortest term option for renewable-based electrical power generation. However, there are still some obstacles that need to be removed to run this sustainable bio-energy engine at full throttle.

Among the available technologies, fluidized beds are proving to be one of the best because of their flexibility, stability, and efficiency. They provide the necessary window of variability needed to handle this diverse renewable fuel.

In general, first category pollutants including PAHs, PCDDs/Fs, CO, and particulate carbon can be easily handled with operating variables and combustor design consideration. Good combustion practices with optimized design considerations in most cases enough to keep unburnt pollutants emissions under environmental norms. Fuel based pollutants (NOx, SOx, dust and metal emissions), however, may need secondary measures. For NOx, air staging together with SCR, SNCR, and reburning delivers high reduction rates (up to 95%). The lower sulfur content in most biomass makes SOx emissions irrelevant, however, sulfur becomes important for its role in corrosion and deposition problems.

The biggest technical challenges that biomass today faces are all related to its ash content. Comparatively higher percentages of alkali metals (potassium) in biomass ash together with chlorine content (especially in herbaceous biomass) are probably the biggest disadvantage associated with this fuel. Biomass ashes melt and sinter at lower temperature due to high potassium and lower calcium content and in combination with other elements like silicon, sulfur etc., they cause the well known biomass related problems; fouling, deposition, corrosion, slagging, and agglomeration (for FBs). As for FBs, they are especially detrimental as agglomeration leads to abrupt shutdowns. Although different remedies including extracting these problematic elements from fuel to different bed additives and use of different bed material (agglomeration) have been suggested and successfully implemented at few units, however, methods need to be improved and new additives need to be found to handle harmful and hazardous compounds out of biomass. Especially extensive research needs to be carried out to find additives/other bed materials to avoid bed agglomeration problems for FBs. High dust and metal emissions problems related to few biofuels (greenhouse residues, demolition wood etc.) have already been rectified with efficient but still expensive solution (ESP, BHPs).

A lot of work is needed to characterize this versatile fuel. Development and standardization of reliable methods to characterize biomass fuel especially biomass ashes is of utmost importance for the successful future of sustainable fuel. Work on the reactor/combustor front is also essential for the plants to be commissioned in the future to make them more robust and adaptable to this renewable fuel class.

In conclusion, further research and development is needed to make biomass economically competitive. Indeed there are problems, but none of these issues represents an insurmountable obstacle for biomass. Governments in both developed and developing countries need to show more commitment for the plants to be commissioned in the future to make them more robust and adaptable to this renewable fuel class.

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References


