

Chapter 2

Biofuel Characteristics and Grate Conversion

Energy crops share many characteristics with other solid fuels, such as coal and wood. Nevertheless, they are clearly differentiated with regard to the fuel chemical properties and, particularly, the ones linked to the inorganic matter. Conversion of the novel fuels might lead to several undesired ash problems during their conversion limiting their applicability for heating purposes. Due to the recent incorporation of energy crops as potential fuels, their combustion behavior is not well-defined yet. Therefore, as a first step of this research, the existing level of knowledge on the aforementioned issues was explored.

This chapter summarizes the theoretical and practical background underneath the work carried out in this research. It has been organized into three main sections. The first one deals with general biofuel characteristics and quality upgrading when biomass is used for heating applications. In the second section, issues related to grate fired conversion technologies are presented. Finally, a review of the inorganic matter aspects involved during biofuel grate conversion is introduced. Throughout this chapter, special emphasis has been given to explore knowledge gained by experiences carried out with alternative biofuels currently being considered to fulfill the European heating market and, particularly, the ones related to *Brassica carinata* and *Populus sp.*, the two energy crops of main interest to this work.

2.1 Characteristics of Biomass and Fuel Quality Upgrading

2.1.1 Main Components in Biomass

Due to its carbohydrate structure, the major elements in biomass are commonly carbon (C), oxygen (O) and hydrogen (H), mentioned according to their decreasing order of abundance. Carbon corresponds to typically between 30 to 60 % on a weight dry basis (wt%, d.b.) of fuel, oxygen is around 30 to 40 wt %, d.b., and hydrogen is the third major constituent comprising from 5 to 7 wt %, d.b. [1–3]. Generally, the

fourth element of the organic matrix is nitrogen (N) and its content is usually less than 2 wt %, d.b [1–3].

Biomass is also formed by inorganic elements, typically denoted as the ash forming matter. Some inorganic elements, such as potassium (K) and sulfur (S), can also be found as part of the fuel organic structure. Concentration of these inorganic constituents vary in a quite broad range, for instance, (S) and chlorine (Cl) are typically found at concentrations from 0.1 to less than 1 wt %, d.b., whereas others, such as lead (Pb), molybdenum (Mo) and boron (B), generally are found as trace elements with a concentration below 0.1 wt %, d.b. [1–3]. These variations may be affected by the growth requirements of biomass. Considering this fact, three main categories can be identified: the major required elements by the plant during growth grouped as macronutrients, which basically comprise K, calcium (Ca), magnesium (Mg), S, N and phosphorus (P); the minor required elements during the plant growth denoted as micronutrients, which involve zinc (Zn), iron (Fe), manganese (Mn), copper (Cu) and Cl; and the beneficial elements, which stimulate growth but are not as essential as the others, or which are essential only for certain species and/or under specific conditions, such as sodium (Na), silicon (Si), and aluminum (Al) [4]. High concentration variability of these inorganic elements is also related to their different association forms in biofuels, which are affected not only by the plant requirements for their growth but also by the biofuel processing steps involved in the whole conversion chain, as is further described.

2.1.2 Association Forms of Inorganic Matter

Basically, inorganic matter in biomass can be inherent (i.e., naturally occurring), which is also formed by several subcategories, or can be incorporated as an extraneous fraction not inherent to the fuel matrix [2, 5, 6]. These association forms are illustrated in Fig. 2.1.

Inherent matter basically refers to assimilation of mineral nutrients during the plant growth [2, 4]. This fraction is primarily incorporated to the biomass matrix as a result of biochemical processes and transport of elements within the plant. Accordingly, inorganic matter reflects the specific nutritional requirements of the plant for metabolism and growth needs, which are mainly dependent on genotype or species cultivated. Mineral nutrients are defined as inorganic elements that have specific and essential functions in the plant metabolism leading to differences on their level of occurrence in most plant types. They can be, for instance, salts absorbed during the plant growth.

As indicated in Fig. 2.1, the inherent inorganic matter is also divided into three association forms [5, 6]:

- salts easily leachable by water: the alkali metals (i.e., Na and K), S, P and Cl tend to be present in the inherent inorganic material as simple inorganic salts that are easily leachable by water and, therefore, generally denoted as water-soluble salts;

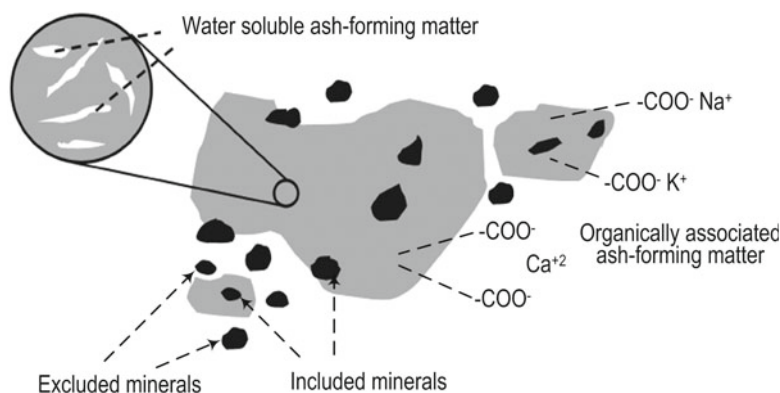


Fig. 2.1 Association forms of ash forming matter in biomass. Adapted from Zevenhoven-Onderwater [5]

- inorganic elements associated with the organic matter: this type of inorganic matter exists as part of the fuel organic structure (e.g., K, S and P). Biomass materials are relatively rich in oxygen containing functional groups, for instance, carboxylic groups, which provide suitable sites for the inorganic species. These forms are typically designated as organically associated matter; and,
- minerals embedded or included in the plant (biomass) structure: inorganic species can be present as very fine particulate forms within the organic structure of some fuels, being generally called included minerals.

The extraneous fraction corresponds to a secondary addition of inorganic elements, which are typically denoted as excluded minerals (see Fig. 2.1). It includes mineral impurities added to biomass mainly because of anthropogenic factors. Contamination of biomass during processing stages is one of the most typical sources of troublesome component addition to biofuels. During their growth and/or cultivation sites typical sources of contamination are, for instance, minerals from sand, soil dust and stones, such as quartz, SiO_2 or feldspar, KAlSi_3O_8 , or deposited particles from nearby industries.

2.1.3 Upgrading Biofuels as Pellets

Biomass may be unsuitable for thermochemical conversion in its raw state. Due to heterogeneity of biofuels, their combustion characteristics may significantly change and, consequently, both design and operational features of efficient combustion systems can be affected. In order to minimize or control these unexpected effects, different methods have been developed to produce more homogeneous and refined biofuels before being supplied to the energy generation stage.

When considering heating applications for biofuels, pelletization is one of the most extended upgrading methods to improve biomass properties used for commercial purposes. Pellets are provided to many commercial sites from a residential-scale and up to the very large scale power generation sectors. Pelletization can be also seen as an alternative to increase contribution of local sources because pellets can be produced as uniform fuels by using one or different biomass sources. All the aforementioned attributes of pelletization were considered to select this densification process as the most suitable upgrading technique for the assessment of the energy crops, brassica and poplar, selected for this research.

During the pelletization process, biofuel properties can be modified within the several stages which are carried out. This process comprises: separation by sieving of extraneous materials in biomass, granulometric reduction, milling, drying, additive addition (if necessary), compression of the raw materials, cooling, fine separation, packaging and storage. As a result of all these process stages, pelletization enhances biofuel homogeneity with respect to particle size, water content and bulk density. This biofuel condition is of great relevance to obtain fully automatic operation and to increase thermal supply stability for achieving complete combustion in small-scale units [7, 8]. Pelletization also improves biomass storage and handling characteristics. Bulk density of biomass is increased up to values typically ranging from 500 to over 600 kg/m³ [9]. This advantage of pelletization is particularly useful for several raw biomass materials, especially grass, straw and sawdust, which have a very low bulk density (usually lower than 150 kg/m³). The higher bulk density of pelletized biofuels minimizes costs for handling operations, basically the ones related to transport from fuel production to consumption locations [10].

Due to the recent incorporation of energy crops, production of these types of sources as pellets is still in a developing state of technological advance. Some experiences have been focused in determining the more suitable conditions for the energy crop pellet production with a maximum level of benefits. Different binding agents have been tested as additives to reduce the operating costs of pelletization and to achieve a higher abrasion resistance [7, 11].

This densification process can be also used for producing blends as a more homogeneous and refined fuels. Fuel blending offers opportunities to achieve synergy benefits by combining different fuel properties. Blending has been used, for instance, for reducing nitrogen content in fuels because of its effect on NO_x emissions [12] or for minimizing the undesired melting behavior of ashes [13].

2.1.4 Control Quality of Pellets and Combustion Performance

In recent decades, the European pellet market has significantly increased as a result of the several possibilities attributed to pelletization. To offer a high operating comfort for the end users, different European standards have been developed not only to include guiding values for product specifications but also to specify threshold

values with regard to thermal efficiency as well as gaseous and particle emissions for combustion units firing standardized pellets [7, 14, 15].

In the product standards, origin of biomass sources as well as some physical and chemical characteristics are considered as main parameters to be controlled. Feedstock quality is crucial to achieve the desired pellet quality and product consistency. For instance, softwoods are the raw materials often preferred for producing woody pellets over other types of woods available, such as hardwoods. This fact is mainly because the higher lignin content of softwoods permits milder pelletization conditions [16]. Compositional differences of pellets can also be affected by different processes involved during pelletization. Producers should use chemically untreated raw materials and avoid binding agents that may add materials containing, for instance, sulphur, which may affect pellet quality, and consequently, their combustion performance.

Regarding biofuel properties specifications, dimensions, particle and bulk density and durability are the most important physical properties used to define pellet quality in the market. Chemical properties include those given by ultimate analysis, and proximate analysis, such as water content (generally below 12 %), lower and higher heating values, ash content, ash elemental analysis and Cl content. Additional properties to control are ash melting point and lignin contents.

Besides the existing European product standards, some local governments have developed their own regulation. Particularly in Austria, significant advances have been done to produce standardized non-woody biofuels based on bark, straw, cereals and blends (agripellets). Standards developed for these type of biofuels are ÖNORM C 4002 for straw pellets, ÖNORM C 4000 for Miscanthus pellets and ÖNORM M 7139 for energy grains [17].

As mentioned previously, besides the product standards, restrictions have been developed to control emissions and thermal performance of the conversion system where biofuels are burned. Performance of combustion systems burning woody biofuels in small scale applications can be tested according to EN 15270 (Pellet burners for small heating boilers—Definitions, requirements, testing, marking). The standard EN 303-5:2012 [15] can be used for combustion units (pellet boilers or integrated-pellet burner systems) up to 500 kW_{th} . In this standard, test methods and emission thresholds for CO, C_XH_Y and particulate matter are defined for combustion of standardized woody and non-woody biofuels, such as the ones based on straw or grains [15]. Therefore, special attention should be paid to emissions and the risk of ash-related problems, such as slagging and corrosion, when non-standardized biofuels are combusted. Austria has defined more restrictive national regulations, which are specific to control combustion of standardized woody and non-woody biofuels produced according to the ÖNORM restrictions mentioned previously and for heating applications up to 400 kW_{th} [15, 17, 18].

2.2 Biofuel Conversion in Grate-Fired Systems

2.2.1 General Characteristics of Grate Technologies

Grate conversion is the most extended fixed bed technology for direct combustion of solid biofuels at commercial scale. The foremost advantage for its commercial applicability is its rather low investment and operating costs with respect to other combustion technologies.

In general terms, grate technologies are appropriated for combustion of heterogeneous biofuels, which are typically characterized by an important amount of ash, a moisture content up to moderate values (i.e., <50 wt %) and, a non-uniform particle size distribution [1, 19, 20]. Nevertheless, the fuel flexibility attributed to commercially available grate technologies is rather limited if biofuels with both high ash content and considerable tendency to unfavorable ash softening behavior have to be combusted [1, 3, 21]. Depending on the conversion unit design and operation, the reliability level of grate systems can be substantially affected when these types of biofuels are converted.

Another drawback attributed to this type of technology is related to its thermal efficiency. Combustion in grate technologies is not as homogeneous as it is in fluidized bed systems and, therefore, a greater excess air level is generally required to obtain equivalent performance. Consequently, thermal efficiency of grate technologies may be generally lower compared to fluidized bed systems [1, 20]. Nevertheless, global efficiency of fluidized bed units is lower than that for the grate systems, basically, because of power demanded for keeping an adequate fluidization condition in the bed.

Grate units are manufactured in a wide range of sizes. Generally, they are categorized as small, medium and higher performance systems [1, 6, 20]. Small-scale heating systems typically comprise thermal outputs from a few kilowatts up to around 100 kW. They are being referred to as household-size and traditionally used in the northern European countries for supplying heating needs of individual dwellings. This category basically includes small stoves for direct heating but it can also involve systems for indirect heating, which implies that the thermal energy available in flue gases is mainly transferred to a circulating fluid. Indirect heating is typically used to cover heating and hot water demands in individual dwellings. Medium performance systems comprise a thermal output from 100 kW up to 1 MW. They are mostly used to provide indirect heating production (including hot water needs) and may involve, for instance, district heating systems, commercial and public sector buildings, and greenhouses and farms. Higher performance units include those over 1 MW up to some around 30 MW. They typically refer to biomass used for power generation but they also applied for district heating systems among other applications.

Generally, grate technologies are mainly comprised of the following key components: the fuel feeding system, the grate itself, the air supply system, the heat exchanger section (in case the energy produced is used for indirect heating applications) and, the ash discharge systems. Particularly, the grate is an essential part of the conversion unit. On the grate, fuel is thermochemically converted into energy by

providing heat and primary air. Other functions attributed to the grate are increasing the stability of the flame over a wide range of flow rates and establishing aerodynamic conditions that ensure uniform and complete combustion.

A well-controlled grate has to guarantee not only a homogeneous fuel distribution over the whole grate but also has to ensure an efficient air supply through different sections under the grate [1, 20]. These two conditions are needed to offer an adequate fuel and primary combustion air mixing and to achieve high burnout and low pollutant emissions. To obtain these requirements, different configurations with regard to the fuel and the primary air supply have been developed in grate systems. As illustrated in Fig. 2.2, fuel and air can be added and distributed in different ways. If fuel is introduced under the grate, the arrangement is called underfeed, also named as bottom fed or downfeed, (see Fig. 2.2a). On the contrary, if fuel is dropped onto the surface of the bed by its own weight, this configuration is called overfeed (see Fig. 2.2b, c). Sometimes, overfeed systems are also referred as top fed or as upfeed units [22–24]. Another configuration of underfeed systems is defined as horizontally fed burners. They are basically similar to underfeed burners but fuel moves horizontally, and consequently, the reaction front is slightly different. A broad range of power sizes from a few kilowatts up to several megawatts can be found in all the three aforementioned cases.

The flow direction of primary air introduced into the combustion unit is another criterion to be considered. In small scale heating units, primary air can be supplied from above being denoted as the downdraft technique [1, 26]. An example of this configuration is, for instance, domestic log firing boilers, which are also named downdraught gasifiers [19, 23, 26]. On the contrary, in updraft or updraught grate units, the primary combustion air is supplied from below the grate and distributed throughout the fuel bed (see Fig. 2.2a, b, c). This is the most widely used technique for small sized up to medium size units [1, 24].

Furthermore, depending on the relative flow direction of fuel and air supply, three different arrangements can be defined to grate systems [23, 27]. As illustrated in Fig. 2.2, if fuel and air are introduced in the same flow direction, they are in a

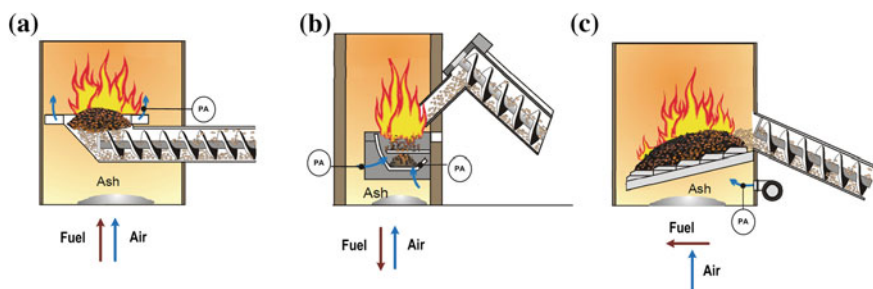


Fig. 2.2 Classification of grate combustors by the relative motion between the fuel bed and the primary air: **a** co-current, underfeed, updraught, **b** counter-current, overfeed, updraught and, **c** cross-current, overfeed, updraught. Adapted from Alakangas [25]

co-current mode (see Fig. 2.2a), whereas if they have opposite flow direction, the arrangement is called counter-current (see Fig. 2.2b). These two modes are mostly considered in small-scale heating systems [1, 24].

A third configuration type and the most commercially used technique in fixed-bed combustion technologies is called cross-current combustion (see Fig. 2.2c) [1, 21]. In this case, the fuel feeding system pushes fuel forward on the grate, while primary air is introduced from underneath the grate [28]. This study has been particularly focused on this type of arrangement and, therefore, special emphasis will be placed on how the combustion process is carried out in this grate configuration.

2.2.2 Combustion Process on the Grate

In grate-fired systems, the fuel bed consists of a huge number of solid particles that are piled up on the grate with a characteristic porosity. During combustion, solid fuel particles undergo heat and mass transfer processes along with various chemical reactions [1, 6, 20]. Conductive, convective and radiative heat transfer may occur within the bed (among solid phases or among solid and gas phases), and/or among the bed, the walls and the flame above the bed. The compositional changes include combustion phases of the solid fuel and the reactions of volatile gases with air [9]. Fuel properties (e.g., moisture and particle size) have a significant influence on the fuel combustion behavior. However, depending on the grate characteristics, some differences are found with respect to air-fuel contact distribution and how ignition is propagated.

The combustion process on stationary sloping-grates has been described by several authors to follow the cross-current combustion pattern [9, 20, 27, 29, 30]. A detailed scheme of this complex process is illustrated in Fig. 2.3. According to Fig. 2.3, fuel undergoes heating and drying followed by devolatilization and partial combustion of the volatile matter and the char. When considering a single fuel particle, the various chemical and thermal reactions occur in sequence. When considering mass feeding to the grate as a fuel bed, particles in different phases coexist at the same time in different parts of the system [31, 32]. As a result, the drying, devolatilization, char oxidation and ash zones appear sequentially for single particles from the bottom to the top of the bed while ignition propagates. These processes occur simultaneously for large fuel particles.

As illustrated in Fig. 2.3, ignition starts at the bed top layer, which is heated up usually by an external heat source or by radiation from the over-bed flame and hot walls. Once the fuel is ignited, the reaction front propagates from the surface down into the bed against the direction of the primary air. The heat generated by homogeneous gaseous reactions and heterogeneous char oxidation is transferred downwards to dry, to heat up and to devolatilize the fresh particles below, allowing the combustion process to propagate. Due to the different flow direction of heat and air, the heat is not transported downwards far from the position where it is released, and consequently, the reaction front is narrow [27]. Since the heterogeneous char

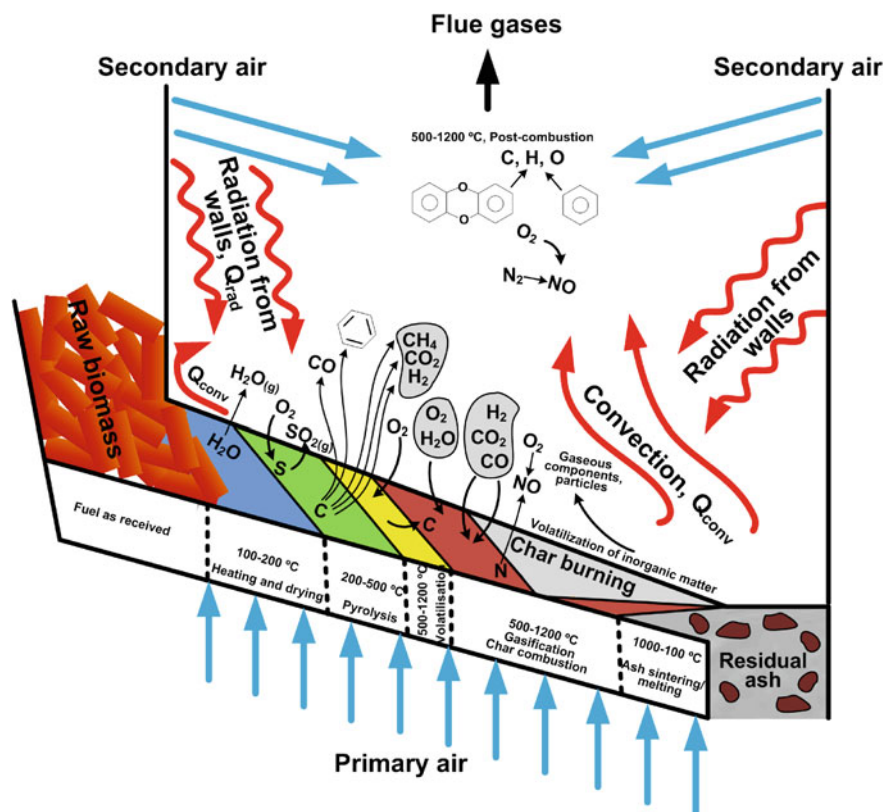


Fig. 2.3 Stages of the fuel conversion in a stationary sloping cross-current grate systems. Adapted from Yin et al. [20] and Salzmann and Nussbaumer [33]

oxidation is relatively slow and oxygen is consumed first by the volatile gases released from the fuel particles, carbonised particles may remain above the ignition front [9].

Once the ignition front reaches the bed bottom, only the oxidation of the remaining char takes place on the upper surface. Therefore, a secondary reaction front (i.e., a char burnout front) appears. It is propagating up towards the surface of the bed, and consequently, depletion of the char layer previously formed occurs by heterogeneous combustion reactions [9]. For traditionally used biomass materials, such as stemwood assortments, the char combustion zone is relatively short because they have very high volatile matter contents. However, substantial variations of the char combustion zone are found in the alternative biofuels, such as the energy crop pellets, mainly affected by fuel properties, for instance, the volatile matter to fixed carbon ratio (VM/FC ratio) or the ash content [1, 9, 29, 34].

As a result of biofuel combustion, the fuel is divided into combustible and incombustible fractions. The combustible fraction of biofuels is converted into energy for heating, power or cooling applications. Incombustible matter is basically responsible of the ash-related effects during biofuel thermal conversion.

2.2.3 Air Requirements and Distribution During Grate Combustion

As mentioned in previous sections, during fuel conversion on a grate, air supply and its distribution play an important role on the achievement of the best combustion system performance. In order to guarantee a slight and a homogeneous fuel bed movement over the grate, low turbulence is suggested for the grate area, sometimes denoted as the *primary combustion zone*. This fact may lead to non-optimal air and flue gas mixing and, therefore, combustion of the gases released from the fuel bed on the grate and a small amount of fuel particles can exist in the freeboard. Based on the well-known “3T criteria”, temperature, residence time and turbulence, a considerably high excess of air tends to be incorporated above the fuel bed on the grate, sometimes called the *secondary combustion zone*. This secondary air (or even tertiary air) addition is useful to the enhancement of gas turbulence and, therefore, air and flue gas mixing [20]. The objective is to obtain almost complete oxidation of gaseous components released from the fuel bed, basically, hydrocarbons (C_XH_Y) and carbon monoxide, CO.

Towards the achievement of these desired conditions at minimum excess air levels, different alternatives have been proposed and tested for the grate systems. Among other options, the air injection arrangement over the combustion chamber cross section, where gases are conducted, should be optimized by using for instance, computational fluid dynamics simulations (CFD). The modeling may be useful to assess diameter, number, positioning, spacing, and orientation of air injection nozzles to offer the desired mixing optimization and, therefore, to minimize the total amount of excess air used to reach as complete combustion as possible in the secondary combustion zone [35, 36].

Furthermore, staged combustion strategies are useful to improve combustion performance of grate systems. Staged combustion can be done as air staging or as fuel staging by introducing air or fuel, respectively, into the system at two or more separated combustion zones [37, 38]. Up to now, air staging strategy has been a widely used alternative for commercial purposes because it is easier to apply and requires low investment compared to other measures.

During air staging strategy, introduction of air can be carried out at two or three levels based on the different air requirements that fuel particles undergo throughout their conversion processes. In Fig. 2.4, an example of air-staged combustion is illustrated. In this case, total air is supplied as primary air added in two different zones and as secondary air. As indicated in this figure, multiple zones of underneath primary air can be considered to enhance combustion control possibilities.

As illustrated in Fig. 2.4, reducing conditions (i.e., oxygen deficiency conditions) are created in the fuel bed conversion on the grate in the primary combustion zone. Biofuels have typically a high proportion of the volatile matter, which favors combustion under sub-stoichiometric conditions (i.e., fuel-rich conditions) in the primary combustion zone. The excess air ratio needed during heating up, drying and initial devolatilization phases corresponds to conditions that resemble pyrolysis process

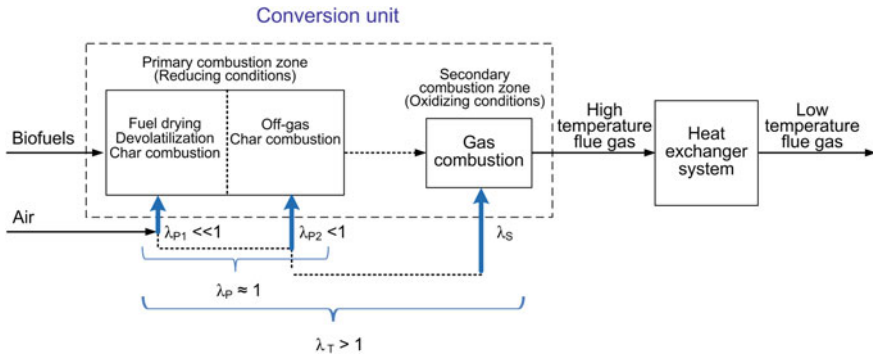


Fig. 2.4 Air staging strategy. Adapted from Friberg and Blasiak [23] and Salzmann and Nussbaumer [37]

(i.e., $\lambda \ll 1$). During final devolatilization and char oxidation phases, air supplied should be referred to as gasification conditions (i.e., $\lambda < 1$) [38]. Based on all these considerations, the λ factor used in the primary combustion zone, λ_P , is suggested to be maintained below the stoichiometric ratio, typically around 0.7–0.95 [12, 39]. Then, after the reducing atmosphere, a higher proportion of air, mostly secondary air and, in some cases, tertiary air, is supplied to the freeboard conversion inside the combustion chamber in the secondary combustion zone. This means that at the same global combustion air to fuel ratio (i.e., λ_T), significant amounts of secondary air are supplied.

In small heating applications, the air-to-fuel ratio at the exit of the conversion system or total λ , λ_T , is typically kept between 1.5 and 2 [39, 40]. In larger combustion scale units and well-controlled systems, total λ tends to be lower between 1.4 and 1.6 [39, 41]. The split ratio of this total air between primary air and secondary air tends to be 40/60 in modern grate-fired boilers burning biofuels, instead of 80/20 in older units, which leaves much more freedom for more advanced secondary air supply and distribution systems [20]. However, combustion experiences carried out with ash-rich fuels with a high slag formation risk have indicated that primary air needs may significantly increase when firing this type of biofuel, because of their specific fuel properties [42–44]. Therefore, special attention should be placed on the grate design when this type of biofuel is combusted.

2.3 Ash-Related Aspects in Grate-Fired Systems

2.3.1 Occurrence of Ash Phenomena and Practical Effects

Some major ash-forming elements can be denoted as the main players in the ash phenomena [2, 3, 39, 45]. With a certain degree of simplification, the main

ash-forming elements are: Si, Ca, Mg, K, Na, P, S, Cl, and Al. They may cause severe operational problems during biofuel conversion in grate units and undesired gaseous and particles emissions.

With regard to operational problems, ash effects in grate systems are closely related to deposit formation. Two main groups of deposits are usually differentiated depending on their particular location inside the system, namely slagging and fouling. Slagging phenomenon usually occur on the hot grate, where radiant heat transfer and the highest temperatures are the dominant conditions. Fouling is basically related to the convection zone of the conversion unit. Besides their location, these two type of deposits are differentiated by specific characteristics (e.g., hardness and composition) and, adverse effects which they may cause on the conversion system performance.

Slagging is generally related to formation of molten ash layers. Partly-fused and/or powdery deposits are denoted as sintered deposits. Some criteria have been defined to classify deposits according to stratification and hardness degree based on strength tests [46, 47]. By contrast, fouling is related to the formation of loose, discrete particles or loosely sintered deposits formed when the flue gas cools down throughout its path inside the convective zone.

Depending on the ash composition in biofuels, residues accumulated on the grates are generally rich in silicate or phosphates compounds [46–48, 48–50]. Although deposits located in the convective zones can be formed by coarse particles, which resemble bottom ash composition, they are typically caused by submicron fly ash particles (aerosols). Deposits formed in these sections can result by homogeneous and heterogeneous interactions among particles and flue gases [45, 51].

Slagging and fouling deposits are also responsible for different problems, which worsen the overall efficiency of the conversion systems and may affect the environment. The formation of substantial fused ash agglomerates on the bed can further interfere with the primary air distribution through the fuel bed and, lead to very poor combustion conditions [42, 44]. This condition worsens the burnout of the char and the quality of the gaseous and emission levels, increases combustion air velocities through the grate area free of ash deposits and, consequently, raises the levels of fly ash carryover (entrainment of bottom ash). Furthermore, the formation of large and fused ash agglomerates can cause difficulties with the removal of the ash from the bed and, downstream problems in the ash handling system. In this case, load reduction and grate cleaning may be required as temporary solutions because of their direct effect on lowering thermal efficiency.

Generally, fouling formation on the surfaces is a much slower process which occurs over a long-term than slag formation but the effects on the system performance may have more severe consequences. Deposits on heat exchanger surfaces reduce heat absorption and, therefore, the flue gas temperature is eventually increased. This fact might contribute to raise metal temperatures in the convective sections and, consequently, the deposition of fused or partially-fused slag in that zone is enhanced as a result of increasing the sticking surfaces of deposits [52]. Accumulation and subsequent natural shedding of large ash deposits on upper combustor surfaces can lead to damage to the grates and heat exchanger structure [6, 50, 53, 54].

A more severe effect attributed to deposit formation is the corrosion phenomenon. In a pure oxidative atmosphere the establishment of an oxide on the surface of metals is often encouraged as it provides a protective layer that limits the rate of metal attack. In the presence of deposits and, in combination with particular constituents of the flue gases, for instance, chlorine and sulfur compounds, the corrosion effects may be promoted [55–59]. Under such conditions, the protective oxide layer becomes involved with the chemical reactions and, eventually, is destroyed or severely damaged. Problems of corrosion can also occur if the temperature of acidic flue gases is too low at the exit of the equipment [55–59]. Water vapor condensation from combustion gases is favored while the flue gas temperature is progressively lowered by the heat transfer.

2.3.1.1 Formation of Deposits on Heat Exchanger Surfaces

Deposits are formed by complex mechanisms and their build-up mechanism involves different phases. The more relevant ones are: formation of an ash particle, transport and attachment of particles to heat transfer surfaces and consolidation of the deposits. Formation of deposits in the convective zones of the conversion unit are particularly related to how particles are transported to the surface. Transport mechanisms basically include thermophoresis, inertial impaction, condensation and chemical reactions. Depending on the processes involved, deposits exhibit specific characteristics. The occurrence of each transport mechanism depends on several factors, such as the physical state of the materials (solid, liquid or vapor), their chemistry and, the conditions inside the conversion system, such as temperature and fluid dynamics [6, 30, 39, 42, 53, 60–62]. A schematic diagram which summarizes the formation of deposits is presented in Fig. 2.5.

Thermophoresis involves the migration of particles from the flue gas to the heat transfer surface as a result of the temperature gradient in the flue gas near to the heat transfer surfaces. By contrast, diffusion is related to mass gradients. Thermophoresis is considered as dominant mechanisms for very small (submicron) particles and, particularly, is attributed to the very initial deposition stages when the local temperature gradients are maximum and when the rate of deposition by inertial impaction is low [6, 60]. Thermophoretic deposits are finer grained and more distributed than those formed by inertial impaction.

Inertial impaction occurs when large particles (i.e., aerodynamic diameter around $10\text{ }\mu\text{m}$ or larger) have sufficient inertia to avoid changes of flue gas direction and, as a result, they impact on the surface and form coarse grained deposits [6, 60].

Condensation takes place when vapours of volatile inorganic species in the flue gases, condense on surfaces cooler than the local gas. Deposits are formed in a very uniform layer even more than those formed by thermophoresis [60]. Condensation may occur by different mechanisms mainly grouped as heterogeneous and homogeneous condensation. The former is mainly associated with vapor condensation on other particles before their attachment on the surfaces. The second one is attributed to the fact that vapor condense homogeneously as the gases cool. Condensation is the

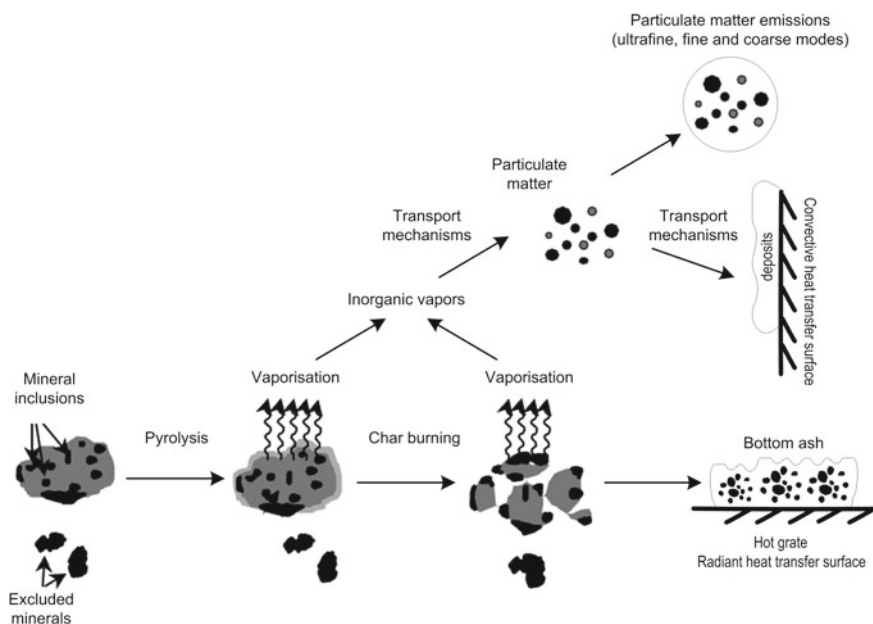


Fig. 2.5 Schematic illustration of ash fraction formation paths. Adapted from Christensen [63]

principal driving mechanism for convective pass fouling and, particularly important for biomass materials with high levels of volatile species [6].

Chemical reactions occur among the already deposited material with components in the flue gas, or less commonly with components in the deposited matter. Therefore, they can be considered as a mechanism by which mass can be accumulated on a deposit. The main chemical reactions regarding ash deposition are sulfation, oxidation and alkali absorption into deposited silica [60].

When a particle has reached the deposit surface, its potential attachment and consolidation on the deposits are dependent on the stickiness of the particle and the surface. Some mechanisms such as erosion or natural shedding (because of erosion and thermal and gravity forces) may decrease the amount of deposit captured on surfaces [50, 64]. Consequently, deposit consolidation on surfaces results from the balance among the total amount of particles attached and removed from the surface.

2.3.2 Behavior of Inorganic Elements During Biofuel Combustion

Parallel to conversion processes of the organic elements in biofuels, inorganic elements undergo complex physical and chemical transformations. Despite knowledge

gained during coal and woody experiences, behavior of the inorganic elements is not completely understood at present.

Basically, inorganic elements in biomass can be divided into two main groups according to their order of reactivity. The first group includes the less reactive elements, Si and the alkaline earth metals, Ca and Mg, which basically remain on the hot grate and, therefore, they are also called the refractory elements. A second group is formed by the more reactive ones, which are easily volatilized (released). In this work, *release* indicates that a chemical element vaporises from the fuel particle and escapes from the fuel bed on the grate. The reactive fraction is also recognized as the most critical one considering implications of the inorganic matter during thermochemical conversion of biofuels. Volatile elements, which are found above 0.1 wt %, d.b., such as Cl, S, Na, K and P, and heavy metals found as trace elements in biofuels, such as Pb, Zn and titanium (Ti), play an important role on the formation of harmful emissions for human health [65–67]. Besides this fact, these elements are mainly responsible for the undesired effects inside the grate combustion unit, which may substantially limit an optimum performance of the system [55–57].

After the initial partitioning of the inorganic components, intermediate species are formed as gas, liquid or solid phases. They may interact in homogeneous or heterogeneous conditions or undergo physical transformations to eventually be retained inside the system as solid compounds or be emitted to the environment as gaseous acidic pollutants, such as $\text{HCl}_{(g)}$ and $\text{SO}_{2(g)}$, and particle emissions.

2.3.2.1 Ash Fractions Formed During Combustion

In general, partitioning of the inorganic species will occur to form gaseous products, such as acidic pollutants and solid ash fractions. The latter exhibit clear differences regarding their particle size and chemical composition.

Considering particle size differences, solid ash fractions can be generally divided into two main groups, residual bottom ash and particulate matter. Bottom ash fraction contains the larger ash particles. The particulate ash fraction, generally called fly ash, comprises two main different categories of particles, which are denoted as supermicron and submicron particulate matter. Supermicron fly ash is formed by particles of aerodynamic diameter $> 1 \mu\text{m}$ and is also typically called the coarse mode. Submicron fly ash (aerosols) can be defined by the fine ($0.1\text{--}1 \mu\text{m}$) and the ultrafine sizes ($< 0.1 \mu\text{m}$). The formation of two modes of submicron particles depends on several factors related to fuel chemistry and operating conditions of the system. Fractions forming the particulate matter are illustrated in Fig. 2.6.

Based on compositional differences, the bottom ash fraction is basically composed of refractory elements, such as Ca and Si, whereas the volatile ones contribute to particle formation. Nevertheless, these fractions overlap and can be found in both regimes. Although Si and alkaline earth elements are nearly fully retained in the residue accumulated on the hot grate, they can also constitute a fraction of supermicron fly ash particles, as a consequence of the entrainment of material from the grate into the flue gases. This fact is mainly related to dynamic characteristics of the

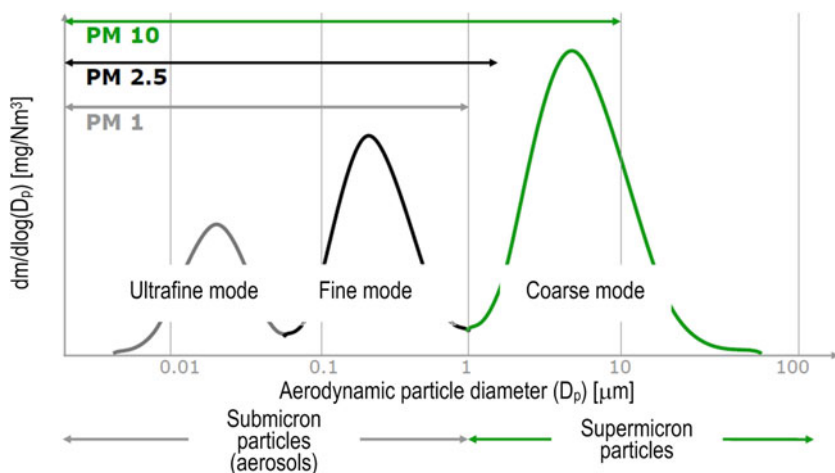


Fig. 2.6 Particulate emissions. Adapted from Brunner et al. [68]

particles, air and gases inside the conversion unit. A fraction of volatile elements can also be retained in bottom ash, as a result of interactions among the inorganic constituents. In general, Al and P can be found in the solid residue remaining on the grates but in low concentrations. Aluminum is not normally found in high concentrations in biomass because it is mainly incorporated as extraneous matter by soil contamination or through fuel processing operations. P content tends to increase in the residual ash in grates (bottom ash) when P-rich fuels, such as rapeseed meal, reed canary grass, cassava stems, or cereal grains (e.g., oat, barley, rye or wheat) are combusted [46, 69–71]. Nevertheless, the volatility of the phosphoric components is assumed to be high; also being found as part of the particulate matter formed from P-rich fuels, basically K-phosphates [65, 71]. The alkali metals, K and Na, as well as Cl and S are a very reactive fraction; however, a fraction of these volatile elements can be also retained in bottom ash [72].

The chemical composition of the coarse fly ash normally resembles the corresponding composition of the bottom ash. As previously mentioned, refractory species are found in the particulate fraction, as a consequence of their entrainment into the flue gas. A degree of condensation of volatile inorganic species, particularly alkali metal sulphates and some heavy metal compounds, commonly occurs on the surfaces of the coarse fly ash particles [6].

The fine and ultrafine modes are mainly formed by a more reactive portion of the ash-forming elements in biofuels, the volatile inorganic species, which are mostly volatilised and released to the gas phase. Eventually, they will form particles, mainly by condensation mechanisms, while the flue gas cools down when passing through the convective stages in the system. The main constituents of submicron fly ash particles are the alkali metals, K and Na, principally as chlorides, sulphates and/or phosphates, and in minor proportion, some heavy metal compounds (if they are found

in the fuel matrix), especially compounds of Zn, Pb and cadmium (Cd) [51, 56, 66, 67, 73].

The residual bottom ash and the particulate matter may lead to different implications during biofuel conversion because of differences in composition and particle size. Bottom ash residues are generally found as partially fused and/or agglomerated matter. K can be partially retained in the bottom ash by interactions with Si (either inherent in biofuels or by contamination with soil components) contributing thereby to ash softening (slag/sintering) [45, 47, 49, 69, 74]. The submicron mode of particles may cause fouling formation or particulate emissions harmful to human health [51, 56, 61, 66, 67, 73, 75, 76]. As a consequence of deposits formed on heating surfaces, corrosion is expected to be promoted [55–59]. Currently, several technologies have been designed for capturing the particulate matter ash fractions [77–79]. At present, collecting efficiencies are mostly limited to particle size above 1 μm . The highest efficiency for particle removal is provided by the electrostatic precipitators (ESP), which can easily exceed 99 % [78, 79].

2.3.2.2 Factors Affecting the Partitioning of the Inorganic Elements

Different studies have been conducted on a wide range of biofuels in order to investigate the behavior of the inorganic elements and, particularly, the volatile S, Cl and K. These three elements not only exist in significant concentration in biofuels, they also play an important role on consequences attributed to the inorganic fraction during biofuel conversion. Recently, incorporation of P-rich alternative fuels and the high reactivity level attributed to P-compounds have reinforced the need to address research efforts on the understanding of the P-release behavior. The reported experiences in the literature have been performed from lab-scale up to full-scale measurements and have resulted in the assessment of several criteria:

- thermochemical conversion process (i.e., pyrolysis, gasification and combustion of biofuels) [80–86],
- combustion technology (i.e., pulverized bed, fluidized bed and fixed bed reactors) [34, 47, 49, 82, 87–89],
- type of fuel feeding as pure biofuel or as blends (co-combustion, combustion of biofuels or combustion of coal and biofuel(s)) [81, 88, 90],
- local gas stoichiometry (i.e., reductive and oxidative atmosphere) [54, 91, 92],
- thermal conditions (e.g., heating rates and temperature) [91, 92],
- particle size [9, 93] and,
- use of additives (e.g., calcium and potassium based additives) [46, 94–97].

Some of the aforementioned experiences have been carried out with novel alternative biofuels, mostly agricultural residues. Cl-release during pyrolysis and gasification was assessed for sugarcane trash, switchgrass, lucerne and rape straw [83]. Alkali release during pyrolysis was reported for wheat and oat straw cultivated with chloride-rich and sulfate-rich fertilizers [84]. Moreover, elemental losses of the main ash-forming elements were evaluated for different ash types obtained from woody fuels

and from wheat and rice straws [72, 98, 99]. Transformations associated to Cl, K, S and P were studied during pyrolysis, combustion and co-combustion of annual crops (e.g., straw from barley, rice, wheat, rape and oat raw materials) [80, 86, 90, 92, 94, 100–103]. At the same time, release quantification methods were developed [91] and applied to woody biomass [104] and to various selected biofuels (including bark, wood chips, waste wood and wheat straw) [105] in order to quantify the Cl, S, K, Na, Zn and Pb release under simulated grate fired conditions. Similar studies were carried out with dedicated waste fractions [54, 106] and with a high-chlorine biomass (corn stover) [107]. Furthermore, specific studies about K speciation were performed on ternary systems K-Ca-Si and K-Ca-P [108]. Influence of additives on K-phosphate behavior was assessed by oat combustion [109]. Different correlations were defined for the release of main-ash forming elements during combustion of wood residues, straw and olive residues with coal [89]. More recently, the influence of additives on the fly ash behavior of P-rich fuels from bioethanol production was evaluated [71].

With regard to the energy crops of main interest to this work, literature is scarce, basically as a result of their recent consideration as biofuels. Regarding brassica, existing research work has been mainly developed within the framework of the HIAL Project *Biofuels for CHP plants, Reduced emissions and cost reduction in the combustion of high alkali biofuels*. The main criteria assessed in these studies were related to the influence of operating conditions [90, 92, 94, 110, 111] and the use of additives [94] on the ash behavior. Experiences implied the assessment of thermal behavior and emissions performance of brassica chips [112], the release of alkali compounds during combustion and co-combustion [90, 111], retention of sulphur in the bottom ash by using sulphur-binding additives [94], ash melting and, finally, the release behavior of inorganic elements. Basically the K, Cl and S releases were studied at laboratory conditions as a function of temperature and ash composition [92, 110]. Concerning poplar, studies in the literature are limited to the characterization of biomass ash behavior and its effects during combustion in a bubbling fluidized bed reactor [113], elemental composition of mineral matter as a function of temperature [98], analysis of ignition front propagation and influencing effects during fuel conversion in a one-dimensional fixed-bed combustor [34]. A summary of these experiences is presented in Tables 2.1 and 2.2.

Based on the knowledge gained by previously mentioned experiences, a close relation is identified to exist among the specific characteristics of the inorganic matter (basically fuel chemistry) and the grate conditions on the partitioning of ash forming elements and their corresponding implications during combustion. The main controlling effects can be grouped into the following categories: compositional differences in fuels [73, 77, 104, 106, 108], their association forms and physical characteristics in the fuel matrix [48, 73, 77, 92, 104, 106, 108], thermodynamic stability of ash compounds and species [80, 100, 115, 116] and, thermal conversion system design and operating conditions affecting the physical environment (e.g., temperature gradient, local gas phase stoichiometry and residence time for the contact between gaseous and solid phases) [92, 98, 116, 117]. Nevertheless, there is still a limited knowledge of the ash chemistry involved, mostly affected by the variability of the inorganic matter found in novel biofuels.

Table 2.1 *Brassica carinata* (brassica) experiences

References	Aim of research	Sample characteristics	Operating conditions implemented
Brassica [34]	Analysis of ignition front propagation and influencing effects during fuel conversion in a one-dimensional fixed-bed combustor	No data are available	<ol style="list-style-type: none"> 1. Setup: bubbling fluidised bed (BFB) combustion pilot plant (1 MW_{th}) 2. Batch feeding 3. Range of temperature: $700\text{--}1000\text{ }^{\circ}\text{C}$ 4. Residence time: No data is available 5. Combustion conditions
Brassica carinata [90]	K, Cl, and S release transformations and interactions during combustion and co-combustion	Powder biomass, 1 mm screen	<ol style="list-style-type: none"> 1. Setup: HPMS, high pressure mass spectrometry analyzer 2. Batch feeding 3. Range of temperature: $800\text{ and }1100\text{ }^{\circ}\text{C}$ 4. Residence time: around 2 min as maximum to the entire combustion process 5. Pyrolysis and combustion conditions 6. Coal blends: 20 and 50 % biomass
Brassica carinata [92]	K, Cl and S transformation and influence of combustion temperature and ash composition	4 g powder biomass, 4 mm screen without fines ($<0.5\text{ mm}$)	<ol style="list-style-type: none"> 1. Setup: laboratory fixed bed reactor 2. Batch feeding 3. Range of temperature: $500\text{--}1150\text{ }^{\circ}\text{C}$ 4. Residence time: around 3 h as maximum to the entire combustion process 5. Pyrolysis and combustion conditions

(continued)

Table 2.1 (continued)

References	Aim of research	Sample characteristics	Operating conditions implemented
Brassica carinata [94]	Retention of sulphur in the bottom ash by using sulphur-binding additives	4 g powder biomass, 4 mm screen without fines (<0.5 mm)	<ol style="list-style-type: none"> 1. Setup: laboratory fixed bed reactor 2. Batch feeding 3. Range of temperature: 800–1100 °C 4. Residence time: around 2.5 h as maximum to the entire combustion process 5. Combustion conditions
Brassica [96]	Assessment of the effect of the addition of several chemical materials (additives) on the sintering behavior of biomass ash	40 g powder biomass. 2 mm screen. Additives were ground to pass by a 0.25 mm sieve	<ol style="list-style-type: none"> 1. Setup: Conventional laboratory temperature controlled oven 2. Batch feeding 3. Range of temperature: 550 and 1000 °C 4. Residence time: 20 h at 550 °C. Obtained ash was heated at 3 °C/min until 1000 °C were reached 5. Combustion conditions
Brassica carinata [110]	Ash melting and ash gas phase-release as a function of temperature	19.5–20.5 mg of ash from powder biomass	<ol style="list-style-type: none"> 1. Setup: STA, simultaneous thermal analyzer 2. Batch feeding 3. Range of temperature: 25–1550 °C

(continued)

Table 2.1 (continued)

References	Aim of research	Sample characteristics	Operating conditions implemented
Brassica carinata [111]	Influence of temperature and fuel composition on alkali release during combustion and co-combustion	Pelletized fuel, 15 mm by 8 mm	<ol style="list-style-type: none"> 1. Setup: CFB, circulating fluidized bed reactor, 25 kW_{th} 2. Continuous feeding 3. Range of temperature: 850, 875 and 900 °C 4. Residence time: around 2 min as maximum to the entire combustion process 5. Pyrolysis and combustion conditions 6. Coal blends: 20 and 50 % biomass
Brassica carinata [112]	Thermal behavior and emissions performance	600 kg of biomass chopped up to 4 cm length	<ol style="list-style-type: none"> 1. Setup: Flat moving grate, 350 kW_{th} 2. Continuous feeding 3. Combustion conditions
Brassica [114]	Assessment of the effect of limestone on the bed agglomeration and sintering tendencies related to combustion of biomass	200 kg/h biomass	<ol style="list-style-type: none"> 1. Setup: bubbling fluidised bed (BFB) combustion pilot plant 2. Continuous feeding 3. Range of temperature: 800 °C 4. Residence time: 8 h under steady state conditions 5. Combustion conditions

Table 2.2 *Populus sp* (poplar) experiences

References	Aim of research	Sample characteristics	Operating conditions implemented
Poplar [34]	Analysis of ignition front propagation and influencing effects during fuel conversion in a one-dimensional fixed-bed combustor	No data are available	1. Set up: bubbling fluidised bed (BFB) combustion pilot plant (1 MW_{th}) 2. Batch feeding 3. Range of temperature: $700\text{--}1000\text{ }^{\circ}\text{C}$ 4. Residence time: No data is available 5. Combustion conditions
Poplar [98]	Elemental composition of mineral matter as a function of temperature	40 mg low ash temperature	1. Set up: tube furnace and thermogravimetric analyzer 2. Batch feeding 3. Range of temperature: $600\text{--}1400\text{ }^{\circ}\text{C}$ 4. Combustion conditions
Poplar [113]	Characterization of biomass ash behavior and their effects during combustion in a bubbling fluidised bed reactor	No data are available	1. Set up: bubbling fluidized bed (BFB) combustion pilot plant (1 MW_{th}) 2. Continuous feeding 3. Range of temperature: $775\text{ }^{\circ}\text{C}$ 4. Residence time: 11.9 h 5. Combustion conditions

References

1. van Loo S, Koppejan J (2002) Handbook of biomass combustion and co-firing. Enschede, Netherlands
2. Vassilev S, Baxter D, Andersen L, Vassileva C (2010) An overview of the chemical composition of biomass. *Fuel* 89(5):913–933
3. Jenkins B, Baxter L, Miles T (1998) Combustion properties of biomass. *Fuel Process Technol* 54(1–3):17–46
4. Marschner H (2002) Mineral nutrients in higher plants. Academic Press, London
5. Zevenhoven-Onderwater M (2001) Ash forming matter in biomass fuels. Ph.D. thesis
6. Livingston W (2006) Biomass ash characteristics and behaviour in combustion systems. MitsuBabcock
7. Obernberger I, Thek G (2004) Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass Bioenergy* 27(6):653–669
8. Passalacqua F, Zaetta C, Janssen R, Pigaht M, Grassi G, Pastre O, Sandovar A, Vegas L, Tsoutsos T, Karapanagiotis N, Fjällström T, Nilsson S, Bjerg J (2004) Pellets in southern Europe. The state of the art of pellets utilisation in southern europe. New perspectives of pellets from agri-residues. In: 2nd World Conference on Biomass for Energy, Industry and Climate Protection, Rome, Italy, pp 1806–1810
9. Ryu C, Yang Y, Khor A, Yates N, Sharifi V, Swithenbank J (2006) Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. *Fuel* 85(7–8):1039–1046
10. Suurs R (2002) Long distance bioenergy logistics. Technical report
11. Mediavilla I (2010) Analisis y optimizacion del proceso de pelletizacion de biomasa y estudio de su comportamiento como combustible en una caldera del sector domestico. Ph.D. thesis
12. Houshfar E, Skreiberg Ø, Todorović D, Skreiberg A, Løvås T, Jovović A, Sørum L (2012) NO_x emission reduction by staged combustion in grate combustion of biomass fuels and fuel mixtures. *Fuel* 98:29–40
13. Mediavilla I, Fernández M, Esteban L (2009) Optimization of pelletisation and combustion in a boiler of 17.5 kW_{th} for vine shoots and industrial cork residue. *Fuel Process Technol* 90(4):621–628
14. European standard CEN/TS 14961: 2005 Solid biofuels—Fuel specifications and classes. European Committee for Standardization (CEN) (2005)
15. European standard EN 303–5:2012: Heating boilers for solid fuels, manually and automatically stoked, nominal heat output of up to 500 kW. Terminology, requirements, testing and marking. European Committee for Standardization (CEN) (2012)
16. Robbins M, Evans G, Valentine J, Donnison I, Allison G (2012) New opportunities for the exploitation of energy crops by thermochemical conversion in Northern Europe and the UK. *Prog Energy Combust Sci* 38(2):138–155
17. Zeng T (2011) National conditions-Austria. IEE/09/758/SI2.558286—MixBioPells. WP4 / D 4.3. Technical report
18. Art 15a B-VG agreement: Precautionary measures regarding small-scale heating systems (2010)
19. Kavalov B, Peteves S (2004) BIOHEAT Applications in the European Union: an analysis and perspective for 2010. Technical report
20. Yin C, Rosendahl L, Kær S (2008) Grate-firing of biomass for heat and power production. *Prog Energy Combust Sci* 34(6):54–725
21. Werther J, Saenger M, Hartge E, Ogada T, Siagi Z (2000) Combustion of agricultural residues. *Prog Energy Combust Sci* 26(1):1–27
22. Oland C (2002) Guide to low emission boiler and combustion equipment selection. U.S. Department of Energy. Oak Ridge National Laboratory, Technical report
23. Friberg R, Blasiak W (2002) Measurements of mass flux and stoichiometry of conversion gas from three different wood fuels as function of volume flux of primary air in packed-bed combustion. *Biomass Bioenergy* 23(3):189–208

24. Fiedler F (2004) The state of the art of small-scale pellet-based heating systems and relevant regulations in Sweden, Austria and Germany. *Renew Sustain Energ Rev* 8(3):201–221
25. Alakangas E (2002) Wood pellets in Finland, technology, economy and market. Technical report
26. Strand M (2004) Particle formation and emission in moving grate boilers operating on woody biofuels. Ph.D. thesis
27. Thunman H, Leckner B (2001) Ignition and propagation of a reaction front in cross-current bed combustion of wet biofuels. *Fuel* 80(4):473–481
28. Ojaniemi A (2002) Design principles of biofuel-fired heating stations of <10 MW. Technical report, OPET Finland
29. Yang Y, Ryu C, Khor A, Yates N, Sharifi V, Swithenbank J (2005) Effect of fuel properties on biomass combustion. Part II. Modelling approach-identification of the controlling factors. *Fuel* 84(16):2116–2130
30. Wiinikka H (2005) High temperature aerosol formation and emission minimisation during combustion of wood pellets. Ph.D. thesis
31. Combustion and gasification of agricultural biomass—technologies and applications. Technical report (1995)
32. Teir S (2002) Modern boiler types and applications. Technical report, Helsinki University of Technology. Department of Mechanical Engineering, Energy Engineering and Environmental Protection
33. Morf L (2003) Thermische Verfahren der Entsorgung. Technical report, TU Wien AWS
34. Porteiro J, Patio D, Collazo J, Granada E, Moran J, Miguez J (2010) Experimental analysis of the ignition front propagation of several biomass fuels in a fixed-bed combustor. *Fuel* 89(1):26–35
35. Brunner T, Obernberger I, Scharler R (2009) Primary measures for low-emission residential wood combustion-Comparison of old with optimised modern systems. In: 17th European Biomass Conference and Exhibition, Hamburg, Germany, pp 1319–1328
36. Weber G, Zygarlicke C (2001) Barrier issues to the utilization of biomass. Technical report
37. Salzmann R, Nussbaumer T (2001) Fuel staging for NO_x reduction in biomass combustion: experiments and modeling. *Energy Fuels* 15(3):575–582
38. Nussbaumer T (2003) Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction. *Energy Fuels* 17(6):1510–1521
39. Obernberger I, Brunner T, Bärthaler G (2006) Chemical properties of solid biofuels-significance and impact. *Biomass Bioenergy* 30(11):973–982
40. Carvalho L, Wopienk E, Pointner C, Lundgren J, Verma VK, Haslinger W (2003) Performance of a pellet boiler fired with agricultural fuels. *Appl Energy* 104:286–296
41. Sommersacher P, Brunner T, Obernberger I (2011) Fuel indexes: a novel method for the evaluation of relevant combustion properties of new biomass fuels. *Energy Fuels* 26(1):380–390
42. Tissari J, Sippulai O, Kouki J, Vuorio K, Jokiniemi J (2008) Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. *Energy Fuels* 22(3):2033–2042
43. Sippula O, Hytönen K, Tissari J, Raunemaa T, Jokiniemi J (2007) Effect of wood fuel on the emissions from a top-feed pellet stove. *Energy Fuels* 21(2):1151–1160
44. Houshfar E, Løvås T, Øyvind S (2012) Experimental investigation on NO_x reduction by primary measures in biomass combustion: straw, peat, sewage sludge, forest Residues and Wood Pellets. *Energies* 5(2):270–290
45. Baxter LL, Miles TR, Jenkins BM, Milne T, Dayton D, Bryers RW, Oden LL (1998) The behaviour of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Process Technol* 54(1–3):47–78
46. Lindstrom E, Sandstrom M, Boström D, Öhman M (2007) Slagging characteristics during combustion of cereal grains rich in phosphorus. *Energy Fuels* 21(2):710–717
47. Öhman M, Boman C, Hedman H, Nordin A, Boström D (2004) Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass Bioenergy* 27(6):585–596

48. Díaz-Ramírez M, Boman C, Sebastián F, Royo J, Xiong S, Boström D (2012) Ash characterization and transformation behavior of the fixed-bed combustion of novel crops: poplar, brassica, and cassava fuels. *Energy Fuels* 26(6):3218–3229
49. Lindström E, Larsson S, Boström D, Öhman M Slagging characteristics during combustion of woody biomass pellets made from a range of different forestry assortments. *Energy Fuels* 24:3456–61
50. Jensen P, Frandsen F, Hansen J, Dam-Johansen K, Henriksen N, Hörlyck S (2004) SEM investigation of superheater deposits from biomass-fired boilers. *Energy Fuels* 18(2):378–384
51. Miles TR, Miles JRTR, Baxter LL, Bryers RW, Jenkins BM, Oden LL (1996) Boiler deposits from firing biomass fuels. *Biomass Bioenergy* 10(2–3):125–138
52. Berndes G, Hoogwijk M, van den Broek R (2003) The contribution of biomass in the future global energy supply: a review of 17 studies. *Biomass Bioenergy* 25(1):1–28
53. Bott T (1995) Fouling of heat exchangers. Elsevier Science, Amsterdam
54. Frandsen F, Pedersen A, Hansen J, Madsen O, Lundtorp K, Mortensen L (2009) Deposit formation in the FASAN Wt E boiler as a function of feedstock composition and boiler operation. *Energy Fuels* 23(7):3490–3496
55. Bankiewicz D, Yrjas P, Hupa M (2009) High-temperature corrosion of superheater tube materials exposed to zinc salts. *Energy Fuels* 23(7):3469–3474
56. Michelsen H, Frandsen F, Dam-Johansen K, Larsen O (1998) Deposition and high temperature corrosion in a 10 MW straw fired boiler. *Fuel Process Technol* 54(1–3):95–108
57. Nielsen H, Frandsen F, Dam-Johansen K, Baxter L (2000) The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Prog Energy Combust Sci* 26(3):283–298
58. Davidsson K, Amand L-E, Leckner B, Kovacevik B, Svane M, Hagstrom M, Pettersson J, Pettersson J, Asteman H, Svensson J-E, Johansson L-G (2007) Potassium, chlorine, and sulfur in ash, particles, deposits, and corrosion during wood combustion in a circulating fluidized-bed boiler. *Energy Fuels* 21(1):71–81
59. Hansen L, Nielsen H, Frandsen F, Dam-Johansen K, Hörlyck S, Karlsson A (2000) Influence of deposit formation on corrosion at a straw-fired boiler. *Fuel Process Technol* 64(1–3):189–209
60. Baxter L (1993) Ash deposition during biomass and coal combustion: a mechanistic approach. *Biomass Bioenergy* 4(2):85–102
61. Sippula O, Hokkinen J, Puustinen H, Yli-Pirilä P, Jokiniemi J (2009) Comparison of particle emissions from small heavy fuel oil and wood-fired boilers. *Atmos Environ* 43(32):4855–4864
62. Ohlström M, Jokiniemi J, Hokkinen J, Makkonen P, Tissari J (2006) Combating particulate emissions in energy generation and industry. Technical report, VTT Technical Research Centre of Finland
63. Christensen K (1995) The formation of submicron particles from the combustion of straw. Ph.D. thesis
64. Zbogor A, Jensen P, Frandsen F, Hansen J, Glarborg P (2006) Experimental investigation of ash deposit shedding in a straw-fired boiler. *Energy Fuels* 20(2):512–519
65. Gaffney J, Marley N (2009) The impacts of combustion emissions on air quality and climate—from coal to biofuels and beyond. *Atmos Environ* 43(1):23–36
66. Fernandez A, Wendt J, Wolski N, Hein K, Wang S, Witten M (2003) Inhalation health effects of fine particles from the co-combustion of coal and refuse derived fuel. *Chemosphere* 51(10):1129–1137
67. Tucker W (2000) An overview of PM 2.5 sources and control strategies. *Fuel Process Technol* 65–66:379–392
68. Brunner T, Bärnthaler G, Obernberger I (2006) Fine particulate emissions from state-of-the-art small-scale austrian pellet furnaces
69. Gilbe C, Öhman M, Lindström E, Boström D, Backman R, Samuelsson R, Burvall J (2008) Slagging characteristics during residential combustion of biomass pellets. *Energy Fuels* 22(5):3536–3543

70. Eriksson G, Hedman H, Boström D, Pettersson E, Backman R, Öhman M (2009) Combustion characterization of rapeseed meal and possible combustion applications. *Energy Fuels* 23(8):3930–3939
71. Wu H, Castro M, Jensen P, Frandsen F, Glarborg P, Dam-Johansen K, Røkke M, Lundtorp K (2011) Release and transformation of inorganic elements in combustion of a high-phosphorus fuel. *Energy Fuels* 25(7):2874–2886
72. Thy P, Jenkins B, Grundvig S, Shiraki R, Leshner C (2006) High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel* 85(5–6):783–795
73. Wiinikka H, Gebart R, Boman C, Boström D, Öhman M (2007) Influence of fuel ash composition on high temperature aerosol formation in fixed bed combustion of woody biomass pellets. *Fuel* 86(1–2):181–193
74. Öhman M, Boman C, Hedman H, Nordin A, Boström D (2004) Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass Bioenergy* 27(6):585–596
75. Frederick J, Vakkilainen E (2003) Sintering and structure development in alkali metal salt deposits formed in kraft recovery boilers. *Energy Fuels* 17(6):1501–1509
76. Andersen K, Frandsen F, Hansen P, Wieck-Hansen K, Rasmussen I, Overgaard P, Dam-Johansen K (2000) Deposit formation in a 150 MWe utility PF-boiler during co-combustion of coal and straw. *Energy Fuels* 14(4):765–780
77. Obernberger I, Biedermann F, Widmann W, Riedl R (1997) Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* 12(3):211–224
78. Strand M, Pagels J, Szpila A, Gudmundsson A, Swietlicki E, Bohgard M, Sanati M (2002) Fly ash penetration through electrostatic precipitator and flue gas condenser in a 6 MW biomass fired boiler. *Energy Fuels* 16(6):1499–1506
79. Zhuang Y, Jin Kim Y, Gyu Lee T, Biswas P (2000) Experimental and theoretical studies of ultra-fine particle behavior in electrostatic precipitators. *J Electrostat* 48(3–4):245–260
80. Jensen P, Frandsen F, Dam-Johansen K, Sander B (2000) Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels* 14(6):1280–1285
81. Srikanth S, Das S, Ravikumar B, Rao D, Nandakumar K, Vijayan P (2004) Nature of fireside deposits in a bagasse and groundnut shell fired 20 MW thermal boiler. *Biomass Bioenergy* 27(4):375–384
82. Tillman D, Duong D, Miller B (2009) Chlorine in solid fuels fired in pulverized fuel boilers—sources, forms, reactions, and consequences: a literature review. *Energy Fuels* 23(7):3379–3391
83. Björkman E, Strömberg B (1997) Release of chlorine from biomass at pyrolysis and gasification conditions. *Energy Fuels* 11(5):1026–1032
84. Davidsson K, Pettersson J, Nilsson R (2002) Fertiliser influence on alkali release during straw pyrolysis. *Fuel* 81(3):259–262
85. Olsson J, Jäglid U, Pettersson J, Hald P (1997) Alkali metal emission during pyrolysis of biomass. *Energy Fuels* 11(4):779–784
86. Risnes H, Fjellerup J, Henriksen U, Moilanen A, Norby P, Papadakis K, Posselt D, Sørensen L (2003) Calcium addition in straw gasification. *Fuel* 82(6):641–651
87. Dahl O, Nurmesniemi H, Pöykö R, Watkins G (2009) Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. *Fuel Process Technol* 90(78):871–878
88. Vamvuka D, Pitharoulis M, Alevizos G, Repouskou E, Pentari D (2009) Ash effects during combustion of lignite/biomass blends in fluidized bed. *Renew Energy* 34(12):2662–2671
89. Shah K, Cieplik M, Bertrand C, van de Kamp W, Vuthaluru H (2010) Correlating the effects of ash elements and their association in the fuel matrix with the ash release during pulverized fuel combustion. *Fuel Process Technol* 91(5):531–545
90. Müller M, Wolf K-J, Smeda A, Hilpert K (2006) Release of K, Cl, and S Species during co-combustion of coal and straw. *Energy Fuels* 20(4):1444–1449

91. van Lith S, Alonso-Ramirez V, Jensen P, Frandsen F, Glarborg P (2006) Release to the gas phase of inorganic elements during wood combustion. Part 1: development and evaluation of quantification methods. *Energy Fuels* 20(3):964–978
92. Knudsen J, Jensen P, Dam-Johansen K (2004) Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. *Energy Fuels* 18(5):1385–1399
93. Bridgeman T, Darvell L, Jones J, Williams P, Fahmi R, Bridgewater A, Barraclough T, Shield I, Yates N, Thain S, Donnison I (2007) Influence of particle size on the analytical and chemical properties of two energy crops. *Fuel* 86(1–2):60–72
94. Lang T, Jensen PA, Knudsen JN (2006) The effects of Ca-based sorbents on sulfur retention in bottom ash from grate-fired annual biomass. *Energy Fuels* 20(2):796–806
95. Steenari B, Lindqvist O (1998) High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. *Biomass Bioenergy* 14(1):67–76
96. Fuel Díaz Arocas P, Gutiérrez Nebot L, Carrasco García JE (2008) The effect of the addition of chemical materials on the sintering of biomass ash. 87(12):2651–2658
97. Aho M, Silvennoinen J (2004) Preventing chlorine deposition on heat transfer surfaces with aluminium-silicon rich biomass residue and additive. *Fuel* 83(10):1299–1305
98. Misra M, Ragland K, Baker A (1993) Wood ash composition as a function of furnace temperature. *Biomass Bioenergy* 4(2):103–116
99. Thy P, Leshner C, Jenkins B (2000) Experimental determination of high-temperature elemental losses from biomass slag. *Fuel* 79(6):693–700
100. Knudsen J, Jensen P, Lin W, Frandsen F, Dam-Johansen K (2004) Sulfur transformations during thermal conversion of herbaceous biomass. *Energy Fuels* 18(3):810–819
101. Knudsen J (2004) Volatilization of inorganic matter during combustion of annual biomass. Ph.D. thesis
102. Knudsen J, Jensen PA, Lin W, Dam-Johansen K (2005) Secondary capture of chlorine and sulfur during thermal conversion of biomass. *Energy Fuels* 19(2):606–617
103. Dayton D, Jenkins B, Turn S, Bakker R, Williams R, Belle-Oudry D, Hill M (1999) Release of inorganic constituents from leached biomass during thermal conversion. *Energy Fuels* 13(4):860–870
104. van Lith S, Jensen P, Frandsen F, Glarborg P (2008) Release to the gas phase of inorganic elements during wood combustion. Part 2: influence of fuel composition. *Energy Fuels* 22(3):1598–1609
105. Frandsen F, van Lith S, Korbee R, Yrjas P, Backman R, Obernberger I, Brunner T, Jöller M (2007) Quantification of the release of inorganic elements from biofuels. *Fuel Process Technol* 88(11–12):1118–1128
106. Pedersen A, van Lith S, Frandsen F, Steinsen S, Holgersen L (2010) Release to the gas phase of metals, S and Cl during combustion of dedicated waste fractions. *Fuel Process Technol* 91(9):1062–1072
107. Johansen JM, Jakobsen JG, Frandsen FJ, Glarborg P (2011) Release of K, Cl, and S during pyrolysis and combustion of high-chlorine biomass. *Energy Fuels* 25(11):4961–4971
108. Novakovic A, van Lith S, Frandsen F, Jensen P, Holgersen L (2009) Release of potassium from the systems K-Ca-Si and K-Ca-P. *Energy Fuels* 23(7):3423–3428
109. Bostrom D, Grimm A, Boman C, Björnbo E, Öhman M (2009) Influence of kaolin and calcite additives on ash transformations in small-scale combustion of oat. *Energy Fuels* 23(10):5184–5190
110. Arvelakis S, Jensen P, Dam-Johansen K (2004) Simultaneous thermal analysis (STA) on ash from high-alkali biomass. *Energy Fuels* 18(4):1066–1076
111. Glazer M, Khan N, de Jong W, Spliethoff H, Schürmann H, Monkhouse P (2005) Alkali metals in circulating fluidized bed combustion of biomass and coal: measurements and chemical equilibrium analysis. *Energy Fuels* 19(5):1889–1897
112. Labalette F, Marsac S, Jacquin C, Lumbreras-Castellano O, Chieze B, Briand S (2010) Evaluation of the performance of triticale and carinata biomasses as biofuels in a french pilot combustion plant. In: 18th European Biomass Conference and Exhibition, Lyon, France, pp 1940–1943

113. Llorente M, Laplaza J, Cuadrado R, García J (2006) Ash behaviour of lignocellulosic biomass in bubbling fluidised bed combustion. *Fuel* 85(9):1157–1165
114. Fernández Llorente MJ, Escalada Cuadrado R, Murillo Laplaza JM, Carrasco García JE (2006) Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass ash agglomeration and sintering. *Fuel* 85(14–15):2081–2092
115. Sørum L, Frandsen F, Hustad J (2003) On the fate of heavy metals in municipal solid waste combustion Part I: devolatilisation of heavy metals on the grate. *Fuel* 82(18):2273–2283
116. Capablo J, Jensen P, Pedersen K, Hjuler K, Nikolaisen L, Backman R, Frandsen F (2009) Ash properties of alternative biomass. *Energy Fuels* 23:1965–1976
117. Boman C, Nordin A, Öhman M, Boström D (2005) Emissions from small-scale combustion of biomass fuels—extensive quantification and characterization. Technical report, Umeå Universitet

Grate-Fired Energy Crop Conversion

Experiences with *Brassica Carinata* and *Populus* sp.

Díaz-Ramírez, M.C.

2015, XX, 194 p. 47 illus., 10 illus. in color., Hardcover

ISBN: 978-3-319-20758-2