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COMBUSTION OF AGRICULTURAL BIOMASS – ISSUES AND SOLUTIONS

Summary

Biomass is one of the oldest energy source known to mankind. Progress made so far in understanding of a rather complex direct combustion process allowed for a constant technology development. Increasingly stringent environmental requirements of the EU, especially in terms of the pollutant emissions, require development of new design solutions of the combustion system for residential hot water boilers fuelled by some form of solid biomass. The emissions are becoming even greater problem if, various residues from agricultural production are used instead of a wooden biomass, as they are becoming more desirable fuel due to their lower cost.

In this paper, various issues related to the combustion of agricultural biomass are discussed. Attention is given to the problems associated with high volatile matter contents, presence of nitrogen, sulphur, chlorine and low ash melting temperatures. At the end, novel design modifications of a conventional residential biomass combustion system are proposed, as the well-known methodologies for combustion and emissions control applied in industrial-scale boilers are in most cases not suitable for small-scale units.

Key words: Agricultural biomass combustion, pollutant emissions, ash related problems, dioxin emission

1. Introduction

The burning of biomass has been common way to generate heat for the millennia and nowadays, due to the growing awareness of greenhouse gas emission and the decline of fossil fuel reserves, it is expected to be very important element in achieving EU's 20-20-20 goals. When implemented appropriately, generating heat and electricity from biomass, has the great potential to offer cost-effective renewable alternative to fossil fuels [1]. Furthermore, compared the other alternatives, biomass is widely available energy source (unlike e.g. geothermal) and it is not of variable and intermittent nature (unlike e.g. solar, wind). Also it has very high energy flux density (e.g. 30 kW/m^2 of heat exchange surface in biomass boiler) compared to other renewables (e.g. 1 kW/m^2 solar irradiation, energy in the wind at 10 m/s). As the EU environmental requirements are becoming increasingly stringent [2] the increase of energy share of biomass burning is strongly depended on scientific and technological developments in the field of combustion technology. The strictest requirements are set in

Directive 2009/125/EC. The Directive prescribes that after 2020 all solid fuel burning appliances have to achieve parameters set for Class 5 in [2].

This requirements are becoming even bigger issue if instead of wooden biomass various residues from agricultural production are used, which are becoming more desirable fuel due to drop in oil and gas prices.

Also, biomass feedstock increases pressure on both agricultural land and forest. Within the last years, competition between food crops and energy crops has been increasing. Using agricultural residues, which are by-product of food production, as an energy source does not increase this competition, and does not require extra land for its production. Furthermore, using agricultural residues as a fuel reduces the possible problems with its disposal. Conventional ways of disposing these residues have generally relied on using them as fodder, as fertilizers after being ploughed into the ground, or burning them completely in uncontrolled conditions on land. Later has a great environmental impact, resulting in enormous amounts of gaseous (CO, NOx, C_xH_y, HC, tar, PAH, dioxins, furans) and dust emissions.

A lot of research has been done on the subject of combustion of this non-conventional biomass. Economical potential of agricultural residues for energy use in Croatia has been determined in [3]. The authors found that the technical potential in Croatia of corn stover is 0.4 million tons and potential of wheat straw is 0.75 million tons. There is also potential in soy strain, olive husk etc. In [4] the authors were comparing emissions obtained from burning of four types of high ash pellet fuels. Authors in [5] analysed gaseous emission from several types of raw and torrefied biomass. Performance of a residential boiler fed with blended olive mill solid waste and pine sawdust is investigated in [6]. Comparison of pollutant emissions from biomass combustion to hard coal have been shown in [7]. Emission from blended biomass pellets are analysed in [8]. Combustion characteristics of miscanthus and other energy crops have also been thoroughly examined. Combustion characteristics of miscanthus are also presented in [9] and for *Miscanthus x giganteus* in [10], where special attention is given to optimization of the harvest time. Ash composition, as the most important parameter while designing the combustion system, is analysed in [11] and [12], whereas in [13] ash melting behaviour is investigated in detail.

In general, biomass is characterized by high content of a volatile matter [14], which is especially true for the most of non-conventional biomass. This means that combustion is expected to be rapid and therefore difficult to control, resulting in high amount of pollutant emissions. For that reason, design and operation principles normally applicable for conventional biomass combustion systems may not be applied here. Combustion chamber should to be constructed in a manner that ensures complete combustion of the volatiles in order to ensure higher combustion efficiency and low emissions of CO, hydrocarbons and PAH (polycyclic aromatic hydrocarbon). The most important issues, related to the pollutant emissions, are the contents of sulphur, nitrogen and chlorine, which are typically much higher compared to wooden biomass. This can lead to formation of gaseous pollutants such as SO_2, NO_x and N_2O and, to some extent, HCl, dioxins and furans.

The ash content varies from one kind of biomass to another. For example, ash content of typical wooden biomass is below 0.5 wt% (weight percent) whereas crops residues can have up to 25 wt% [14]. Generally, due to the ash content of non-conventional biomass, which is typically 2-6 times higher compared to conventional biomass, care must be given in incorporation of an efficient ash removal system in order to reduce the particulate pollution. A particular ash related problem is its low melting point during the combustion which can result in agglomeration, fouling, scaling and consequently corrosion of the heat exchanger surfaces [15].

For combustion of non-conventional biomass numerous designs exist with typical thermal power up to several MW. Despite the relatively high annual production of this kind of

biomass (unused by-products from various bio-based sources amounts to a total of 2.8 billion tons/year in the EU), current level of their utilization as a main fuel for direct combustion systems is very low. The reason is that this type of biomass is mostly produced and used locally and often has low bulk density. For example, the bulk density of chopped straw is 50-120 kg/m^3 [16]. Those values are very low compared with the bulk density of wood, which is in a range of 170-600 kg/m^3 [17] and due to the resulting high transportation costs and yield dependence on the climatic conditions it is often uneconomical to use it as a main fuel in bigger power stations, at least without conditioning. This agrees with the IRENA report [18] where it is pointed out that in 2030 biomass might amount for 20% of the world's total energy needs. The key to this scenario lies in the use of locally sustainable sources, whereby 40% of the biomass feedstock comes from waste and agricultural residues.

Therefore, the potential of using non-conventional biomass is in small-scale boilers, e.g. residential solid-fuel burning appliances. Obstacle for using this kind of biomass in residential units is that existing solutions for pollutant emission reduction and handling the combustion of high ash biomass are in most cases, due to their high investment, operation and maintenance cost, not applicable for small-scale units. In order to overcome these problems there are two possibilities. First involves intelligent fuel blending in order to overcome ash and emissions related problems. Authors in [14] propose blending it with coal while new investigations [11] found that blending it with peat also yields positive results. Second possibility involves the new cost-effective design solutions for high ash biomass combustion systems.

2. Combustion process

In this section the general mechanism of solid biomass combustion (moisture evaporation, devolatilisation, combustion of the volatiles and char combustion) is described. Small solid particle of biomass entering hot oxidizing atmosphere ignites and burns in a way shown in Fig. 1. The process can be divided into three main stages: heating up to a temperature where evaporation of moisture and oils occur (1); decomposition of the carbonaceous structure in which volatile gases and char are produced (2). Formed volatiles burn as a diffusion flame around the particle and as their production declines, oxygen penetrates to the surface and char combustion begins (3).
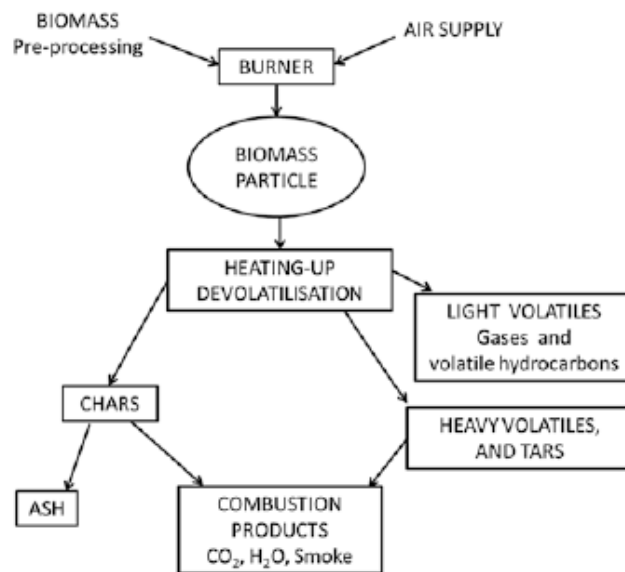

Fig. 1 Main steps in combustion of small biomass particle [19]

Moisture content is an important factor in the combustion process. Typically, newly cut woods contain up to about 50-70 wt% moisture, present as bound (about 30 wt%) and free water in the pores and capillaries. Ambient drying for considerable amount of time can lower the moisture content to about 10–20 wt%. Additional reduction in moisture content can be achieved in the dry-kilns. Upon heating moisture and oils contained in biomass undergo evaporation. This heating process is, beside moisture content, determined by surrounding temperature, size and density of the particle.

Particle devolatilisation is a process in early stages of combustion which starts when the particle reaches a sufficient high temperature for chemical decomposition to occur. The most part of the solid particle is released in the form of volatiles (inorganic species such as CO, CO_2, H_2O and gases such as methane and other hydrocarbons). During this process tar and char is formed. From a pollution point of view the problem is whether the volatile gases and tars burn completely out in the combustion chamber or are emitted in the ambient. For biomass, devolatilisation starts at temperatures of about 160-250 °C (Fig. 2).
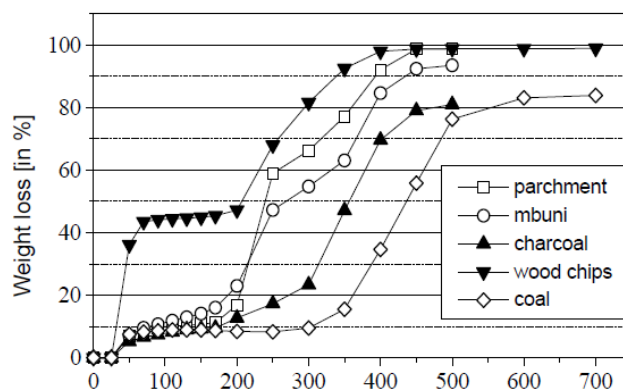

Fig. 2 Temperature resolved weight loss analysis [14]

Solid biomass consists of three major components: cellulose (crystalline polymer of glucose), hemicellulose (mixture of amorphous polymer of 5- and 6-carbon sugars) and lignin. Lignin is a random three-dimensional phenolic polymer of which there are three classes based on different phenyl-propane monomeric units (guiacyl $C_9H_{10}O_2$, p-hydroxy-phenol $C_{10}H_{12}O_3$ and syringyl $C_{11}H_{14}O_4$) [19]. Due to the increasing number of methoxy groups, the C/H and C/O ratios are significantly different (C/H ratios are 0.90, 0.83 and 0.78 whilst the C/O ratios are 4.5, 3.3 and 2.75 respectively).

Different types of biomass contain different amounts of the above mentioned monomeric units (softwoods are based on guiacyl, hardwoods are based on guiacyl/syringyl and grasses on p-hydroxy-phenols) [19]. The differing C/H and C/O ratios implies not only the difference in higher heating values (HHV), but also the tendency to form various pollutants so the exact quantities of these species determine the combustion processes and its environmental impact.

During devolatilisation, hemicellulose compounds react first, then the cellulose and at the end lignin [19]. The fact that the devolatilisation of biomass (especially most of the agricultural biomass) takes place at low temperatures is an indication that this type of fuel ignites instantaneously, when exposed to the high furnace temperatures. The key factor here is the moisture content, which has been found to increase the devolatilisation time [20-22]. The combustion of the volatiles would be the dominant step during the combustion of agricultural residues and related biomass.

The char formation and combustion is also important process in biomass combustion. This process is partially responsible for the formation of NO_x and CO in the flue gases [19].

Furthermore, it determines the physical and chemical structure of the char which in turn determines its fragmentation resulting in the emission of the carbonaceous particulate matter (dust).

3. Pollutant formation

Pollutants are formed in parallel with the main combustion reactions from the N, S, Cl, K and other trace elements contained in the volatiles and char (Fig. 3).
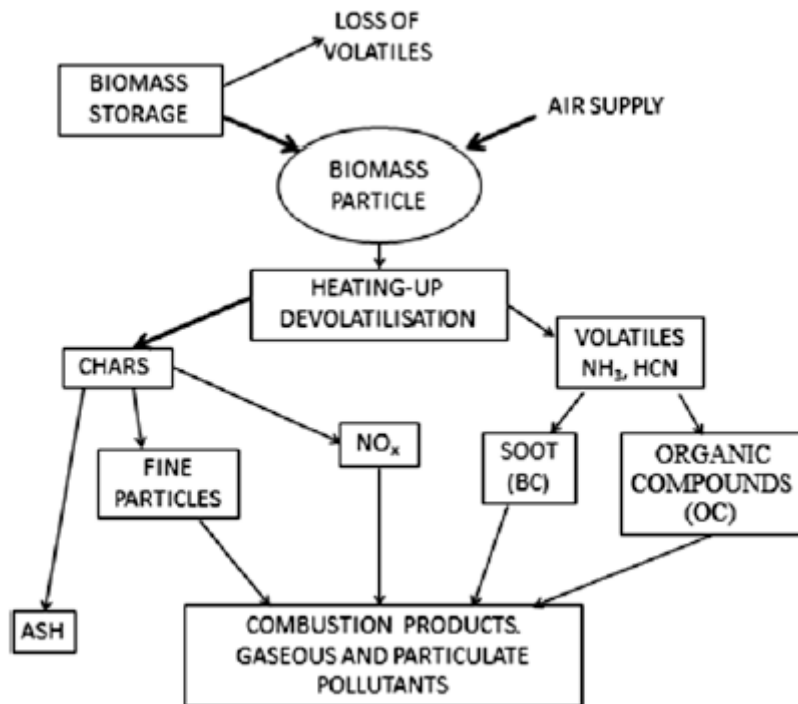

Fig. 3 Formation of pollutants during the biomass combustion [19]

The pollutant emissions from biomass can be classified in two groups. The first group consists of the unburnt pollutants, which are mainly influenced by the combustion equipment and process. The other group consists of pollutants which are mainly influenced by the fuel properties.

If the combustion is incomplete, due to factors such as local low temperatures, poor mixing with oxygen, moisture content, too short residence time and etc., products such as CO, C_xH_y, HC, tar, PAH, soot and char particles are released. These substances are emitted from all biomass fuels, but the released amount depends on furnace design, fuel used and/or operating conditions.

NO_x production during the combustion of fossil fuels is already well known and in case of coal combustion arises from the main mechanism: thermal-NO_x (from high temperature oxidation and atmospheric N_2), prompt-NO_x (from the reaction of fuel derivated radicals and atmospheric N_2) and fuel-NO_x (from oxidation of nitrogen chemically bound in the fuel). The contribution of the first two, whose mechanism route is well known, in total amount of NO_x produced in most biomass combustion systems are below 30% [23].

The majority of the NO_x in biomass combustion is produced from the fuel bound nitrogen which can be present in biomass as inorganic nitrate and ammonium ion, amino compounds (includes proteinaceous fraction), heterocyclic purines, pyrimidines and pyrroles [19]. Fuel-nitrogen will be released in the combustion process, during both the devolatilisation and in the char combustion stage. NO_x formation during the volatile

combustion can be controlled by stoichiometry control (staged combustion and flue gas recirculation), whereas NO_x formation from char combustion is not as easy to control. Authors in [4] and [8] found that NO_x emissions from biomass increases with the increase of nitrogen content in the fuel and that logarithmic correlation between nitrogen content and NO_x emission can be presumed. This correlation and the empirical potentials of several different measures for NO_x reduction are shown on Fig. 4. NO_x emissions from energy crops can also, to a certain degree, be controlled by an informed choice of the harvest time. Authors in [10] analyzed combustion properties of *Mischanthus x giganteus* from three different harvest times and concluded that the winter harvest is optimal regarding the fuel nitrogen content.
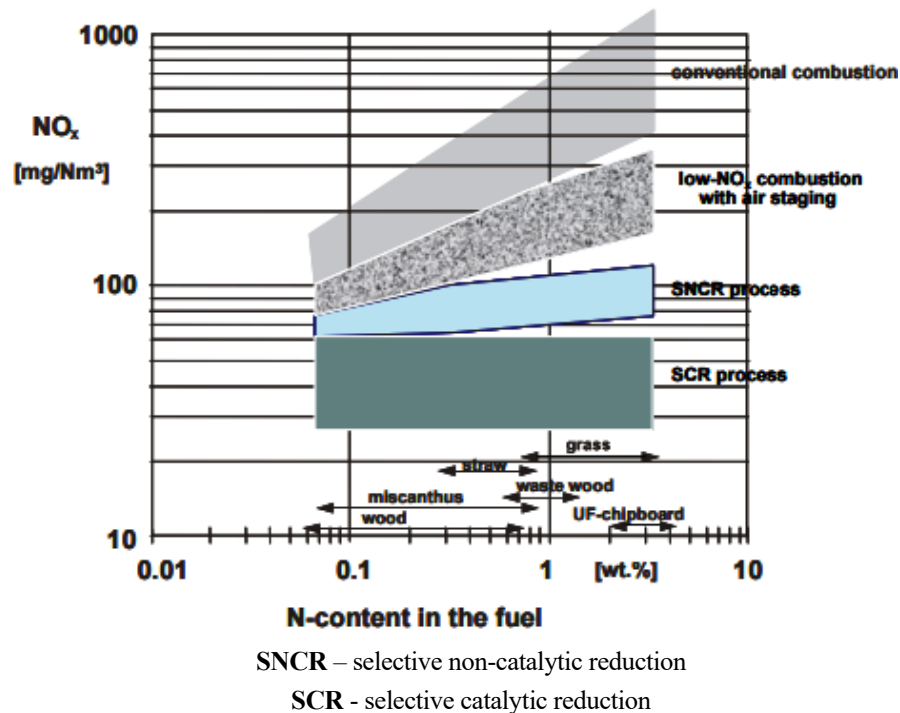

SNCR – selective non-catalytic reduction

SCR - selective catalytic reduction

Fig. 4 Relation between fuel-N content, NO_x emission reduction measures and NO_x emissions [24]

Biomass usually contains small amounts of sulphur (0.1 - 0.5 wt% dry plant matter, which is small compared with most of coals), so small emissions of SO_2 are expected while burning biomass. Chlorine concentration in biomass ranges up to 2 wt% (dry plant matter) and this high concentrations, which can be found in some straws, represent a major combustion and environmental problem. Both Cl and S are present both as organo-compounds, but mainly as inorganic salts (particularly potassium salts). Chlorine reacts with metals such as K and Na, forming vapors and aerosols, which can during the cooling processes lead to deposits on the furnace walls. Chlorine, in form of HCl, can also react with organic constituents producing dioxins [25]. Dioxins and dioxin-like compounds are compounds that are highly toxic and environmental persistent organic pollutants. The various reaction steps in dioxin formation are given in Fig. 5.

In general, the formation of dioxins is very complex. Essentially any hydrocarbons present in the hotter regions of flue gases can rearrange to give benzene and then phenols and phenoxy radicals (under oxidizing circumstances) which can then combine to give dioxin precursors. However, as long as combustion is complete, by decreasing the amount of C/H/O species and ash in the flue gases, the environmental problem can be minimized. Furthermore, as the dioxins are not chemical substances of high thermal stability, authors in [26] proved that temperatures greater than 900 °C and oxygen deficiency can bring to the complete

decomposition of dioxins and other dioxin-like compounds. On the other hand, most of the emitted dioxins and dioxin-like compounds are formed behind the combustion zone in so called de novo synthesis, at the temperatures below 500°C, as a result of a series of catalytic reactions proceeding on the surface of dust that contains metals such as Cu, Fe, Ni, Al, Zn [25].
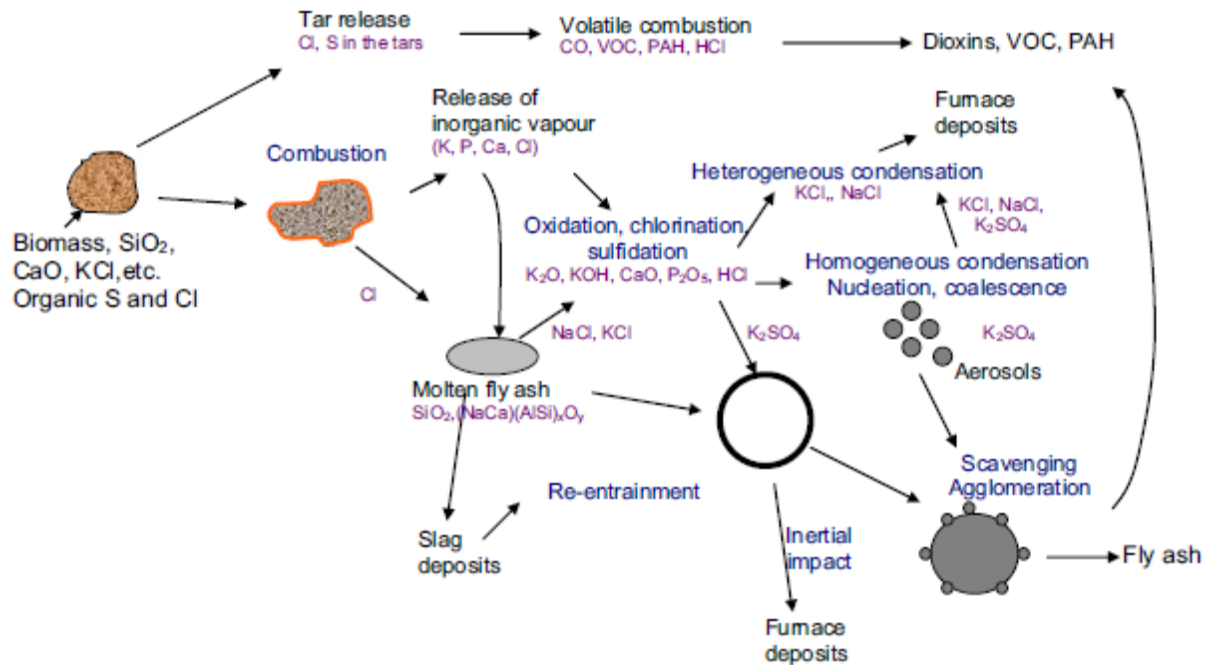

Fig. 5 Aerosol, deposits and pollutant formation pathways for K, Cl and S compounds [27]

4.   Problem of low ash melting point

Non-conventional biomass usually has high content of alkali oxides and salts which consequently contribute to the low ash melting sintering temperature. These low melting temperatures of some types of biomass pose serious burning appliances operation problems which includes agglomeration, fouling, slagging and in some cases corrosion of heat exchanger surfaces. Therefore a careful analysis of ash melting properties should be the first step in choosing the adequate combustion system and combustion conditions for a given biomass.

Typically agricultural residues and energy crops have higher K_2O content compared to conventional biomass or coal [14]. This is manly attributed to the use of fertilizers in agricultural industry. The effect of the K_2O content on the ash melting point is presented in Table 1. Since the ash consists of a mixture of different inorganic compounds, it has no well-defined melting point and the melting process takes place over a wide temperature range starting with the initial deformation temperature. It is seen that straws from rye, oat and barley, with high contents of K_2O have much lower melting temperatures compared to the wheat straw, which have lower content of K_2O.

Table 1 Ash melting temperatures for some straws [28]

Material	Straws			
	Wheat	Rye	Oat	Barley
K_2O (wt% in ash)	6.6	19.2	40.3	40.3
Initial deformation temperature (°C)	900-1050	800-850	750-850	730-800
Hemisphere temperature (°C)	1300-1400	1050-1150	1000-1100	850-1050
Flow temperature (°C)	1400-1500	1300-1400	1150-1250	1050-1200

If no experimental data of ash melting behavior is available, molar ratio of (Si+P+K)/(Ca+Mg) used in [11] gives first information ash melting tendencies. It has been proved to be more accurate than well-known Si/(Ca+Mg) ratio, especially for P-rich fuels (Fig. 6). As it can be seen on Fig. 6 most of the non-conventional biomass have ash sintering temperature well below 1000 °C (molar ratio (Si+P+K)/(Ca+Mg) > 3) and burning this kind of biomass in burners designed for burning conventional biomass, due to the clogging problems, is practically impossible.
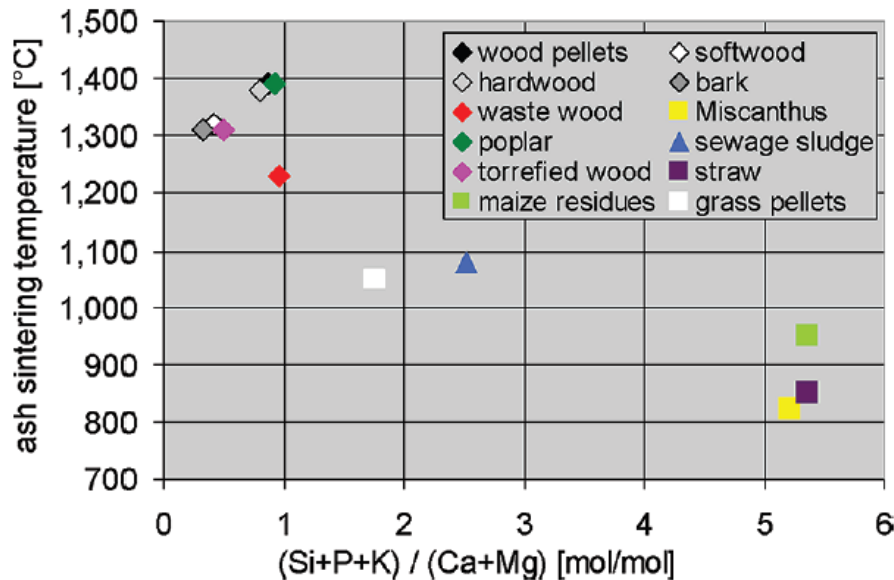

Fig. 6 (Si+P+K)/(Ca+Mg) molar ratio versus ash-sintering temperature for different biomass fuels [29]

Some ash constituents can react with flue gases forming a variety of compounds which may form deposits on the water cooled heat exchanger surfaces leading to fouling and slagging. These deposits, if containing certain chemicals, can also create corrosion and erosion problems.

5. Handling of fuels with low ash melting point

Two design solutions for handling the combustion of non-conventional biomass are used in small scale boilers. First solution is the design solution of heating appliances that keeps the temperature in furnace below the biomass ash sintering temperature [14]. This can be ensured by using water cooled walls and grates or flue gas re-circulation and careful design which avoids direct contact of flue gases and hot temperature surface. It can also be presumed that such design solutions can effectively reduce the NO_x emission as well. On the other hand, such solution, due to lowering the temperature in the combustion zone, should increase the emission of unburned pollutants (CO, C_xH_y, PAH).

Second solution is the use of so-called rotary combustion chamber burners (Fig. 7) or similarly working devices. This kind of burners are particularly suitable for burning of fuels with high content of non-combustible impurities without the need to continuously manually remove agglomerate or slag, also ensuring an efficient combustion due to permanent rotation of the grate which consequently contributes to better fuel and air mixing.
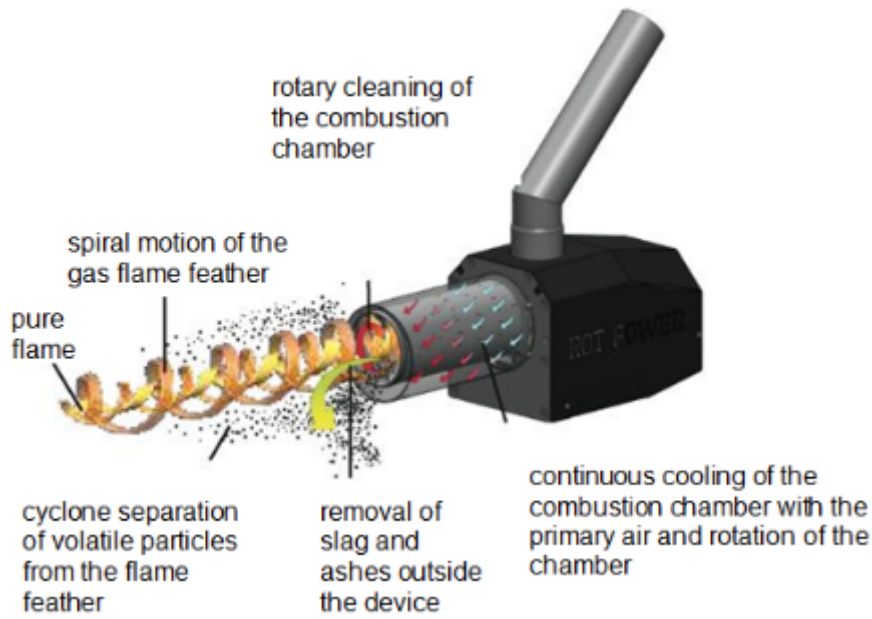
Fig. 7 Rotary combustion chamber burner [30]

6.   Novel modifications of the combustion system

In Commission regulation (EU) 2015/1189 emission of dioxins and furans are not identified as significant in case of solid fuel boilers. The same regulation also states that non-woody biomass boilers are exempted, because there is insufficient European-wide information to determine appropriate levels for "Eco-design" requirement. The regulation clearly states that such boilers may have significant environmental impact, such as dioxin and furan emissions. Having that in mind, care must be given to design the cost-effective combustion system which ensures low dioxin emission when burning non-conventional biomass, especially Cl-rich fuels.
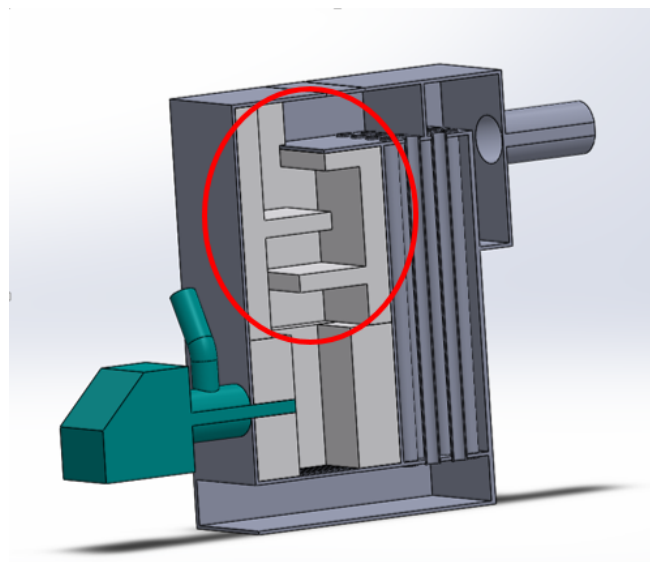

Fig. 8 Cross section of novel combustion system – installed obstacles and insulated combustion chamber

To ensure destruction of dioxins temperature in combustion zone must be maintained above 900 °C for sufficient amount of time (high resistance period). This can be achieved by installing various obstacles to flue gas steam flow in order to increase the flow path and by insulating the whole combustion chamber (Fig. 8). Installed obstacles may also serve as an

efficient measure for the dust emission reduction. By insulating the entire (or almost the entire) combustion chamber, cold spots, which contribute to the generation of CO and C_xH_y, can be to a great extent avoided. Negative consequence of this measure is the increase of pressure drop and necessary increase of convection heat exchange surfaces in order to achieve the same heat output.

Some mechanisms of dioxin formation (formation from precursors in the fly ash and de novo synthesis) can potentially be controlled by porous ceramic media installed behind the combustion zone, preferably where the flue gas temperatures are still above 700 °C (Fig. 9). This porous media acts as a filter and due to its high specific surface should control the condensation of various volatiles and aerosols. When choosing this porous media, care must be given to its porosity and operating temperatures (resistance to thermal and chemical attack). In order to be effective, such high-temperature filtration media must be sufficiently porous, to maintain the pressure drop in acceptable limits for a certain time, and on the other hand it has to provide high particulate extraction efficiency.
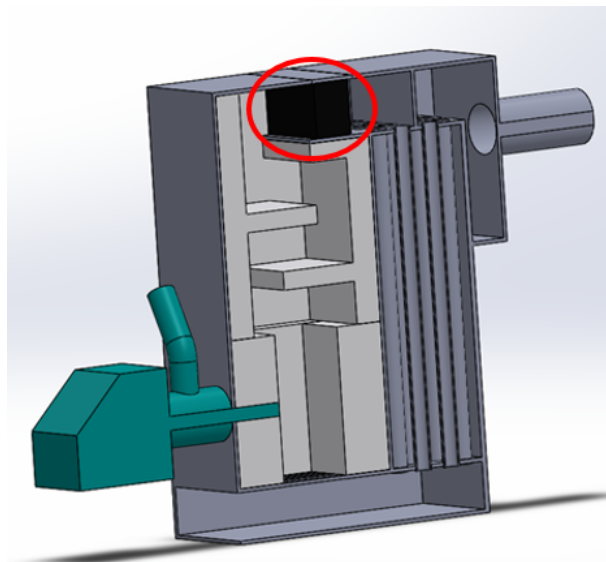

Fig. 9 Cross section of novel combustion system – installed porous ceramic filter

Filter efficiency and pressure drop increases with the hours in operation. Also, in most cases boiler operation is temperature regulated through ON/OFF cycles as a function of current water content temperature. This is commonly characterized by frequent start-stop cycles where most of soot is generated. Furthermore, agricultural biomass has significant amount of fuel ash and high concentrations of dust emissions are expected. Filter cleaning can be achieved with help of gravity (filter is placed so that flue gas flow is in opposite direction of gravity) and/or with air counter-current flow (in periods when boiler not in operation). Cleaning can also be accomplished by porous media catalytic coating, which facilitates the combustion of CO, C_xH_y and carbon particles captured on filter. To ensure more efficient cleaning mechanism, filter may have a built-in electric heater that can occasionally be turned on resulting in the raise of the filters surface temperature in order to enable the complete burn-out of captured unburned particles and other pollutants.

7. Conclusion

In this paper, several investigations regarding the combustion and emission characteristics of agricultural biomass are presented.

It has been pointed out that the current utilization of non-conventional biomass is very low whereby it is used mostly locally due to its low bulk density. From the reviewed

literature, it can be concluded that the high volatile matter has dominant impact on the overall combustion process and, therefore, on design and operation parameters of the combustion system. Due to the higher N, S, Cl and ash content compared to the conventional biomass, higher emission of NO_x, SO_2, dioxin and dust are expected. Problems regarding the low ash melting temperatures are discussed and empirical formula, based on fuels chemical composition that provides first information on ash melting tendencies is given.

At the end, several solutions for handling combustion of solid fuels with low ash sintering temperatures have been proposed, as well as the novel modification of the combustion system which, in theory, should ensure cost-effective low dioxin emissions when burning Cl-rich fuels (most of non-conventional biomass). The proposed modifications can also be to some degree, implemented in existing appliances for burning of conventional biomass.

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