Evaluation of the utilization of woodchips as fuel for industrial boilers

Leonel J. R. Nunes[a,b], Radu Godina[c,*], João C. O. Matias[a,b], João P. S. Catalão[d]

a DEGEIT, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
b GOVCOPP, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
c UNIDEMI, Department of Mechanical and Industrial Engineering, Faculty of Science and Technology (FCT),Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal
d INESC TEC and Faculty of Engineering of the University of Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

Abstract

This study aims to evaluate the implications of the use of maritime pine non-debarked wood chips as an alternative solid fuel in industrial boilers in Portugal, highlighting the energy properties and chemical composition of the produced ash. Several samples are collected from different sources, on which a proximate analysis is carried out to determine the volatile matter content, fixed carbon content, ash content and higher heating value (HHV). The chemical composition of the ash samples is determined by the scanning electron microscope (SEM) method. Then, empirical indices were used to assess the utilization of the ash and its tendency to create slagging and fouling deposits in industrial boilers during the combustion process. From the obtained results it was concluded that the use of maritime pine non-debarked wood chips can contribute significantly to the formation of slagging and fouling phenomena in industrial boilers. These phenomena will be responsible for increasing the number of technical stoppages of the equipment and for the increase in maintenance costs.

1. Introduction

Among the advantages of the use of renewable energy is the reduced pollution, it is decentralized and thus closer to energy consumers, and is available in all countries, albeit with different capacity and potential. The use of renewable energy also leads to a reduction in energy costs (Mendonça et al., 2018), as the availability of most renewable resources is almost unlimited (solar, wind, geothermal, hydro, marine) or economical (biomass) (Husmann et al., 2018).

The utilization of biomass is drawing attentions worldwide as a renewable energy source mainly due to the scarcity of fuels of fossil origin and to the up surging related environmental problems (Maraver et al., 2013). The search for alternative sources for the production of thermal energy with less environmental impact led biomass to occupy a very important role compared with other forms of renewable energy (Riaza et al., 2012). Biomass thereby has great importance in the production of thermal energy. This biomass for energy purposes
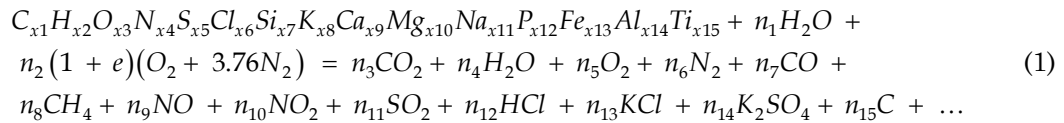
* Corresponding author
E-mail address: rd@ubi.pt (Radu Godina).

mainly comes direct from the forest in all its forms, namely that one processed into wood chips after forestry operations (Adanez et al., 2012).

These wood chips are used directly as fuel in thermal energy production through combustion. In this thermal conversion process, organic elements present in the fuel suffer total or partial oxidation, transforming the chemical energy into thermal energy (Ahmadi et al., 2014).

Combustion is composed by a group of complex phenomena that involves occurrences of mass and heat transfer that promotes simultaneous chemical reactions and fluid flow. These predictions are crucial for process design and control, and require deep knowledge about fuel characteristics and how these will influence the evolution of combustion. The general reaction that occurs during biomass combustion in the presence of air may take the form presented in the following equation (1), where the first reactant represents a generic biomass fuel (Jenkins et al., 1998) as:

$$
\begin{aligned}
& C_{x1}H_{x2}O_{x3}N_{x4}S_{x5}Cl_{x6}Si_{x7}K_{x8}Ca_{x9}Mg_{x10}Na_{x11}P_{x12}Fe_{x13}Al_{x14}Ti_{x15} + n_1H_2O + \\
& n_2(1+e)(O_2 + 3.76N_2) = n_3CO_2 + n_4H_2O + n_5O_2 + n_6N_2 + n_7CO + \\
& n_8CH_4 + n_9NO + n_{10}NO_2 + n_{11}SO_2 + n_{12}HCl + n_{13}KCl + n_{14}K_2SO_4 + n_{15}C + \ldots
\end{aligned}
\tag{1}
$$

Biomass is usually a very complex and heterogeneous material that produces complex and heterogeneous by-products during the combustion process. During combustion, biomass particles with different organic and inorganic compositions will behave differently, and for that prediction based on the average composition of the fuels will be misleading (Mosier et al., 2005).

Combustion systems have very important environmental issues that must be considered, with emphasis on the production of ash that is a solid residue of the process and does not participate in the reactions. Several studies make reference that, in the biomass of forest origin, the ash content represents the percentage of mineral compounds that can be found in the fuel. This ash content is directly influenced by such factors as: the environmental conditions during growth, the species, the part of the tree used (bark, leaves, logs), and age of the tree. The main chemical elements that can be found in biomass ash are K, Ca, P, Si, Al, Fe, Ti, Na and Mg (Vassilev et al., 2010).

These elements can form large slagging areas on the thermal exchange surfaces of the industrial boilers and can lead to malfunctioning and a reduction in heat transfer efficiency. In addition, depositions can generate fouling areas and corrosion that accelerate the wear of the heat transfer surfaces and even the boiler structure (Vassilev et al., 2012).

The creation of large deposits in furnaces and boilers will conduct to a number of operational contrarieties such as slagging and fouling in the convective zones of the boiler. The deposition of melted or partially melted ashes on the furnace wall and burner quarls, reduces heat absorption and leads to increased exhaustion gases temperature. This, in turn, results in overheating and fouling of the secondary super-heater, causing the formation of sintered deposits on the pendant super-heater tubes. As a consequence, the process of deposition of ashes provoke a decrease in boiler efficiency, decreased availability (unexpected shut-downs), and higher maintenance costs provoked by pipe blockage, erosion and corrosion in inner walls, contributing to substantial financial losses (Park and Lee, 2013; Vassilev et al., 2014, 2013a, 2013b, 2013c).

Slagging formation potential depends on the fusion capacity of the chemical elements present in the ash. Alternatively, fouling starts with the sintering process, resulting in much harder deposits that are more difficult to remove over time (Ahmadi et al., 2013).

Slagging and fouling phenomena, jointly with feeding system blockage, humidity of fuel, temperature levels, among others, are some of the causes for unexpected equipment shutdown due to efficiency decreasing. Furthermore, ash deposition also potentiates corrosion problems and consequent lifetime reduction of the equipment. The anticipation of problems related with the deposition of ashes is one of the major technical concerns during boiler project and design. The difficulties observed in the past involving the prediction of ash behaviour and the changes fuel use patterns, highlighted the need to have a better knowledge about the mechanisms involved in ash deposition (Egolfopoulos et al., 2014).

Concerning an energetic perspective, the selection of a biomass form to produce energy is almost always made considering only the energy content of the fuel. In contrast, the effect of the biomass forest ash in the combustion process in boilers is still understudied and the probability of generating slagging and fouling can derail its use, mainly due to the significant increase in maintenance costs of the equipment (Al-Sulaiman et al., 2012; Chen et al., 2012; Xu et al., 2004).

The formation of ash deposits can be roughly estimated from the chemical composition of the fuel and how inorganic material present in the fuel is associated (Figure 1). Biomass fuels are intrinsically more reactive than coal due to its usually higher oxygen and organic volatile content. The combination of higher content of oxygen and volatile matter in biomass indicates a potential for creating larger amounts of inorganic vapours during combustion. Volatilization occurs at lower temperatures and large amounts of inorganic vapours are released during combustion. The division of inorganic compounds influences ash properties and behaviour in a boiler (Baxter, 1993).

See Figure 1 at the end of the manuscript.

Many biomass fuels contain high concentrations of elements that are bound within the fuel in an easily vaporizable form. Alkali and alkaline earth metals, together with Si, Cl and S present in biomass, can cause unwanted reactions forming low melting point species that lead to problems like ash slagging and fouling (Figure 2). These elements within biomass vaporize during combustion to produce gaseous inorganic compounds. A part of these species are retained in the char during devolatilization and are vaporized in the char combustion phase. These gaseous components can then condensed homogeneously to form a sub-micron fume of fine ash particles, produced due to nucleation of refractory oxides, commonly Mg, Ca, Fe, Si and Al (Miles et al., 1996). The particles then grow due to coagulation and heterogeneous condensation of alkali vapours, particularly Na, and K, on the surface of the particles. The vapours may also condense on fragmented fly ash particles or directly onto the surface of the process equipment (Zhu and Zhuang, 2012).

See Figure 2 at the end of the manuscript.

The resulting ash has a bimodal size distribution containing a sub-micron and a residual size fraction (Baxter, 2005; Sarofim et al., 1977; Williams et al., 2012). The sub-micron fraction is largely a result of the homogeneous nucleation of volatilized inorganic species. For fly ash produced during biomass combustion the sub-micron fraction is expected to be larger

than for fly ash produced during coal combustion due to the larger content of volatile inorganic species in biomass (Christensen et al., 1998).

In biomass fuels, even though a large fraction of the inorganic material may occur as ions attached to the organic matrix, distinct minerals may also be present, and the most frequently occurring of those are silicates of Na, K, Ca and Mg. Silicates are not expected to volatilize during combustion (Bhutto et al., 2013; Valmari et al., 1998).

This motive itself justifies a novel analysis that allows the definition of how far a material with high energy potential can be used as fuel, but also considering the analysis of the ash. In this way, the main objective of this research is to evaluate possible implications for industrial boilers in Portugal of maritime pine (*Pinus pinaster*) wood chips, one of the forest biomass forms with the highest potential to be used as fuel, considering its energy properties and the chemical composition of the ash.

2. Materials and Methods

2.1. Sampling and samples preparation

In this study, five different non-debarked maritime pine wood-chip samples used as fuel in industrial boilers were analysed (Figure 3). Sampling and the preparation of the samples was conducted in order to be representative of the combustion process in the different boilers, with several samples collected directly from the bottom grate covering the entire combustion surface. The samples collected in each furnace were mixed and homogenized before chemical analysis in order to represent the average value.

See Figure 3 at the end of the manuscript.

All ash samples were collected in two furnaces (one with 3 MWth and the other with 1.5 MWth) fed by the same fuel system that previously transformed the pine wood chips into sawdust. This sawdust is injected into the furnace and burnt in suspension (Figure 4). The temperature in the furnace is in average higher than 850ºC. Only the bottom ashes were collected and analyzed.

See Figure 4 at the end of the manuscript.

2.2. Characterization of the collected samples

As in what concerns to the need for standardized methods of analysis that conduct to accurate and consistent evaluations of fuel properties, biomass is similar to other fuel forms. The proximate analysis to determine moisture (%ar), ash (%db), fixed carbon (%db) and volatile matter (%db) was undertaken following standards EN14774-2, EN14775 and EN15148. High Heating Value (HHV) was achieved with a Parr 6400 calorimeter.

2.3. Chemical composition of the ash

Proximate analyses (ash, volatiles, moisture, and fixed carbon) and ultimate analyses (carbon, hydrogen, carbonates, sulphur and oxygen) are routine analyses for biomass. Typically, the main elements analysed are Si, Al, Fe, Ca, Mg, Na, K, P, Mn and S. These analyses are reported as oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, P_2O_5, MnO and SO_3). These oxide analyses are extensively used to determine the slagging propensity of the coal, mineral composition and to predict the viscosity of the fly ash particles and of the slagging deposits. Typical slagging prediction ratios are the acid/base ratio, slagging index, slagging factor and fouling index (Menon and Rao, 2012).

The characterization of mineral materials present in fuels, ashes and other type of related depositions can be achieved with mineralogical analysis and microscopic techniques. One of these is X-ray diffraction, which is used to identify the main crystalline phases in these materials. Scanning electron microscopy (SEM) is an analytical method that allows the identification of the microstructure and chemistry of ashes and other mineral deposits.

Several slagging and fouling indexes are available for the assessment of the propensity of fuel ashes to form deposits (Tortosa Masiá et al., 2007). These indexes are based on the ash content and the chemical composition of the ashes, or on the results of laboratorial tests using small samples of the fuel. These indexes have been developed for the characterization of coals,

and, with proper modifications, are applied to other solid fuels, such as waste forms and biomass fuels, and to the ash produced by the co-firing of biomass with coal (Dai et al., 2012).

The ash samples collected were analysed using a Phenom ProX desktop scanning electron microscope, where the sample structures were physically examined and their elemental compositions determined.

2.4. Slagging and fouling indexes of ash in industrial boilers

The same methods used for the estimation of the characteristics of ashes deposits are based on coal ash chemistry. These convectional analytical methods are not capable to give conclusive information about the mineral compounds that coals may contain (Wigley et al., 1990).

In this study, several empirical indexes were used to evaluate the behaviour of the ash and its tendency to generate slagging and fouling deposits on the inner walls of the boilers, furnaces and tubing during combustion. These indexes were originally developed for fossil fuels, but have also been used for biomass fuel analysis in several recent studies (Degereji et al., 2012; Fang et al., 2010; Yang et al., 2014).

Several slagging indexes are related with the ash fusibility behaviour, and the traditional indexes are based on the chemical composition of the ashes, mainly being used the ratio of the acidic metal oxides, (SiO_2 and Al_2O_3) to the basic oxides (Fe_2O_3, CaO, MgO, Na_2O and K_2O). These indexes give an overview of the fusion temperature of the ashes, which is then used to classify the ash in terms of its propensity to form melted slag deposits. Knowing the limitations of the mentioned approaches, these are still widely applied for fuel specification and boiler design and operation. For the majority of biomass fuels, K is the most abundant alkali metal and, as for the case of Na, exists in a form that enhances volatilization. For this reason fouling indexes used to characterize biomass fuels tend to be related with the total alkali content present in the fuel (Thomas et al., 2011).

The indexes used are described by the following equations:

1) **_Slagging Index (B/A):_** is the base-acid relation used to measure the slagging occurrence tendency caused by the fuel ash and numerically it is found by the Equation 2 (Erickson et al., 1995):

$$\frac{B}{A} = \left(\frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3} \right) \tag{2}$$

Equation 2 was developed for fossil fuels with low phosphorus (P) content. In a later study, and following the methodology previously presented, the P content was also considered in the relation presented in Equation 3 (Benson and Harb, 1993):

$$\frac{B}{A} + P = \left(\frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{SiO_2 + TiO_2 + Al_2O_3} \right) \tag{3}$$

where a relation B/A<0.5 indicates a low propensity for slagging; 0.5<B/A<1.0 indicates medium propensity for slagging; B/A=1.0 (expressed by the values in between 1.0<B/A<1.75) indicates high propensity for slagging and B/A>1.75 indicates severe propensity for slagging.

2) **_Fouling Index (FI):_** represents the propensity for fouling formation in industrial boilers and is represented in Equation 4:

$$FI = \left(\frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3} \right) \times \left(Na_2O + K_2O \right) \tag{4}$$

where FI<0.6 indicates a low propensity for fouling; 0.6<FI<40 indicates a high propensity for fouling and FI>40 indicates a severe propensity for fouling.

3) **_Alkali Index (AI):_** represents the quantity of alkali oxides in the fuel per unit of energy (kg/GJ), and is represented in Equation 5 (McLaughlin et al., 1996; Müller et al., 2013):

$$AI = \left(\frac{1 \times 10^6 \times Ash\% \times \left(K_2O + Na_2O \right)\%}{HHV \left(\frac{kJ}{kg} \right)} \right) \tag{5}$$

where AI<0.17 indicates low propensity for slagging and fouling; 0.17<AI<0.34 indicates a high propensity for slagging and fouling and AI>0.34 indicates severe propensity for slagging and fouling.

3. Results and Discussion

3.1. Energy characterization of the biomass

The process of ash formation is mainly dependent on the residence time and temperature to which the biomass particle has been submitted. Acquired physical properties of the ash particle usually indicate if it will bind to the surfaces where it is expected occurs the transfer of heat. At the same time, localized chemical reactions may also contribute to the transformation process of the ashes and thereby to the final physical properties of ash particles (Gani et al., 2005).

In Table 1 the results of the energy characterization of the biomass samples are presented.

See Table 1 at the end of the manuscript.

As can be seen in Table 1, the percentage of volatile matter is above 70%, and is as expected for these biomass forms and desirable in the direct combustion process (Pronobis, 2005).

The obtained values for fixed carbon varied between 19% and 21.6%, also assumed to be normal for this type of biomass (Benson et al., 1993).

Concerning the ash content, it is possible to verify that the obtained values varied between 1.73% and 1.92%, which can be considered high when compared with other forms of biomass also used as fuel in industrial boilers . Bark tends to contribute to higher ash content compared to debarked wood, as has been shown in previous studies, because higher nutrient and contamination content accumulates (Mohod et al., 2011).

HHV varied between 10.82 MJ/kg and 12.60 MJ/kg. This variation in the obtained values is accepted because there are differences between the moisture content of the samples that varied respectively between 28.50% and 49.10%, provoking the difference in HHV. These values are in accordance with the results presented in several previous studies (Huo et al., 2014).

3.2. Chemical composition of the ash

Chemical composition of the ash of the studied samples is characterized by the variation in some of the inorganic compounds that are presented in Table 2 as mineral oxides.

See Table 2 at the end of the manuscript.

As can be verified, the differences are mainly in SiO_2, Al_2O_3 and Fe_2O_3, which can be justified by the different origins and sources of the biomass, namely mainland regions or littoral areas where contamination with sandy materials is more frequent. In fact, pine logs are supplied to this industrial plant where the furnaces are installed from two distinct locations, being one location from the sandy lands near the sea, while the remaining one is from the nearby mountains, located about 20 km far from the sea, where schist soils are predominant. When arriving to the plant, logs are separated according to its provenience in order to create production batches before being transformed into wood chips. In the lab analysis it is possible to confirm that by the percentages of silica and alumina present in the ashes, as well as for the higher amount of ashes produced, may indicate indirectly a higher presence of sandy materials.

3.3. Ash tendency for slagging and fouling in industrial boilers

There still are many areas of uncertainty where daily operation experience helps to take decisions concerning the transposition from laboratorial results to final decisions concerning boiler design (Bhuiyan and Naser, 2015).

A very good option to predicting the deposit effects more accurately is with small-scale combustion tests where the conditions present in industrial scale boilers are simulated. Combustion tests allow the evaluation of the ash formation and deposition process, as well as a more detailed characterization of the deposits (Bryers, 1996).

Test results can be used to define the parameters for boiler design if the sample used in the tests is representative of the totality of the ashes produced. Variability in the deposit and

its impact on the fuel properties are very important factors that must be evaluated (Hotta et al., 2012).

It is possible to verify that was no difference in the occurrence tendency of slagging in industrial boilers compared to the indexes with and without phosphorus oxide (Table 3).

See Table 3 at the end of the manuscript.

As can be observed in Table 3, with the exception of Sample 1, all the remaining samples present a high tendency for slagging and fouling. This difference may be justified by the origin of the used fuel. Ashes coming from biomass originated far away from littoral have lower SiO_2, and the presence of Al_2O_3 may vary according to soil composition. In the majority of the cases, the presence of these oxides can be justified by contamination occurred during forestry operations such as trees cutting and recess, where usually the logs are dragged over the soil (Keefe et al., 2014). Such contamination at the first sight may be perceived as insignificant. It can, however, greatly contribute to a larger amount of ash produced during the combustion process. This means that it will lead to the production of ashes that will suffer, most noticeably, vitrification phenomena (Lapuerta et al., 2015). This phenomena is caused by the fact that the melting temperature of the ash decreases, in direct relation to the increase in the content of several alkali metals, namely Na and K (Lapuerta et al., 2015).

4. Conclusions

In this paper the objective was to evaluate the implications of the use of maritime pine non-debarked wood chips as an alternative solid fuel in industrial boilers in Portugal, highlighting the energy properties and chemical composition of the produced ash. The slagging and fouling phenomena comprise a large number of variables that affect ash deposition in several forms. Several samples were collected from different sources, on which a proximate analysis was carried out to determine the volatile matter content, fixed carbon content, ash content and higher heating value (HHV). The chemical composition of the ash

samples was determined by the SEM – scanning electron microscope – method. The results showed that the overall tendency points to a high probability of slagging and fouling when non-debarked maritime pine wood chips are used as fuel. The results obtained in this work show the occurrence of slagging and fouling phenomena provoked by several chemical elements, such as alkali metals, in consonance with several authors which demonstrated that debarking the logs before shredding will significantly reduce the ash content in the woodchips, reducing that way the quantity of chemical elements that contribute to the occurrence of slagging and fouling phenomena in industrial boilers and tubing which in turn will contribute to increasing maintenance technical stoppages, as well as increasing maintenance costs associated with equipment operation.

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Captions

Figure 1 – Melted ashes deposit in a biomass boiler furnace that uses pulverized sawdust as fuel.

Figure 2 - Slagging and fouling phenomena in the surface of a temperature probe of a biomass boiler.

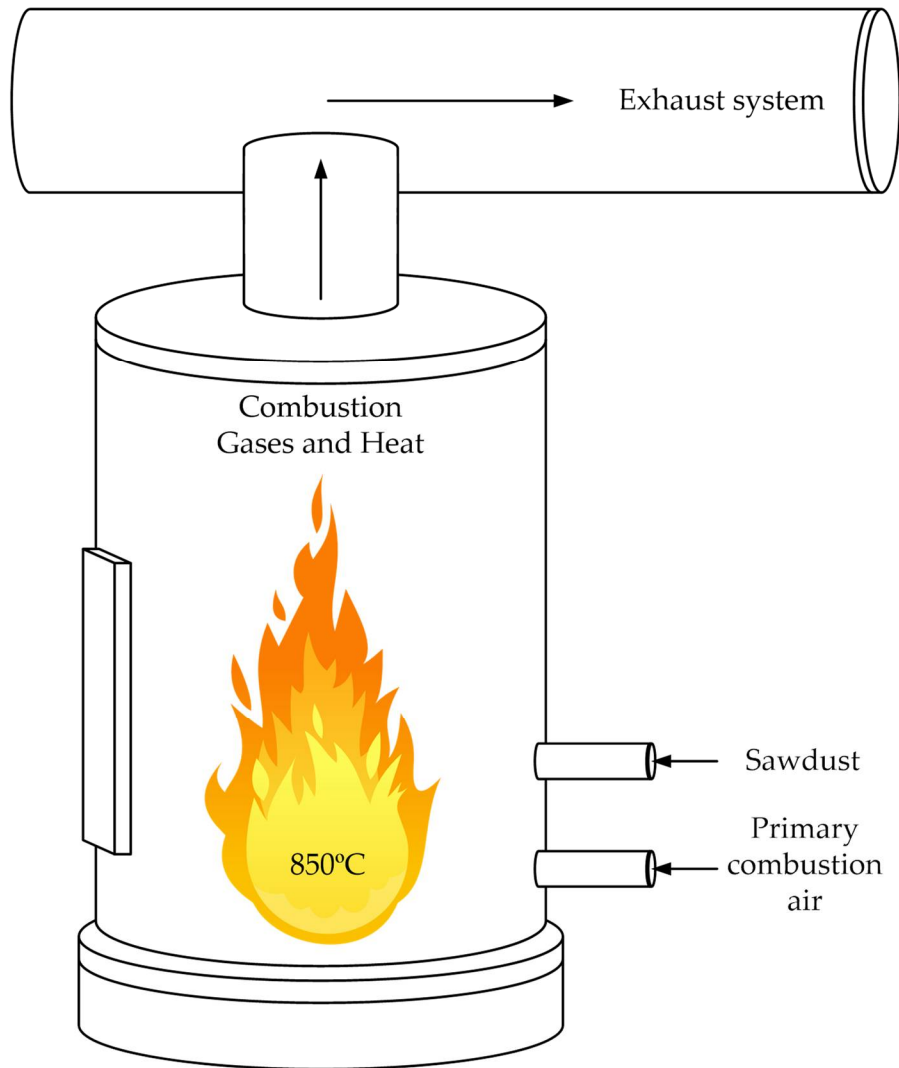Figure 3 – Common visual aspect of the *Pinus pinaster* woodchips used in this study.

Figure 4 – Structure of the furnaces where the ash samples were collected.

Tables

Table 1. Proximate analysis and HHV for maritime pine non-debarked wood-chip samples (all determinations are as received – on a wet basis).

Samples	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Moisture (%)	43.30	47.80	28.50	39.70	49.10
Volatile matter (%)	76.90	77.80	79.30	80.60	77.70
Fixed carbon (%)	21.60	20.90	20.10	19.00	20.60
Ash (%)	1.53	1.25	1.82	1.76	1.70
HHV (MJ/kg) (wood as received)	11.90	11.10	14.80	12.60	10.82

Table 2. Chemical composition of the ash.

Oxides (%)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
SiO_2	42.57	45.63	19.65	10.91	24.60
Al_2O_3	15.30	10.96	11.16	18.33	12.66
CaO	3.92	9.23	3.64	1.82	7.56
P_2O_5	0.96	0.91	1.23	1.03	1.15
Fe_2O_3	8.72	13.23	41.43	30.45	7.29
K_2O	4.58	8.79	9.23	10.30	6.56
MgO	6.96	6.30	8.23	8.62	12.44
TiO_2	1.21	0.98	1.34	1.50	1.12
Na_2O	3.17	3.56	3.56	4.71	4.21
MnO	0.00	0.00	0.00	0.00	1.15

Table 3. Quantitative and qualitative analysis of ash slagging and fouling.

Samples	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Quantitative analysis					
Slagging index	0.46	0.71	2.06	1.82	0.99
Slagging index + P	0.48	0.73	2.09	1.85	1.02
Fouling index	3.59	8.82	26.29	27.30	10.68
Alkali index	0.11	0.20	0.19	0.21	0.19
Qualitative analysis					
Slagging index	Low	Medium	Severe	Severe	Medium
Slagging index + P	Low	Medium	Severe	Severe	High
Fouling index	High	High	High	High	High
Alkali index	NP	P	P	P	P

Where: NP – Not Probable; P – Probable; VP – Very Probable