

Biomass combustion systems: a review on the physical and chemical properties of the ashes

L.J.R. Nunes ^{a,b}, J.C.O. Matias ^a, J.P.S. Catalão ^{a,c,d*}

^a University of Beira Interior, R. Fonte do Lameiro, 6201-001 Covilhã, Portugal

^b YGE – Yser Green Energy SA, Área de Acolhimento Empresarial de Loureiro/Úl, Lote 17, 3720-075 Oliveira de Azeméis, Portugal

^c INESC-ID, R. Alves Redol, 9, 1000-029 Lisbon, Portugal

^d IST, University of Lisbon, Av. Rovisco Pais, 1, 1049-001 Lisbon, Portugal

Abstract

Biomass as an energy source contributes to a decrease in the dependence on imported fossil fuels, while at same time, adding value to the countries where biomass fuel sources thrive, in addition to providing a source of renewable energy. Knowledge of the behaviour of fuel is essential in order to design and operate equipment safely and efficiently. In particular, knowledge about mineral content is essential because the ashes play an important role in the dynamics of the generation system. Through knowledge of the chemical composition and physical properties of the ashes, it is possible to predict the tendency to form deposits in the boiler components, as well as their potential to cause corrosion, erosion and abrasion. The behaviour of the ashes in the system is highly dependent on fuel, particularly when it comes from industrial waste or energy crops. These fuels have a higher mineral content, particularly sodium (Na), potassium (K), phosphorous (P) and chloride (Cl). They also have higher ash content with a low melting point and high corrosion potential. This paper focuses on the characteristics of the ashes derived from the combustion of biomass, with particular attention paid to the chemical transformations at high temperatures, as well as its effect on the combustion equipment. Emphasis is placed on the potential problems that occur when biomass-burning technologies are used for energy crops, in order to avoid catastrophic failures. It concludes with recommendations for the management, control and prevention of problems associated with ash.

© 2015 Elsevier Ltd. All rights reserved.

Keywords: Biomass, combustion, ashes, corrosion

1. Introduction

In today's world, there is a growing interest in the use of biomass for energy purposes [1–5]. The reasons include economic, political and environmental concerns, as well as the need to provide energy using renewable resources, reduce dependence on foreign fossil fuels, create more jobs per unit of energy produced and considerably reduce the environmental impact [6–10]. The majority of biomass waste products actually available are deprecated and may potentially be used as an energy source. In addition, many types of biomass forms can be grown as energetic crops to be consumed on-site, eliminating the dependence on third parties to supply raw materials [11].

To achieve a stable energy generation system, the requirements imposed by the fuel should be well known in order to allow for the adaptation of the burning technologies, particularly when it concerns industrial waste biomass forms or energy crops that, by its chemical composition, have different behaviours than other biomass types [12]. These fuels have a higher content of minerals, including sodium (Na),

* Corresponding author at: Department of Electromechanical Engineering, University of Beira Interior, R. Fonte do Lameiro, 6201-001 Covilhã, Portugal.
Tel.: +351 275 329914; fax: +351 275 329972.

E-mail address: catalao@ubi.pt (J.P.S. Catalão).

potassium (K), phosphorous (P) and chloride (Cl), a high ash content with low melting point and a high corrosion potential [13].

The objective of this paper is to present a review about the development of the research related to biomass ashes and its effects in thermal conversion equipment. The ashing process and its physical and chemical characteristics, as well as the mechanisms of ash deposition and metallurgical damage caused by chloride gas combustion active corrosion are described. Ways to prevent or minimise the problems caused by ash deposition in biomass-fuelled boilers are also presented and analyzed.

2. Ash formation mechanisms

The elements that form the ashes are present in biomass as salts that are chemically bonded to the carbon structure (inherent ash), or they can come with biomass as mineral soil particles that have been caught during growth or are swiped during harvest and transport (foreign ash) [14]. The inherent ash components are homogeneously distributed in the fuel and are much more mobile than the trapped ash compounds, and therefore, they react chemically during combustion [15]. A fraction of these ash-forming compounds are volatilised and become part of the gas phase [16]. The volatilised amount depends on the characteristics of the fuel, the atmosphere surrounding the particle and the burner technology [17]. For example, a high combustion temperature and a reducing atmosphere enhance the volatilisation of environmentally relevant elements, such as heavy metals (Zn, Pb, etc.) [18].

Metals and metal oxides are partially evaporated at high temperatures within the fuel particles, and they become an active part of the reactions during the gas phase [19]. During its tour in the boiler fire, channels will precipitate at low temperatures and will nucleate on the surface as fine particles of CaO. They then become part of the gases in what is called “fly-ash” (size $<1\mu\text{m}$). Due to a reoxidation–nucleation–coalescence process, these particles agglomerate, composing an ash type larger than $10\ \mu\text{m}$ known as coarse fly-ash [20].

Fig. 1 shows the typical grate furnace with bottom ashes being formed.

See Fig.1 at the end of the manuscript.

Non-volatile ash compounds that remain in the still-combusting particles may be melted and coalesced on or in the surface of the particle, depending on the temperature and chemical composition of both the

particle and the surrounding gases [21]. This results in ash particles that have a wide range of compositions, sizes and characteristics related to the original mineral. Depending on the density and size of these particles, the technology used and the speed of the gases, a fraction of these ashes can be entrained by the gases, but in general, the majority is deposited on the grid, forming the so-called “grate ashes” [22], as seen in Fig. 2.

See Fig. 2 at the end of the manuscript.

3. Chemical composition of the ashes

The ash content of different forms of biomass is varied, and can be as low as 0.5% on a dry basis for some species of pulpade wood, or up to 20% for some cereal or forestry and agriculture waste, particularly if they are contaminated with inert materials like small stones or rock dust [23]. The ash composition is dominated by SiO_2 and CaO , and less oxides of Mg, Al, K and P. The ash from plants with long reproductive periods, such as trees, by the dynamic flow of nutrients to the soil, have a very different mineral composition than plants that are harvested several times a year, such as energy crops or cereals. The latter contain large quantities of oxides with low melting points, particularly K and P [24], and also contain substantially lower levels of heavy metals [25]. Table 1 presents the ash average composition obtained from the combustion of some of the most common biomass forms available in Portugal.

See Table 1 at the end of the manuscript.

Due to complex alterations between K, Cl, P, Si and Ca, each element cannot be evaluated individually without including interactions between different oxides and equilibrium compositions, which are also highly dependent on the type of biomass, operational conditions and generated steam parameters. For example, a Cl content of less than 0.1% is not enough to avoid corrosion problems with heaters if you are dealing with a high temperature steam [29].

The most used technique for ash-related research involves using air-cooled steel probes simulating heating tubes or heat exchangers where ash will be deposited during biomass combustion, monitoring ash deposition rate, as well as allowing the collection of fly ash deposit for further analysis, as described in several studies [30–40].

The ashes originated from biomass combustion after being collected are usually characterized using several laboratorial techniques, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDX), and ion chromatography (IC) [41].

ICP-AES, XRF and SEM-EDX are usually applied to analyze the major elements present in the fuel ash and deposits, including Si, Al, Fe, Ca, Mg, Ti, Na, K, P, Cl and S [37,45–49], as well as Pb and Zn for some fuels [42].

4. Physical and chemical behaviour of the ashes

The inorganic components that support biomass can be evenly distributed in the organic fuel, as inorganic component grains in the fuel particles and as foreign material brought to the process [43].

During the combustion process of the particle, the balance of the ash's inorganic fraction that is formed then undergoes a series of simultaneous physical and chemical transformations in order to form ash particles as a result of segregation, evaporation, precipitation, nucleation and coalescence processes. These particles have a wide spectrum in terms of size, shape and composition. This depends on many factors, primarily the morphology and composition of the fuel, the combustion temperature and residence time.

During combustion several chemical and physical changes of the minerals at high temperature occur [44]. Silica will melt partially or totally and will interact chemically with other components of the ash, primarily forming alkali metal silicates (K and Na). Alumina-silicates will suffer partial or total fusion. Carbonates, oxalates, chlorides and other salts will be decomposed. Alkali metals and other heavy metals will be volatilised. The particles will suffer fragmentation by thermal shock and rapid emission of gases, as well as the mineral particles will coalesce and agglomerate.

The type of combustion equipment used is also relevant in terms of the behaviour of the ash, since the combustion conditions are different. For example, in moving bed equipment, ash fusion may not be so troublesome as it is in fixed-bed situations, as there is less coalescence of the molten particles. Details of each type of biomass-burning technology, along with its corresponding effects, can be found in several research and technical studies [45].

One of the most important features of the ash of biomass is its behaviour at high temperatures, particularly its melting behaviour. The mechanisms of fusion and agglomeration of ash particles on burners' grates and particle agglomeration processes on moving bed and fluidised bed burners are very important and must be taken into account when they are designed [46]. The melting behaviour of the ash is also an important factor in determining the propensity of the different fuels to form deposits of slag or ash vitrification, either on the grate or the boiler surface walls.

Phase diagrams are a good starting point to study the behaviour of the ash at high temperatures, where the influence is shown having a composition at the melting temperature, determined by the system design. Several studies use the ternary system CaO-SiO₂-K₂O phase diagram, where the melting temperatures of all possible compositions are plotted [47]. In these diagrams, woody biomass ash is presented as having high melting points and behaviour that is insensitive to changes in the composition [48], while typical fast-growing biomass ash, which is high in K, is presented as being dominated by eutectic system characteristics with low temperatures and large variations in composition [49].

Several studies demonstrated [50–56] that the laboratorial tests should evaluate at least two key temperatures: a temperature where 15% of the mass is liquid (considered to be the temperature at which the particles begin to soften, allowing agglomeration of ash deposits) and a temperature where 70% of the mass is liquid (considered to be the temperature at which the ash flows like a liquid).

The liquid–solid performance of the ash is a very complex phenomenon and depends primarily on its chemical composition. Another study shows that for points away from the eutectic point, fusion occurs over a range of several hundred degrees, and the influence of the Cl content in the ash is an important factor in the melting temperature in which solids begins to soften. For example, ashes without Cl or with a very low Cl content begin to melt at 800 °C and are completely liquid at 1000 °C. On the other hand, ashes with Cl content near 20% begin to melt at 600 °C and are fully molten at 800 °C [57].

There are other indices that are more related to the tendency of ashes to deposit on the surface of the equipment walls due to their melting point, which are also available for the evaluation of the fuels' behaviour [58–61].

5. Ash-related problems

In practical terms, the problems related to ash in the biomass combustion systems of burners and boilers are associated with [62] the formation of partially melted ash agglomerates, and their influence on the grate and slag deposits in the equipment at high temperatures, the formation of ash deposits in low temperature zones of the exchange surfaces in boilers where there are convective sections, the accelerated corrosion and erosion of the metal on the side of the gases, the emission of ash in the aerosol state (fly-ash), as well as its formation and control, and the use, handling and disposal of ash waste from the biomass equipment.

In general, the nature of the problems and their impact on the performance of the combustion equipment depends on the characteristics of the fuel (mainly ash content and chemical composition), as well as the design and operation of combustion equipment and boilers [63].

Ash behaviors during combustion are closely related with the characteristics of biomass fuel (e.g., high K, Cl and moisture content, low S content, etc.), which usually lead to greater ash-related challenges for almost all burner types when firing biomass materials. Some major negative impacts of the increased ash deposition by biomass combustion on the efficiency and operation of a combustion system can be summarized as follows [64]:

- Decrease in the burner efficiency. The increased ash deposition as well as the changed properties of the ash deposits containing low-melting compounds such as K, Na, S and Ca would form a kind of coating on the bottom ash particles, which is partly in a liquid form, and begin to bind the particles together like glue, leading to agglomeration of the ash particles in the combustor. Moreover, deposition of fused or partially fused ash deposits on the heat exchanger surfaces will retard the boiler heat transfer, leading to a decline in the combustor thermal efficiency, and its capacity too.
- Damage to the burner. Ash deposits may grow to the extent that the flue gas flow may be restricted. This could cause mechanical damage of the burner components, and more importantly, the ash deposits are associated with corrosion at high temperatures. Even for large pulverized fuel furnaces, the ash deposition on burner components and divergent surfaces could result in an interference with the burner light-up and operation. Again, the accumulation and subsequent shedding of large ash deposits on the upper furnace and the steam tubes surfaces could restrict gas flow and thus damage the components of the combustion system.

- Maintenance problems. Severe deposits would require premature shut-down for maintenance. Unplanned outages for off-load cleaning are required for removing ash deposits. Moreover, the build-up of accumulations of ash deposits on heat transfer surfaces also lead to increased burner exit gas temperatures, reducing efficiency.

6. Ash deposition dynamics

When burning fuels with a high ash content and chemical composition that promote corrosive effects on boilers, is important to recognise that the ash is an important factor to consider in the equipment design and conception [65]. It is necessary to locate the points where the ash tends to deposit and study the gas flow system with due care. The problems associated with ash deposition during the operation of the equipment occur on all burners and biomass boilers, with the following situations occurring most frequently [66]:

- Agglomeration of ash particles in the grate or fluidised bed due to poor combustion conditions, defluidisation, ash removal and handling problems.
- Deposition of ash in the components of the burner and interfering with the stability of the process.
- Accumulation of large amounts of partially or totally melted ashes that interfere with the operation of the system. This results in unscheduled boiler shutdowns, as evident in Fig. 3, illustrating the vitrified ash sample taken from a thermal fluid boiler operating with wood pellets.
- Partially or entirely molten ash deposition on the walls of the boiler heat exchanger, which reduces heat transfer, increasing the gas temperature and decreasing the boiler efficiency.
- Accumulation and subsequent fall of large ash deposits in the upper parts of the furnace, causing damage to the combustion system components.

See Fig. 3 at the end of the manuscript.

These ash slag formations occur at relatively high temperatures ($> 800^{\circ}\text{C}$) on the walls of refractory or heat exchange surfaces, occurring relatively quickly (in a matter of hours when conditions are favourable) involving the deposition and agglomeration of solid particles or partially melted ashes on each other [67]. Accumulations of these deposits also occur on the convection surfaces of boilers, known as fouling, both at high and at low temperatures. The formation of ash deposits on the surfaces of heat exchangers at temperatures in the vicinity of 800°C to 1000°C involves a slow deposition process of partially molten ash,

in which the growth of the layering occurs during the operating days, generally depositing species of alkali metal oxides. The formation of deposits on the heat exchange surface occurs at low temperature, by the deposition of material on the walls perpendicular to the gas flow [68].

It is now clear that the processes involving ash deposits on burners and boilers operating with biomass are very complex phenomena, depending on the characteristics of the ashes and of the burner [69]. The design of both the burner and the boiler will be particularly important where convection will occur and should be appropriately adapted to the characteristics of the ashes [70]. The design and operation of the combustion and cleaning systems are very important. It is preferable to avoid the deposition of ash, or at least to keep it in a very low level instead of using cleaning methods, but these should be exhaustively used during equipment stop programs where the boiler and convective areas must be thoroughly cleaned of ash [71]. There are monitoring systems and automatic cleaning systems for ashes that can be integrated with the optimisation and control of the operation [72].

7. Impact of ash deposition in biomass systems

7.1 Chemical impact: corrosion

Corrosion processes occurring on the side of the smoke in the boilers are very complex, as they occur at high temperatures and under conditions involving large variations of temperature and composition. For those reasons, the processes are extremely difficult to study and monitor. However, because of the great importance for the design and operation of biomass combustion plants, these processes have been the subjects of several recent studies in laboratories, pilot plants and on the industrial scale [73–78].

Several research works demonstrated that Cl has a catalytic effect, which leads to the dissociation of the steel material in the heat exchangers, even when the temperatures of the tubes are low (100 to 150 °C) [79]. This problem seems to be accentuated in those fuels that have a Cl:S molar ratio higher than 2, where the absence of S enhances the formation of chlorides, having a catalytic effect on the corrosion [80]. In general, the corrosion rate at the boiler tubes is affected by several factors: the material of the tubes, the gas compositions and temperatures, the heat transfer rate, the dynamics of bottom ash, and the physical and chemical properties of the deposition [81].

7.2 Corrosion mechanisms

It is common for biomass boilers to have a high rate of corrosion when metal temperatures exceed 500°C [82]. A number of corrosion mechanisms coexist and may occur simultaneously, including reaction processes between the metal and the metal oxides with gaseous species of Cl and O, reactions involving the alkali metal salts solid phase (K and Na), and reactions with ash in the liquid phase and during phase changes [83]. An example of this type of corrosion is presented in Fig. 4.

See Fig. 4 at the end of the manuscript.

The operating experience with biomass demonstrates that the most severe corrosion is commonly associated with deposits of ash containing alkali metal chlorides on the heating change surfaces [84]. These deposits are responsible for significantly high rates of wear in metals, with reactions occurring below the melting point of KCl, and other ash mixtures with low eutectic points (KCl-NaCl-FeCl₂ systems) [85].

Another reaction, which is likely to increase the corrosion processes in biomass boilers, is the sulfation of the deposits in contact with SO₂/SO₃ in the gases that generate HCl through the metal surface, according to Eq. 1 [86]:



The gaseous HCl can then diffuse to the surface and react to form metal chlorides. This mechanism occurs when fuels are low in S and significantly higher in Cl content [87]. Cereals are much more prone to corrosion, having a ratio of Cl:S that promotes corrosion.

Other studies [88-90] describes the mechanism of corrosion in the presence of Cl as "active oxidation," and as the main factor that is responsible for accelerated corrosion rates in boiler tubes. The study describes the condensation process' enrichment of alkali metal chlorides in the pipe surface. In addition, the study illustrates that the chlorides react with SO₂ and SO₃ in the gas to form sulphate with subsequent generation of gaseous Cl, according to Eq. 2 and Eq. 3:



This generated Cl may also partially react with available oxygen as shown in Eq. 1, or it may directly react with the iron in the tubes to form FeCl₂. These chlorides can react with available oxygen and regenerate the gaseous Cl, holding or even accelerating the pace of corrosion according to Eq. 4, Eq. 5 and Eq. 6:



This study shows that these reactions are responsible for the generation of gaseous Cl in the adjacent metal surface, resulting in severe corrosion.

A number of corrosion on-site tests in plants working with biomass boilers have been carried out in recent years. These assays involve exposing the test metals to flue gas for a period of time long enough to note corrosion effects [91–97].

Another study were performed where accelerated corrosion tests in boilers using fuels, such as straw, with ash levels around 5% to 7%, Cl levels between 0.3% and 0.5%, a S content lower than 0.2% and K content of up to 2% [98]. The heaters alloys were exposed to the combustion gases at temperatures between 450°C and 620°C and showed that measured corrosion rates are insensitive to the materials used, even when tested in Cr-Ni-Mo steels, reaching values of oxide penetration equivalent to 8mm per year.

The evaluation of different systems using biomass generation was reported by another study [99], where failures were observed on heaters prior to the first year of operation, due to active corrosion by Cl.

7.3 Corrosion preventive and corrective measures

In burners combusting biomass waste with a high content of alkali metal materials, chlorides and low sulphur content will undergo significant corrosion in areas, even at low steam temperature in the vicinity of 500 to 550 °C. There are a number of steps that can be taken in order to prevent and reduce corrosion [100], such as the control of the vapour temperature in the design of the boiler to a level at which the corrosion rate is acceptable, the use of additives that alter the chemistry of the combustion gases and thus the

deposition of ash and the selection of more corrosion-resistant alloys to the heat exchangers and other boiler parts.

7.4 Physical impact: erosion/abrasion

Erosion and abrasion of the components of the boiler and other equipment in plants where a biomass system is used in all scales of operation are predominantly associated with the presence of ashes that have hard particles, particularly those that are harder than steel and refractory materials used for the interior of the boilers. The only mineral species that is commonly found in biomass that falls into this category is quartz, so only these materials, or others contaminated with quartz will cause significant erosion and abrasion [101].

The fly-ash ashes primarily tend to be very thin and relatively soft, and thus are not considered to be particularly abrasive or erosive. For this reason, the processes of erosion and abrasion tend to be less important than they are in coal combusting equipment. However, there are some cases where erosion and abrasion can be significant [102]:

- The use of some materials, such as agriculture waste, which have ashes that have a high silica content, resulting in abrasion problems in the boilers' components.
- The formation of molten material, particularly in the bottom ash, can cause grate erosion and abrasion on mechanical components and pneumatic ash handling systems.
- In biomass boilers suffering severe fouling problems in convective zones, the gases will circulate with higher speeds due to the narrowing of the passage.
- Overall, the experience shows that erosion and abrasion of the ash from biomass is lower than in other conventional power generation systems.

8. Final utilisation and/or disposal of ashes

The increased use of biomass as fuel for the generation of heat and power has required the use of ash for beneficial purposes in order to minimise the negative environmental and economic impacts that may occur. For a sustainable use of biomass, both domestically and on an industrial scale, it is important to recognise the fact that the ash can largely be returned to the soil, renewing and replacing the extracted nutrients,

especially P and K [103]. If, for some reason, no ash can be recycled to its place of origin or be used as fertiliser, there are other potential uses, including, for example, as additives for the production of building materials [104].

9. Conclusions

The composition of ashes from biomass is dominated by SiO_2 and CaO , and contains lesser amounts of Mg, Al, K and P oxides. The ash from plants, such as trees, that have long reproductive periods, have a mineral composition very different from plants that are harvested several times a year, such as cereals, due to the dynamic flow of nutrients within the earth. The latter contain large quantities of oxides with low melting points, mainly K and P. In addition, they also contain substantially lower levels of heavy metals.

During the combustion process of the particles, the balance of the inorganic fraction of the ash formed undergoes a series of simultaneous physical and chemical transformations to form ash particles, as a result of segregation, evaporation, precipitation, nucleation and coalescence processes. The resulting ash has a wide spectrum in terms of size, shape and composition of the ash. This depends of many factors, primarily the morphology and chemical composition of the fuel, the combustion temperature and the residence time. The minerals chemical and physical transformations occurring at high temperatures include melting, decomposition of volatile compounds and the fragmentation, coalescence and agglomeration of mineral particles.

When burning fuels with high ash content and chemical compositions that promote corrosive effects on boilers, it is important to recognise that the ash is an important consideration in the equipment design phase. Many studies have demonstrated that Cl has a catalytic effect, which leads to the dissociation of the steel pipe material in the heat exchangers, even when the temperatures of the tubes are low (100 to 150 °C). This problem seems to be accentuated in those fuels with a Cl:S molar ratio higher than 2, where the absence of S enhances the formation of chlorides, having a catalytic effect on the corrosion. In these cases, it was found that the measured corrosion rates are unaffected by the materials used, even when Cr-Ni-Mo steels were tested, reaching values of equivalent oxide penetration of 8mm per year.

To achieve sustainable and stable development, the combustion technologies must be known and adapted to the requirements imposed by the fuel, particularly when it comes to industrial wastes or energy

crops, which, by their chemical composition, have different behaviours than do other forms of biomass. These fuels have a higher mineral content, especially K, P and Cl, a high ash content with a low melting point, and a high corrosive potential.

Many research studies contribute to the ash formation and deposition subjects for biomass thermal conversion covering different types of boilers and a large number of biomass species. Nevertheless, detailed reactions of the alkali elements during the combustion processes aren't yet completely well-known. Many questions, such those concerning what type of reactions occur before the fly ash makes contact with the heater exchange surface, or what are the practical and cost-effective means to retard these reactions, still remain unanswered.

Acknowledgements

This work was supported by FEDER funds (European Union) through COMPETE and by Portuguese funds through FCT, under Projects FCOMP-01-0124-FEDER-020282 (Ref. PTDC/EEA-EEL/118519/2010) and UID/CEC/50021/2013. Also, the research leading to these results received funding from the EU Seventh Framework Programme FP7/2007–2013 under grant agreement no. 309048.

References

- [1] Ruiz, J. A., et al. "Biomass gasification for electricity generation: Review of current technology barriers." *Renewable and Sustainable Energy Reviews* 18 (2013): 174–183.
- [2] Abuelnuor, A. A. A., et al. "Characteristics of biomass in flameless combustion: A review." *Renewable and Sustainable Energy Reviews* 33 (2014): 363-370.
- [3] Saidur, R., et al. "A review on exergy analysis of biomass based fuels." *Renewable and Sustainable Energy Reviews* 16.2 (2012): 1217–1222.
- [4] Sahu S.G., Chakraborty N., Sarkar P. "Coal–biomass co-combustion: An overview." *Renewable and Sustainable Energy Reviews* 39 (2014): 575-586.
- [5] Nunes L.J.R., Matias J.C.O., Catalão J.P.S. "A review on torrefied biomass pellets as a sustainable alternative to coal in power generation." *Renewable and Sustainable Energy Reviews* 40 (2014): 153-160.
- [6] Abbasi, T., and Abbasi, S. A. "Biomass energy and the environmental impacts associated with its production and utilization." *Renewable and Sustainable Energy Reviews* 14.3 (2010): 919–937.

- [7] Laser, M., and Lynd, L. R. "Comparative efficiency and driving range of light- and heavy-duty vehicles powered with biomass energy stored in liquid fuels or batteries." *Proceedings of the National Academy of Sciences* 111.9 (2014): 3360–3364.
- [8] Zanon, A. J. V., et al. "Physical and colorimetric changes in *Eucalyptus grandis* wood after heat treatment." *BioResources* 9.1 (2013): 293–302.
- [9] Zabalza B., Ignacio, A. V. C., and Usón, A. A. "Life cycle assessment of building materials: Comparative analysis of energy and environmental impacts and evaluation of the eco-efficiency improvement potential." *Building and Environment* 46.5 (2011): 1133–1140.
- [10] Fernando, A. L., et al. "Environmental impact assessment of energy crops cultivation in Europe." *Biofuels, Bioproducts and Biorefining* 4.6 (2010): 594–604.
- [11] Corma, A., et al. "Production of high-quality diesel from biomass waste products." *Angewandte Chemie* 123.10 (2011): 2423–2426.
- [12] Liu, X., et al. "Pilot-scale anaerobic co-digestion of municipal biomass waste and waste activated sludge in China: Effect of organic loading rate." *Waste Management* 32.11 (2012): 2056–2060.
- [13] Sheth, P. N., and Babu, B. V. "Production of hydrogen energy through biomass (waste wood) gasification." *International Journal of Hydrogen Energy* 35.19 (2010): 10803–10810.
- [14] Hansen, U. E., and Nygaard, I. "Sustainable energy transitions in emerging economies: The formation of a palm oil biomass waste-to-energy niche in Malaysia 1990–2011." *Energy Policy* 66 (2014): 666–676.
- [15] Merlino, G., et al. "Shifts of microbial community structure during anaerobic digestion of agro-industrial energetic crops and food industry byproducts." *Journal of Chemical Technology and Biotechnology* 87.9 (2012): 1302–1311.
- [16] Williams, A., et al. "Pollutants from the combustion of solid biomass fuels." *Progress in Energy and Combustion Science* 38.2 (2012): 113–137.
- [17] Vassilev, S. V., et al. "An overview of the chemical composition of biomass." *Fuel* 89.5 (2010): 913–933.
- [18] Vassilev, S. V., et al. "An overview of the composition and application of biomass ash. Part 1. Phase-mineral and chemical composition and classification." *Fuel* 105 (2013): 40–76.
- [19] Vassilev, S. V., et al. "An overview of the composition and application of biomass ash: Part 2. Potential utilisation, technological and ecological advantages and challenges." *Fuel* 105 (2013): 19–39.
- [20] Boström, D., et al. "Ash transformation chemistry during combustion of biomass." *Energy & Fuels* 26.1 (2011): 85–93.

- [21] Nordgren, D., et al. "Ash transformations in pulverised fuel co-combustion of straw and woody biomass." *Fuel Processing Technology* 105 (2013): 52–58.
- [22] Teixeira, P., et al. "Use of chemical fractionation to understand partitioning of biomass ash constituents during co-firing in fluidized bed combustion." *Fuel* 101 (2012): 215–227.
- [23] Garba, M. U., et al. "Modelling of deposit formation and sintering for the co-combustion of coal with biomass." *Fuel* 113 (2013): 863–872.
- [24] Pengthamkeerati, P., and Satapanajaru, T. "Analysis and modeling of column operations on reactive dye removal onto alkaline-treated biomass fly ash." *Desalination and Water Treatment* [ahead-of-print] (2013): 1–8.
- [25] Pengthamkeerati, P., et al. "Alkaline treatment of biomass fly ash for reactive dye removal from aqueous solution." *Desalination* 261.1 (2010): 34–40.
- [26] Vassilev, Stanislav V., Christina G. Vassileva, and David Baxter. "Trace element concentrations and associations in some biomass ashes." *Fuel* 129 (2014): 292–313.
- [27] Febrero, Lara, et al. "Characterisation and comparison of biomass ashes with different thermal histories using TG-DSC." *Journal of Thermal Analysis and Calorimetry* 118.2 (2014): 669–680.
- [28] Huang, S., et al. "The physicochemical properties and catalytic characteristics of different biomass ashes." *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 36.4 (2014): 402–410.
- [29] Pisa, I., and Lazaroiu, G. "Influence of co-combustion of coal/biomass on the corrosion." *Fuel Processing Technology* 104 (2012): 356–364.
- [30] Yildiz, Güray, et al. "Effect of biomass ash in catalytic fast pyrolysis of pine wood." *Applied Catalysis B: Environmental* 168 (2015): 203–211.
- [31] Rizvi, T., et al. "Prediction of biomass ash fusion behaviour by the use of detailed characterisation methods coupled with thermodynamic analysis." *Fuel* 141 (2015): 275–284.
- [32] Gu, Haiming, et al. "Interaction between biomass ash and iron ore oxygen carrier during chemical looping combustion." *Chemical Engineering Journal* 277 (2015): 70–78.
- [33] Qin, Ke, and Henrik Thunman. "Diversity of chemical composition and combustion reactivity of various biomass fuels." *Fuel* 147 (2015): 161–169.
- [34] Reinmöller, Markus, et al. "Relationship between ash fusion temperatures of ashes from hard coal, brown coal, and biomass and mineral phases under different atmospheres: A combined FactSage™ computational and network theoretical approach." *Fuel* 151 (2015): 118–123.
- [35] Pengthamkeerati, P., and T. Satapanajaru. "Analysis and modeling of column operations on reactive dye removal onto alkaline-treated biomass fly ash." *Desalination and Water Treatment* 54.1 (2015): 227–234.

- [36] Fuller, A., et al. "Results of fly ash quality for disposal options from high thermal shares up to pure biomass combustion in a pilot-scale and large scale pulverized fuel power plants." *Renewable Energy* 75 (2015): 899-910.
- [37] Zhang, Guanjun, et al. "Ash melting behavior and slag infiltration into alumina refractory simulating co-gasification of coal and biomass." *Fuel* 139 (2015): 457-465.
- [38] Lanzerstorfer, Christof. "Chemical composition and physical properties of filter fly ashes from eight grate-fired biomass combustion plants." *Journal of Environmental Sciences* 30 (2015): 191-197.
- [39] Lanzerstorfer, Christof. "Cyclone fly ash from a grate-fired biomass combustion plant: Dependence of the concentration of various components on the particle size." *Fuel Processing Technology* 131 (2015): 382-388.
- [40] Fournel, S., et al. "Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops." *Applied Energy* 141 (2015): 247-259.
- [41] Zhou, Chuncai, et al. "Investigation on thermal and trace element characteristics during co-combustion biomass with coal gangue." *Bioresource technology* 175 (2015): 454-462.
- [42] Liu, Na, et al. "Sampling procedure in a willow plantation for chemical elements important for biomass combustion quality." *Fuel* 142 (2015): 283-288.
- [43] Eberhardt, T. L., and Pan, H. "Analysis of the fly ash from the processing of wood chips in a pilot-scale downdraft gasifier: Comparison of inorganic constituents determined by PIXE and ICP-AES." *Biomass and Bioenergy* 51 (2013): 163-168.
- [44] Abraham, R., et al. "Physicochemical characterization and possible applications of the waste biomass ash from oleoresin industries of India." *Fuel* 109 (2013): 366-372.
- [45] Li, L., et al. "Heavy metal characterization of circulating fluidized bed derived biomass ash." *Journal of Hazardous Materials* 233 (2012): 41-47.
- [46] Wiinikka, H., Grönberg, C. and Boman, C. "Emissions of heavy metals during fixed-bed combustion of six biomass fuels." *Energy & Fuels* 27.2 (2013): 1073-1080.
- [47] Tan, Z., and Lagerkvist, A. "Phosphorus recovery from the biomass ash: A review." *Renewable and Sustainable Energy Reviews* 15.8 (2011): 3588-3602.
- [48] Koukouzas, N., Ketikidis, C. and Itskos, G. "Heavy metal characterization of CFB-derived coal fly ash." *Fuel Processing Technology* 92.3 (2011): 441-446.
- [49] Piotrowska, P., et al. "Fluidized-bed combustion of mixtures of rapeseed cake and bark: The resulting bed agglomeration characteristics." *Energy & Fuels* 26.4 (2012): 2028-2037.
- [50] Míguez, J. L., et al. "Review of technology in small-scale biomass combustion systems in the European market." *Renewable and Sustainable Energy Reviews* 16.6 (2012): 3867-3875.

- [51] Meijer, I. S. M., et al. "The influence of perceived uncertainty on entrepreneurial action in the transition to a low-emission energy infrastructure: The case of biomass combustion in the Netherlands." *Technological Forecasting and Social Change* 77.8 (2010): 1222–1236.
- [52] Zhang, L., Schmetterer, C. and Masset, P. J. "Thermodynamic modeling of the CaO-SiO₂-M₂O (M= K, Na) Systems." *High Temperature Materials and Processes* 32.3 (2013): 223–228.
- [53] Colombari, P., et al. "Vegetable ash as raw material in the production of glasses and enamels, for example the contemporary vegetable ashes from Burgundy, France." arXiv preprint arXiv:1012.1504 (2010).
- [54] Vigier, K. D. O., and Jérôme, F. "Choline chloride-derived ILs for activation and conversion of biomass." *Production of Biofuels and Chemicals with Ionic Liquids*. Springer Netherlands, 2014. 61–87.
- [55] Pang, C. H., et al. "An automated ash fusion test for characterisation of the behaviour of ashes from biomass and coal at elevated temperatures." *Fuel* 103 (2013): 454–466.
- [56] Fryda, L., et al. "Study on ash deposition under oxyfuel combustion of coal/biomass blends." *Fuel* 89.8 (2010): 1889–1902.
- [57] Teixeira, Paula, et al. "Uncertainty estimation to evaluate mass balances on a combustion system." *Accreditation and Quality Assurance* 17.2 (2012): 159-166.
- [58] Vamvuka, D., and Kakaras, E. "Ash properties and environmental impact of various biomass and coal fuels and their blends." *Fuel Processing Technology* 92.3 (2011): 570–581.
- [59] Braga, R. M., et al. "Characterization and comparative study of pyrolysis kinetics of the rice husk and the elephant grass." *Journal of Thermal Analysis and Calorimetry* 115.2 (2014): 1915–1920.
- [60] Brunner, T., et al. "Advanced biomass fuel characterization based on tests with a specially designed lab-scale reactor." *Energy & Fuels* 27.10 (2013): 5691–5698.
- [61] Bodí, M. B., et al. "The wettability of ash from burned vegetation and its relationship to Mediterranean plant species type, burn severity and total organic carbon content." *Geoderma* 160.3 (2011): 599–607.
- [62] Sommersacher, P., Brunner, T. and Obernberger, I. "Fuel indexes: A novel method for the evaluation of relevant combustion properties of new biomass fuels." *Energy & Fuels* 26.1 (2011): 380–390.
- [63] Cherney, J. H., and Verma, V. K. "Grass Pellet Quality Index: A tool to evaluate suitability of grass pellets for small scale combustion systems." *Applied Energy* 103 (2013): 679–684.
- [64] Kumar, Anil, et al. "A review on biomass energy resources, potential, conversion and policy in India." *Renewable and Sustainable Energy Reviews* 45 (2015): 530-539.
- [65] Leino, T. J., et al. "Experiences from a novel sensor for fireside corrosion monitoring during grate combustion of corn stover/wood chip blends." *Energy & Fuels* 27.10 (2013): 5653–5662.

- [66] Lamberg, H., et al. "Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials." *Energy & Fuels* 27.11 (2013): 7044–7053.
- [67] Mendivil, M. A., et al. "Chemical characterization of pruned vine shoots from La Rioja (Spain) for obtaining solid bio-fuels." *Journal of Renewable and Sustainable Energy* 5.3 (2013): 033113.
- [68] Yu, C., et al. "Experimental determination of agglomeration tendency in fluidized bed combustion of biomass by measuring slip resistance." *Fuel* 128 (2014): 14–20.
- [69] Gogebakan, Z., et al. "Investigation of ash deposition in a pilot-scale fluidized bed combustor co-firing biomass with lignite." *Bioresource technology* 100.2 (2009): 1033–1036.
- [70] Weber, R., et al. "On predicting the ash behaviour using Computational Fluid Dynamics." *Fuel Processing Technology* 105 (2013): 113–128.
- [71] Tamura, M., et al. "Computationally predicted performance of pulverised coal fired boilers and study of ash deposition phenomenon." ASME 2011 Power Conference collocated with JSME ICOPE 2011. American Society of Mechanical Engineers, 2011.
- [72] Shao, Y., et al. "Ash deposition in co-firing three-fuel blends consisting of woody biomass, peat, and lignite in a pilot-scale fluidized-bed reactor." *Energy & Fuels* 25.7 (2011): 2841–2849.
- [73] Panayotis, D. E. and Liati, A. "Soot and ash layer characteristics in ceramic diesel particulate filters." *Advances in Science and Technology* 65 (2011): 225–231.
- [74] Wang, X., et al. "Deposition and corrosion problems of biomass fired boiler." *Measuring Technology and Mechatronics Automation (ICMTMA), 2011 Third International Conference on*. Vol. 1. IEEE, 2011.
- [75] Abreu, P., Casaca, C. and Costa, M. "Ash deposition during the co-firing of bituminous coal with pine sawdust and olive stones in a laboratory furnace." *Fuel* 89.12 (2010): 4040–4048.
- [76] Naganuma, H., et al. "Control of ash deposition in solid fuel fired boiler." *Fuel Processing Technology* 105 (2013): 77–81.
- [77] Bashir, M. S., et al. "Ash transformation and deposit build-up during biomass suspension and grate firing: Full-scale experimental studies." *Fuel Processing Technology* 97 (2012): 93–106.
- [78] Vélez, F., et al. "A technical, economical and market review of organic Rankine cycles for the conversion of low-grade heat for power generation." *Renewable and Sustainable Energy Reviews* 16.6 (2012): 4175–4189.
- [79] Metzger, M., and Polakow, G. "A survey on applications of agent technology in industrial process control." *Industrial Informatics, IEEE Transactions on* 7.4 (2011): 570–581.
- [80] Symonds, R. T., et al. "Pilot-scale study of CO₂ capture by CaO-based sorbents in the presence of steam and SO₂." *Industrial & Engineering Chemistry Research* 51.21 (2012): 7177–7184.

- [81] Hellsmark, H., and Jacobsson, S. "Realising the potential of gasified biomass in the European Union—Policy challenges in moving from demonstration plants to a larger scale diffusion." *Energy Policy* 41 (2012): 507–518.
- [82] Chen, L., Yong, S. Z. and Ghoniem, A. F. "Oxy-fuel combustion of pulverized coal: Characterization, fundamentals, stabilization and CFD modeling." *Progress in Energy and Combustion Science* 38.2 (2012): 156–214.
- [83] El-TaibHeakal, F., Fouda, A. S. and Radwan, M. S. "Inhibitive effect of some thiazazole derivatives on C-steel corrosion in neutral sodium chloride solution." *Materials Chemistry and Physics* 125.1 (2011): 26–36.
- [84] Razali, N. A. M., et al. "Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: A review." *Renewable and Sustainable Energy Reviews* 16.7 (2012): 4951–4964.
- [85] Dengler, J. E., Doroodian, A. and Rieger, B. "Protic metal-containing ionic liquids as catalysts: Cooperative effects between anion and cation." *Journal of Organometallic Chemistry* 696.24 (2011): 3831–3835.
- [86] Paul, S., and Harvey, M. D. F. "Corrosion testing of Ni alloy HVOF coatings in high temperature environments for biomass applications." *Journal of Thermal Spray Technology* 22.2–3 (2013): 316–327.
- [87] Kim, M-G, et al. "Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing." *Nature Materials* 10.5 (2011): 382–388.
- [88] Backman, R., et al. "The effect of peat ash addition to demolition wood on the formation of alkali, lead and zinc compounds at staged combustion conditions." *Fuel Processing Technology* 105 (2013): 20–27.
- [89] Peng, C., Guo, Z. and Zhang, F. "Equilibria in the quaternary system KCl– NaCl– CaCl₂– H₂O at 283.15 K." *Journal of Chemical & Engineering Data* 56.5 (2011): 1793–1797.
- [90] Bian, S. F., Wang, Y. Z. and Tian, S. L. "Ash characteristics analysis during co-combustion of biomass and coal." *Applied Mechanics and Materials* 130 (2012): 838–841.
- [91] Dai, S., et al. "Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization." *International Journal of Coal Geology* 94 (2012): 3–21.
- [92] Brossard, J. M., et al. "Superheater fireside corrosion mechanisms in MSWI plants: Lab-scale study and on-site results." *Materials and Corrosion* 62.6 (2011): 543–548.
- [93] Harvey, D., et al. "Mitigation of biomass-induced corrosion of superheatertubes using thermal spray coatings." *CORROSION* 2013 (2013).
- [94] Montgomery, M., et al. "In situ corrosion testing of various nickel alloys at Måbjerg waste incineration plant." *Materials and Corrosion* 64.1 (2013): 14–25.

- [95] Retschitzegger, S., et al. "Assessment of online corrosion measurements in combination with fuel analyses and aerosol and deposit measurements in a biomass combined heat and power plant." *Energy & Fuels* 27.10 (2013): 5670–5683.
- [96] GuidiNissim, W., et al. "Long-term biomass productivity of willow bioenergy plantations maintained in southern Quebec, Canada." *Biomass and Bioenergy* 56 (2013): 361–369.
- [97] Abanades, J. C., Alonso, M. and Rodríguez, N. "Biomass combustion with in situ CO₂ capture with CaO. I. Process description and economics." *Industrial & Engineering Chemistry Research* 50.11 (2011): 6972–6981.
- [98] Montgomery, M., et al. "Experiences with high temperature corrosion at straw-firing power plants in Denmark." *Materials and Corrosion* 62.7 (2011): 593–605.
- [99] Balan, G., Losurdo, M. and Spliethoff, H. "Experimental study of high-temperature chlorine-induced corrosion in dependence of gas velocity." *Energy & Fuels* 27.10 (2013): 5628–5639.
- [100] Amir, M. K., et al. "Corrosion prevention in boilers by using energy audit consideration." *Applied Mechanics and Materials* 532 (2014): 307–310.
- [101] Song, J. H., et al. "Study on air preheater corrosion problem of CFB biomass directed-fired boiler in Zhanjiang Biomass Power Plant." *Applied Mechanics and Materials* 291 (2013): 294–299.
- [102] Lit, Q. H., Zhang, Y. G. and Meng, A. H. "Design and application of novel horizontal circulating fluidized bed boiler." *Proceedings of the 20th International Conference on Fluidized Bed Combustion*. Springer Berlin Heidelberg, 2010.
- [103] Ilyushechkin, A. Y., et al. "IGCC solids disposal and utilisation." *Final Report for ANLEC Project 5-0710-0065*. (2012).
- [104] Knapp, B. A., and Insam, H. "Recycling of biomass ashes: Current technologies and future research needs." *Recycling of Biomass Ashes*. Springer Berlin Heidelberg, 2011. 1–16.

Figure captions



Fig. 1. Ash formation over a furnace grate fuelled with wood pellets.



Fig. 2. Vitrified bottom ashes in a burner fuelled with sawdust.



Fig. 3. Vitrified ash collected in a thermal oil boiler fuelled with woodchips.



Fig. 4. Equipment corrosion.

Tables

Table 1. Composition of ashes obtained from the combustion of the most common biomass forms [26-28].

Fuel	Cl	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃
Wood pellets	NA	4.30	1.30	1.50	5.90	8.50	55.90	0.60	16.80	0.10	3.90	1.30
Olive husk	0.20	32.70	8.40	6.30	NA	4.20	14.50	26.20	4.30	0.30	2.50	0.60
Wheat straw	3.60	48.00	3.50	0.50	NA	1.80	3.70	14.50	20.00	NA	3.50	1.90
Olive kernel	NA	67.70	20.30	0.05	NA	0.05	0.50	11.2	0.15	0.05	NA	NA
Pine woodchips	0.60	45.80	4.60	2.90	NA	3.60	25.70	0.60	8.20	0.30	3.40	4.20